Electrospun Nanofiber Reinforced Composites: Fabrication and Properties

Dissertation

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To my family

Work while you work; Play while you play; This is the way; To be cheerful and gay.

—M. A. Stoddart

工作时工作，玩乐时玩乐，依此方法做，轻松与欢乐。

—斯道达特

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List of symbols and abbreviations

AcOH	acetic acid
ATR-IR	attenuated total reflectance spectroscopy
BPDA	3,3’,4,4’-biphenyltetracarboxilic dianhydride
C	concentration
CA	contact angle
CMC	ceramic matrix composites
CNFs	cellulose nanofibers
CNTs	carbon nanotubes
CNWs	cellulose nanowhiskers
DMF	N,N’-dimethylformamide
ECNB	electrospun carbon nanofiber bundles
FA	formic acid
FRP	fiber reinforced polymer composites
FT-IR	fourier transform infrared spectroscopy
g	gram
GPa	giga pascal
h	hour
H-bonding	hydrogen bonding
J	joule
l	length
l_c	critical fiber length
Kg	kilogram
kV	kilovolt
LBL	layer-by-layer
L/d	length to diameter
m	meter
MF	melamine-formaldehyde
mg	milligram
min	minute
MJ	meta joule

MMC	metal matrix composites
MPa	mega pascal
MWNT	multiwalled carbon nanotubes
nm	nanometer
NP	nylon-6/PMMA
NT	nylon-6/TPU
ODA	4,4’-diamino diphenyl ether
OMC	organometallic compounds
OPEFB	oil palm empty fruit bunches
PA	phosphoric acid
PA-6	polyamide-6, nylon-6
PA-66	polyamide-6,6, nylon-6,6
PAA	poly(amic acid)
PAN	polyacrylonitrile
PBI	polybenzimidazole
PBO	zylon, polybenzoxazole
PCL	polycaprolactone
PDA	*p*-phenylene diamine
PEEK	poly(ether ether ketone)
PEO	poly(ethylene oxide)
PET	poly(ethylene terephthalate)
PI	polyimide
PIPICOF	PI/PI nanofiber composite films
PLA	poly(lactic acid)
PMC	polymer matrix composites
PMDA	pyromellitic dianhydride
PMIL	Polymer melt infiltration lamination
PMMA	poly(methyl methacrylate)
PP	polypropylene
PVA	poly(vinyl alcohol)
RIs	refractive indexes
s	second
SBR	styrene-butadiene rubber

LIST OF SYMBOLS AND ABBREVIATIONS

SEM	scanning electron microscopy
T	temperature
$\mathbf{T_{5\%}}$	temperature at which 5% weight loss took place
$\mathbf{T_d}$	decomposition temperature
TGA	thermogravimetric analysis
TPU	thermoplastic polyurethane
UV	ultraviolet
UV-Vis	ultraviolet-visible spectroscopy
VGCNF	vapor grown carbon nanofibers
wt	weight
wt%	weight percent
$\mathbf{^oC}$	degree Celsius
$\boldsymbol{\varepsilon}$	strain
$\boldsymbol{\rho}$	density
µm	micrometer
$\boldsymbol{\sigma}$	stress

Summary/Zusammenfassung

Summary

This dissertation presents research related to the use of electrospun nanofibers for reinforcement of mechanical properties of polymers, like thermoplastic polyurethane (TPU), melamine-formaldehyde (MF) and polyimide (PI). Nylon-6 and PI electrospun nanofibers are excellent candidates for reinforcement purposes as they possess excellent mechanical properties. Both long and short electrospun nanofiber reinforced composites were prepared and the effects of the fiber contents, the fabricating methods, and use of continuous and/or short nanofibers on the wetting behavior, mechanical properties, thermal and optical properties were investigated in the present work.

Chapter 1 provided a general introduction of fiber reinforced polymer composites and electrospinning technology. The classification, the mechanical properties and the fabrication methods of fiber reinforced polymer composites were introduced. Nanofibers as a special kind of fibers have been attracting more and more attention in fiber reinforced polymer composites due to their excellent mechanical properties compared to the traditional fibers. The affecting factors on the properties of fiber reinforced polymer composites were also introduced in **Chapter 1**.

Chapter 2 is the cumulative part of the thesis subdivided into 4 parts. Each part is the summary of the published work in different peer-reviewed journals.

In **Section 2.1**, electrospun nylon-6 nanofiber mats were used to reinforce melamine-formaldehyde (MF) by dip-coating combined with hot-pressing (method 1) and passing the MF solution through nylon-6 nanomats combined with hot-pressing (method 2). The resulted composite films by both methods presented synergistic effects in tensile strength and toughness compared to the pure MF resin. The wetting behavior of the samples (produced by methods 1 and 2) led to quite different effects

on the morphology and mechanical properties of the composites. Depending on the loading amount of nylon-6 nanofibers, the effect between MF and nylon-6 could be considered as fiber reinforced MF or MF glued nylon-6 fibers. **Section 2.2** highlighted a novel layer-by-layer procedure for making high performance nylon-6 nanofiber reinforced TPU composites. The fast wetting of nylon-6 nanofibers by a TPU/N,N'-dimethylformamide (DMF) solution greatly improved the interfacial interaction between nylon-6 nanofibers and the TPU matrix, and led to a significant improvement in mechanical properties like tensile strength, E modulus, elongation at break and toughness. The enhancement was achieved without sacrificing the transparency of TPU by just using very small amounts (even as small as 0.4 wt%) of nylon-6 nanofibers.

Section 2.3 and **2.4** focused on the initial investigations of using short electrospun nanofibers as reinforcement. A liquid processing technique was applied to prepare short electrospun nanofibers and their dispersions. The pre-loaded very small amount of short nanofibers (< 5 wt%) gave rise to significant enhancement effects without sacrificing the transparency. In **section 2.3**, a comparison study by using short nylon-6 nanofibers to reinforce TPU and poly(methyl methacrylate) (PMMA) was provided. The interaction of hydrogen bonding (H-bonding) and the homogeneous distribution of short fibers between nylon-6 nanofibers and the TPU matrix led to a stronger interface compared to nylon-6/PMMA composites and better reinforcement effects were observed in nylon-6/TPU composite than in nylon-6/PMMA composites. **Section 2.4** described the self-reinforced PI composites and compared the enhancement in mechanical properties by short PI nanofibers and PI nanofiber mats. The solubility difference between PI and its precursor, polyamic acid (PAA) provided the opportunity to prepare self-reinforced composites. As compared to using PI nanofiber mats as reinforcement, the short PI nanofiber reinforced PI composites showed better mechanical properties due to the much better dispersability of short nanofibers. Quite less amounts of short PI nanofibers than nanofiber mat were required to achieve similar enhancement of the composites, i.e. 38 wt% of PI nanofiber mat compared to 2 wt% of short PI nanofibers were required to achieve almost the same tensile strength.

Chapter 4 presents an outlook about the problems and challenges in electrospun nanofiber reinforced polymer composites. Future work about electrospun nanofiber reinforced composites could be focused on (1) how to prepare strong nanofiber with excellent mechanical properties; (2) the effect of diameter and aspect ratio of nanofibers on the properties of nanofiber reinforced polymer composites; (3) how to enhance the nanofiber/matrix interaction and (4) how to prepare super strong electrospun carbon nanofibers as reinforcements.

Zusammenfassung

Diese Dissertation beschreibt einige Entdeckungen zu elektrogesponnenen nanofaserverstärkten Polymerkompositen, bei denen zum einen kontinuierliche und kurze Nylonnanofasern zur Verstärkung von Melaminformaldehyd (MF) bzw. thermoplastischer Polyurethane (TPU) eingesetzt und zum anderen kontinuierliche und kurze Polyimid-(PI)-nanofasern zu selbstverstärkenden PI-Kompositen umgesetzt wurden. Insbesondere der Einfluss von Fasergehalt, Fertigungsmethoden und der Einsatz von kontinuierlichen bzw. kurzen Nanofasern wurde im Hinblick auf Benetzungsverhalten, mechanische Eigenschaften, thermischen und optische Eigenschaften untersucht.

Diese Dissertation befasst sich mit Forschung im Zusammenhang mit der Verwendung von elektrogesponnenen Nanofasern zur Verbesserung der mechanischen Eigenschaften von Polymeren, wie thermoplastischem Urethan (TPU), Melaminformaldehyd (MF) und Polyimid (PI). Nylon-6- und PI-Nanofasern sind hervorragende Beispiele für Verstärkungszwecke, da sie exzellente mechanische Eigenschaften besitzen. Composite verstärkt sowohl mit langen als auch kurzen elektrogesponnenen Nanofasern wurden hergestellt und die Auswirkung auf Fasergehalt, Verarbeitungsmethode, Benetzungsverhalten, mechanische Eigenschaften und andere Eigenschaften in dieser Arbeit untersucht.

In **Kapitel 1** wurde eine allgemeine Einführung zu faserverstärkten Polymercompositen und den Grundlagen des Elektrospinnens gegeben. Die Klassifizierung, die mechanischen Eigenschaften und Verarbeitungsmethoden von faserverstärkten Polymerkompositen wurden hier diskutiert. Nanofasern, als besondere Art von Fasern, haben im Bereich der faserverstärkten Polymercomposite, aufgrund ihrer ausgezeichneten mechanischen Eigenschaften im Vergleich zu herkömmlichen Fasern, mehr und mehr Aufmerksamkeit auf sich gezogen. Die Faktoren, die die Eigenschaften von faserverstärkten Polymercompositen beeinflussen, wurden ebenfalls in **Kapitel 1** beschrieben.

Das **Kapitel 2** enthält den kumulativen Teil der Arbeit und enthält vier Teile. Jeder dieser Teile stellt eine Zusammenfassung eines in einer begutachteten Zeitschrift veröffentlichen Artikels dar.

In **Sektion 2.1** wurden Methoden zur Herstellung von mit elektrogesponnenen Nylon-6-Nanofasermatten verstärktem MF diskutiert. Zum Verstärken wurden einerseits Tauchbeschichtung und Heißpressen (Methode 1), andererseits Durchführen einer MF-Lösung durch Nylon-6-Nanofasermatten gefolgt von Heißpressen (Methode 2) eingesetzt. Die daraus erhaltenen Kompositfilme zeigten synergetische Effekte in Bereichen von Zugfestigkeit und Zähigkeit verglichen mit reinem MF-Harz. Die Benetzungseigenschaften der Proben (hergestellt durch Methoden 1 und 2) führten zu gänzlich anderen morphologischen und mechanischen Eigenschaften. Abhängig von der Beladungsmenge mit Nylon-6-Nanofasern konnte das System als faserverstärktes MF oder als mit MF verklebte Nylon-6-Fasern betrachtet werden.

In **Sektion 2.2** wurde ein neues Layer-by-Layer-Verfahren zur Darstellung von mit TPU verstärkten Hochleistungs-Nylon-6-Nanofaser-Kompositen beleuchtete. Die schnelle Benetzung der Nylon-6-Nanofasern mit einer TPU/ N,N’-dimethylformamide (DMF)-Lösung verbesserte die Grenzflächeninteraktion zwischen Nylon-6 und der TPU-Matrix deutlich und führte zu einer Steigerung der mechanischen Eigenschaften, wie Zugfestigkeit, E-Modul, Bruchdehnung und Zähigkeit. Diese Verbesserungen konnten ohne Verlust der Transparenz von TPU erreicht werden, da bereits Anteile von 0.4 gew.% der Nylon-6-Nanofasern ausreichten.

In **Sektion 2.3** und **2.4** lag das Augenmerk auf den anfänglichen Untersuchungen zu kurzen elektrogesponnenen Nanofasern als Verstärkung. Eine nasschemische Technik wurde eingesetzt, um kurze elektrogesponnene Nanofasern und ihre Dispersionen herzustellen. Bereits geringe Mengen von kurzen Nanofasern (< 5 gew.%) führten zu signifikanten Verbesserungen der Eigenschaften, ohne die Transparenz der Proben zu kompromittieren. In **Sektion 2.3** wurde eine Vergleichsstudie zur Herstellung von mit Nylon-6-nanofaserverstärktem TPU bzw. poly(methyl methacrylate) (PMMA) diskutiert. Die Wechselwirkungen, aufgrund von Wasserstoffbrückenbindungen und die homogene Verteilung der kurzen Fasern zwischen den Nylon-6-Nanofasern und der TPU-Matrix führten zu einer stärkeren Verknüpfung der Grenzflächen und somit zu besseren Verstärkungseffekten verglichen mit den Nylon-6/PMMA-Kompositen. In **Sektion 2.4** wurden sich selbst-verstärkende PI-Komposite beschrieben und die Verbesserungen durch den Einsatz von kurzen PI-Nanofasern und PI-Nanofasermatten verglichen. Die Löslichkeitsunterschiede zwischen PI und seinem Präkursor, Polyamidocarbonsäure (PAA) ermöglichte die Darstellung von sich selbst-verstärkenden PI-Nanofasern. Diese zeigten, aufgrund der besseren Dispergierbarkeit, bessere mechanische Eigenschaften als die mit PI-Nanomatten verstärkten Komposite. So wurden zur Erzeugung ähnlicher mechanischer Eigenschaften deutlich geringere Mengen PI-Nanofasern benötigt, was z.B. im Falle gleicher Zugfestigkeit in 2 gew.% Nanofasern gegenüber. 38 gew.% Nanofasermatten zum Ausdruck kam.

Kapitel 4 gibt einen Ausblick über die bestehenden Probleme und Herausforderungen bei durch elektrogesponnene Nanofasern verstärkten Polymerkompositen. Weitere Arbeiten könnten in den folgenden Bereichen liegen: (1) Wie lassen sich stabile Nanofasern mit exzellenten mechanischen Eigenschaften herstellen? (2) Untersuchung des Einflusses von Durchmesser und Aspektverhältnis von Nanofasern auf die Eigenschaften von Nanofaser-verstärkten Polymerkompositen (3) Wie lassen sich die Wechselwirkungen zwischen Nanofasern und Matrix verbessern? (4) Wie lassen sich elektrogesponnene Kohlenstoff-Nanofasern als Verstärkung einsetzen?

1. Introduction of fiber reinforced polymer composites

1.1. Motivation

Electrospinning is the most effective state-of-the-art method for the generation of continuous polymer nanofibers and nanofiber nonwovens. The nanofibers/nanofiber materials fabricated using this technology have a large surface area, large porosity, high aspect ratio of length to diameter and high molecular orientation along fiber axis, making them very useful in many applications such as energy storage, healthcare, biotechnology, environmental engineering, defense and security. The quite high-speed developments in electrospinning technology in the last few years, on the one hand, make the modifications on the morphology of the nanofibers possible by varying the processing parameters; on the other hand, have enhanced the production from few grams to kilos of nanofibers/nanofiber nonwovens in short time. Such developments not only promote application areas like filtration, textile manufacturing, medical application, etc., but also make possible the use of these fibers for making fiber reinforced composites.

Electrospun polymeric nanofibers have excellent mechanical properties which is high enough for making fiber reinforced composites. For example, single electrospun nylon-6 nanofiber displayed high tensile strength of 200-400 MPa and tensile modulus of 1-5 GPa[1-3]. Single electrospun polyimide nanofiber presented greater tensile strength of 1000-2500 MPa and tensile modulus of 20-90 GPa[4, 5]. The mechanical properties of these two kinds of nanofibers were much higher than those of other commercial polymers. Therefore, the electrospun nanofibers as reinforcements are attracting more and more attention in the last few years. Until now, only few countable studies have been available in the literatures. The limited data from the previous reports can’t give an enough and comprehensive impression on the effect of electrospun nanofiber on polymer matrix. For this fairly new area of electrospun nanofiber reinforced polymer composites, more studies are required in different directions, such as developing novel processing methods, modifying the morphology of the reinforcements, the wetting behavior of nanofibers and matrix, the interaction between nanofibers and matrix, fabrication of short electrospun nanofibers and short electrospun nanofiber reinforced composites, which are highlighted in the present thesis.

1.2. General introduction

Composites are one of the most fascinating and popular materials known to human. Composite materials are made from two or more distinct components with different chemical, physical and mechanical properties, but when combined, possess better properties than those of each individual components used alone. Composites materials have many advantages [6-12], such as high specific strength and modulus, ease of fabrication, high design flexibility, good resistance to fatigue and corrosion, desirable thermal expansion characteristics, and economic efficiency. Because of the outstanding properties, the composites materials have been widely used in aerospace industry, military industry, automobile industry, construction materials and other engineering applications[10-17].

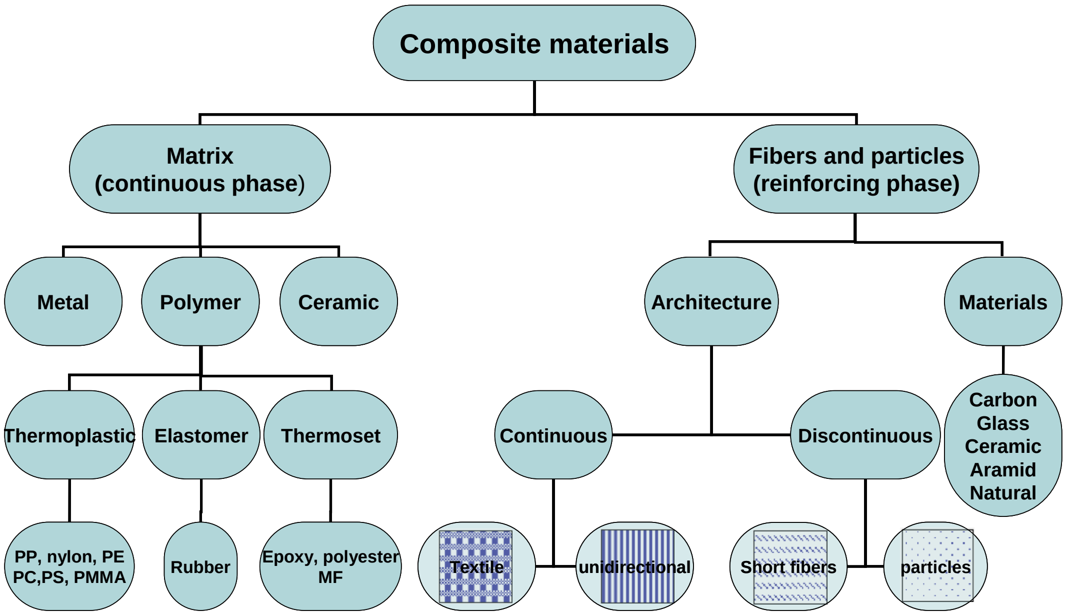

Figure 1- 1 Composition of composite materials.

Typical composite materials usually are composed of a continuous phase called matrix and one or more discontinuous phases known as reinforcement or reinforcement materials[18, 19], as shown in **Figure 1-1**. In most cases, the discontinuous reinforcement phase is harder, stronger, stiffer, and more stable than the continuous matrix phase. Polymers, metals and ceramics can be used as matrix. Polymer matrices usually have poor mechanical and thermal properties, metals have intermediate strength and stiffness but high ductility, and ceramics have high strength and stiffness but fragility[18-21]. The matrix materials surround the reinforcement to maintain the reinforcement in the proper positions and protect the reinforcement from abrasion and environment erosion. Particles, flakes, fibers and fiber sheets can be used as reinforcement materials. The reinforcements impart their special physical and mechanical properties to enhance the matrix properties. Particles, flakes and discontinuous fibers generally have a random orientation in the matrix, which provide the resulted composites isotropic properties, while continuous fibers and fiber sheets can be aligned in the matrix to endow the composites anisotropic properties.

The composites can be divided into two distinct levels based on the matrix materials or the reinforcement materials[18, 19]. The first level of classification refers to the matrix materials, including ceramic matrix (CMC), metal matrix (MMC), and polymer matrix (PMC) composites. The second level of classification is based on the reinforcements, including particulate reinforced composites, fiber (continuous and discontinuous) reinforced composites, and hybrid material reinforced composites.

1.3. Traditional fiber reinforced polymer composites

Among the different classes of composite materials, fiber reinforced polymer composites (FRP) play a crucial role in civil infrastructure and high-tech equipment for aerospace industry, military industry, civil engineering area and so on[6, 7, 13, 22-27]. In the last 30 years, FRP have gradually, partially or completely replaced the traditional engineering materials such as wood, metal, glass, and even ceramics in a few areas of applications[27-31]. FRP composites are defined as a combination of polymer resins, acting as matrix or binders, and strong and stiff fibers, acting as the reinforcement. By appropriately selecting the types of the polymer resins and the reinforcement fibers and using different processing technology, the physical properties of the FRP composites can be versatilely tailored[32]. The fibers for traditional fiber reinforced composites often have a diameter in micrometer range[33-36]. At the beginning, the main functions of fibers are to bear the load and provide high strength, high modulus, high stiffness, and thermal stabilities to the FRP composites, while the polymer matrix has functions of binding the fibers, holding the position of fibers, transferring the load to the fibers by adhesion/friction, and protecting the fibers from environment damages. Besides focusing on the improvement of mechanical properties, in many cases, the FRP composites also can be imparted other functional properties, such as optical properties[37, 38], electrical properties[39, 40] and conductivity[41, 42] by tailed modifying the fibers or matrix.

Depending on the properties and the types of the fibers, the FRP composites can be sorted out into several classes. By varying the length of the fibers, continuous and discontinuous (short) fibers can be applied to the FRP composites. Continuous fibers usually are easier to handle to be oriented in the FRP composites[43], while short fiber reinforced composites also have attracted significant attention owing to their advantages in easy processing, high-volume production and desirable mechanical properties[44]. Another classification of FRP composites is based on the types of the fiber materials, including natural fibers and synthetic (organic fibers and inorganic fibers)[45]. As shown in **Figure 1-2**, a wide range of different fibers can be applied as reinforcement or fillers[45]. Natural fibers are environment friendly and have huge resources including plant fibers (cotton, sisal, jute, bamboo, coir, kenaf, flax, wood etc.) and animal fibers (silk, wool, alpaca wool, camel hair, etc.). Inorganic fibers (glass, boron, ceramic, carbon, metal, etc.) are of high stiffness, high modulus, and good thermal stability. Compared to inorganic fibers, organic fibers (aramid, nylon, polyimide, polybenzoxazole, polybenzimidazole etc.) have low density, flexibility and elasticity.

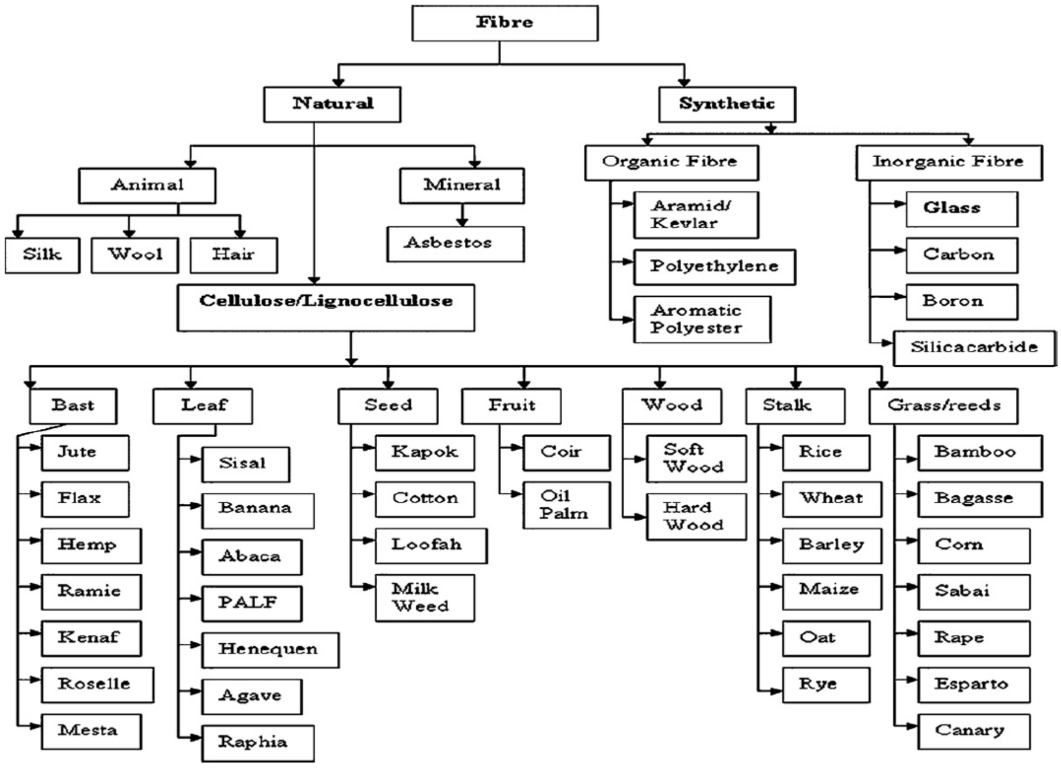

Figure 1-2 Classification of natural and synthetic fibers[45].

1.3.1. Natural fiber reinforced composites

In last several decades, extensive research has been done on natural fibers as an alternative reinforcement in polymer composites[22, 45-50]. The natural fibers used for polymer composites have advantages of low cost, low density, comparable high mechanical properties, renewability, recyclability and bio-degradability, which make them suitable for fabricating composites to apply for leisure equipment, constructions, sports, packages and so on[45, 50]. However, the natural fibers also have many disadvantages like lower strength especially impact strength, variable quality (influenced by weather), poor moisture resistant which causes swelling of the fibers, lower durability, poor fire resistant, and poor fiber/matrix adhesion[45, 50]. Generally, the poor adhesion between natural fiber and polymer matrix come from the incompatibility between the hydrophilic natural fibers and the hydrophobic polymer matrix. There are many reports focused on the modification of the fiber surface by using compatibilizers or coupling agents to improve the adhesion between the natural fibers and polymer matrix[22, 46, 49, 51, 52]. **Table 1-1** presents the mechanical properties of natural fibers and commercially important glass fibers that could be used for composites. The natural fibers present comparable to or even better than glass fibers as considering the specific modulus (modulus per unit specific density) and the elongation at break. Therefore, with the main purpose of replacing glass fibers in the past two decades many natural fibers such as jute[51, 53], bamboo[54, 55], kenaf[56, 57], rice husk and straw[58-61], sisal[62], pineapple[63, 64], coir[65, 66], banana[67], flax[68], silk[69], coconut[70] etc., have been studied as reinforcements.

Table 1-1 Mechanical properties of natural fibers and glass fibers[45].

Fibers	Density (g/cm^3)	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
OPEFB	0.7-1.55	248	3.2	2.5
Flax	1.4	800-1500	60-80	1.2-1.6
Hemp	1.48	550-900	70	1.6
Jute	1.46	400-800	10-30	1.8
Ramie	1.5	500	44	2
Coir	1.25	220	6	15.25
Sisal	1.33	600-700	38	2-3
Abaca	1.5	980	-	-
Cotton	1.51	400	12	3-10
Kenaf (bast)	1.2	295	-	2.7-6.9
Kenaf (core)	0.21	-	-	-
Bagasse	1.2	20-290	19.7-27.1	1.1
Henequen	1.4	430-580	-	3-4.7
Pineapple	1.5	170-1527	82	1-3
Banana	1.35	355	33.8	5.3
E-glass	2.5	2000-3500	70	2.5
S-glass	2.5	4570	86	2.8

1.3.2. Synthetic fiber reinforced composites

Of all the synthetic fibers used for polymer composites, four main classes of fibers, including glass fibers, carbon fibers, aramid fibers and nylon fibers are the best known reinforcements used for composites. **Table 1-2** is a summary of mechanical properties of the above glass, carbon, aramid and nylon fibers.

Table 1- 2 Mechanical properties of glass, carbon, aramid and nylon fibers.

Fiber	Tensile strength (MPa)	Tensile modulus (GPa)	reference
E-glass	2000-3500	70	[45]
S-glass	4570	86	[45]
Carbon	3950	238	[71]
Kevlar	2900	70-112	[72]
Nomex	590-860	7.9-12.1	[72]
Nylon-6	210	1.1	[73]

1.3.2.1. Glass fiber reinforced composites

Glass fibers are the most common used reinforcement in high performance composite applications due to their excellent combination properties (low density, resistance to chemicals, insulation capacity, easy to fabricate, high strength and stiffness) and relatively low cost comparing to other kinds of fibers[23,74]. However, the disadvantages of glass fibers for composites are from the relatively low modulus, which makes the glass prone to break when applying high tensile stress for a long time (**Table 1-2**). Glass fibers can be processed in the form of mats, tapes, fabrics (woven and nonwoven), continuous and chopped filaments, roving and yarns for composites applications. Vipulanandan et al. studied the glass fiber mat reinforced epoxy coating for concrete in sulfuric acid environment[75]. The results showed that the lifetime of the coated concrete in 3% sulfuric acid could be extended by more than 70 times without failure occurring. Pıhtılı et al. compared the effect of load and speed on the wear behavior of woven glass fabrics and aramid fiber reinforced composites[76]. The wear in the woven 300 glass fabric-reinforced composites was lower than the woven 500 glass fabric-reinforced composites when keeping all test parameters constant and the wear of the aramid fiber-reinforced composites was lower than the woven glass fabric-reinforced composites. Many researchers studied the effect of fiber length on the properties of glass fiber reinforced polymers[77-79]. Ohsawa et al. proposed that if the average length of the broken pieces (l) could be measured, the critical fiber length (l_c) could be expressed as $l_c = 4/3l$. His studies also showed that the critical fiber length greatly increases with increasing temperature and the apparent shear strength at the interface decreased linearly with increasing temperature. Gupta et al. proved that the fiber lengths of 0.4-0.8 mm were necessary for better fiber dispersion and better interfacial adhesion. An investigation from East Coast Fibreglass Supplies presented that the formation of the glass fiber had significant effect on the mechanical properties of glass fiber reinforced polyester (**Table 1-3**).

Table 1- 3 Tensile strength of glass fiber reinforced polyester composites.

Glass fiber reinforced polyester composites	Specific gravity (g/cm^3)	Tensile Strength (MPa)
Polyester resin	1.28	55
Chopped strand mat laminate 30% E-glass	1.4	100
Woven roving laminate 45% E-glass	1.6	250
Satin weave cloth laminate 55% E-glass	1.7	300
Continuous roving laminate 70% E-glass	1.9	800

1.3.2.2. Carbon fiber reinforced composites

Carbon fibers are one kind of the important high performance fibers used for composites[7, 80, 81]. Carbon fiber (7.5 µm) possess ultrahigh tensile strength of 3950 MPa, Young's modulus of 238 GPa[71]. **Table 1-4** lists some characteristic properties of some typical carbon fibers. Three precursors, rayon, polyacrylonitrile (PAN) and pitch, were used to manufacture carbon fibers by high temperature pyrolysis[81]. Carbon fiber reinforced composites were mainly applied in aerospace and automobile industry due to their outstanding mechanical properties, conductivity, low density, high temperature resistance, and long service life[7, 80, 82]. Many studies had been focused on the carbon fiber reinforced composites. Fu et al. reported an 100% increase of tensile strength and 900% increase of tensile modulus respectively of carbon fiber reinforced polypropylene than pure polypropylene[71]. Voigt et al. reported a high performance carbon fiber reinforced melamine-formaldehyde (MF) composites with tensile strength of 500 MPa and modulus of 60 GPa, which were 11 times and 7 times of the pure MF resin respectively [83]. Lee et al. applied carbon fibers into high speed boring bar and found that the dynamic stiffness of the composite boring bar was about 30% higher than that of the tungsten carbide boring bar[84]. Corrêa and coworkers studied the effect of incorporation of carbon fibers (diameter: 8-10 µm) in the thermoplastic elastomers[33]. As the manufacturing technology of carbon fibers improved, the carbon fiber reinforced composites were applied in small consumer products as well, such as fishing rods, badminton rackets, helmets, laptops, tent poles and snooker cues.

Table 1- 4 Properties of some typical carbon fibers[81].

Characteristic	Isotropic pitch-based fiber	Mesophase pitch-based fiber	PAN fiber	Vapor grown carbon fiber	Nanofiber
Diameter (µm)	14.5	6.5	10	5-8	0.05
Density (g/cm3)	1.57	1.81	2.0	2.0	2.1
Tensile strength (MPa)	600	2500	2100	4000	12000
Young’s modulus (GPa)	30	300	520	300	600

1.3.2.3. Aramid fiber reinforced composites

Aramid is an abbreviation for aromatic polyamide. Aramid fibers are a class of high performance synthetic fibers, which were usually applied in aerospace industry, military industry and civil engineering applications[72, 85]. Aramid fibers have high performance properties like superior mechanical resistance because (1) due to the high ratio of stretching and drawing during the fiber preparation process, the molecules in aramid fibers are highly oriented along the longitudinal direction (2) due to the special chemical structure with large amount of intramolecular hydrogen bonds, the aramid fibers have very high crystallization tendency[72, 85]. Besides the excellent mechanical properties, the aramid fibers have other outstanding properties like good resistance to abrasion/organic solvents, good thermal stabilities (no melting point, degradation starts from 500 ^{o}C, low flammability), and electric insulation[72, 85]. The disadvantages of aramid fibers include, sensitivities to UV radiation/acids/salts, and difficulties for cutting and machining. The most commercial aramid fibers are well-known as Kevlar and Nomex. Many reports were focused on using aramid fibers as reinforcements. Takayanagi et al. compared effect of the incorporation of the Kevlar fiber and surface-modified Kevlar fiber on the mechanical properties of polyethylene composites[86]. Better reinforcement was found after modifying the surface of Kevlar fiber by carboxymethyl group. Kutty and coworkers studied the effect of fiber loading and orientation on the mechanical behavior of Kevlar fiber-filled thermoplastic polyurethane[87]. Improved strength and significant improvement on modulus of the composites at higher fiber content were observed. Alonso et al. compared the effect of reinforcement of glass fibers and Nomex fibers on the mechanical performance of epoxy foams[88]. İçten and coworkers using woven Kevlar fiber to reinforce epoxy and applied the composite in pinned joints[89]. Kato et al. [90] and Bolvari et al. [91] used aramid fiber to improve the wear resistance of brake pads and polyamide 6,6 respectively.

1.3.2.4. Nylon fiber reinforced composites

Nylon is a big family of aliphatic polyamides, which were produced from a variety of diamines and dicarboxylic acids[92]. Nylon fiber was produced in 1935 by Wallace Carothers at DuPont's research facility at the DuPont Experimental Station and the first synthetic fiber to be commercialized in 1939[93]. In the nylon family, nylon-6,6 and nylon-6 are the most two common members. Although nylon-6,6 was synthesized from polycondensation of adipic acid and hexamethylene diamine while nylon-6 from ring opening polymerization of ε-caprolactam, both of these two nylons have similar outstanding properties, such as high melting temperature (above 200 ^{o}C), excellent mechanical properties including abrasion resistance, high strength and toughness, light weight, resistance to chemicals, and ease to be processed. Those two nylons are widely used as fibers commercially in all of the world. As one class of reinforcement, nylon-6 fiber (100 µm) has quite excellent tensile strength of 210 MPa, tensile modulus of 1.1 GPa and elongation of 90% (**Table 1- 2**) [73]. Therefore, many studies were focused on using short and continuous nylon fibers to reinforce polymers[94-106]. Thermal, rheological, and mechanical properties of short nylon fiber reinforced different rubbers were systematically studied by Seema and Kutty[94-99], Senapati[100], Sreeja[101, 102], Wazzan[103], Lin et al.[104] and Rajesh et al[105]. Kantz and Corneliussen found that low volume fraction of continuous nylon-66 fibers could significantly increase the tensile yield strength, elongation at yield and impact strength in polypropylene composites[106]. John et al. compared the effect of reinforcement of glass, aramid, and nylon fibers on the conventional acrylic resin and the results showed that all reinforced specimens had better flexural strength than the pure resin[107].

1.3.2.5. Short fiber reinforced composites

Short fibers applied for reinforcing polymer composites have a fiber length to diameter ratio much less than that the continuous long fibers have. Short fibers for composites have an appropriate length which is neither too low to give up their fiber properties nor too high to make them entangle with each other[108-110]. Compared to continuous fibers, short fibers have many advantages for preparing composites[108-110]. Short fibers can be prepared from many resources, such as natural plants, aramid polymers, nylon series polymers, carbon, glass and the offcut of the long fibers/fiber textiles. Short fibers have lower price than continuous fibers. The amount of the short fibers in composites can be preloaded, which means ahead of the fabrication of the composites, precise amount of short fibers can be incorporated into the composites. Short fibers can be easily incorporated into the polymer matrix and flexible design methods can be applied to prepare short fiber reinforced composites. Generally, to provide best reinforcement, the short fibers should be homogeneously dispersed in the polymer matrix by melt-blending and solution casting[108-110]. There are many reports on reinforced rubber composites via different short fibers, such as glass[111], silk[69, 112], jute[113, 114], coconut[70], coir[115], nylon[116], aramid[117-120] and polyethylene terephthalate[121]. Rezaei studies the effect of fiber length on the thermomechanical properties of polypropylene composites reinforced by short carbon fibers[122]. Two types of short fibers (aromatic polyamide and carbon) were applied to reinforce thermoplastic polyurethane by Corrêa et al[33]. Jancar et al. compared the toughening effect of denture based composites reinforced by short polyvinyl alcohol (PVA) fibers, S2-glass fibers and Kevlar 29 fibers[123].

1.4. Nanofiber reinforced polymer composites

1.4.1. Why nanofibers as reinforcement?

As described in **section 1.3**, the reinforcing fibers for traditional fiber reinforced composites usually come from the natural, glass, carbon, aramid and nylon fibers, which often have big diameter in the range of tens to hundreds micrometers[7, 23, 45, 72-74, 80, 85, 93]. However, when the fiber diameter decreases from micrometers (10-100 µm) to submicrons or even nanometers (1000×10^{-3} - 1×10^{-3} µm), the fibers will present amazing characteristics[124, 125] and provide amazing properties into the composites.

The first characteristic is that the pore size of the fiber nonwoven linearly decreases with the fiber diameter decreases (**Figure 1-3**)[126]. From **Figure 1-3A** and **3B**, an obvious conclusion could be obtained that fiber nonwoven with fiber diameter of 309 nm had pore size of about 1-2 µm while bigger pore size of more than 5 µm were observed from the fiber nonwoven with fiber diameter of 520 nm. **Figure 1-3C** gave a linear fitting based on the relationship between geometric pore size and fiber diameter. From the extension of the linear fitting, we could speculate that a reduction of fiber diameter from about 50 µm to 200 nm would cause a pore size reduction from 400 µm to 1 µm. This characteristic could gave valuable guidance on the selectivity of the nonwovens for the control of the fiber content in the composites.

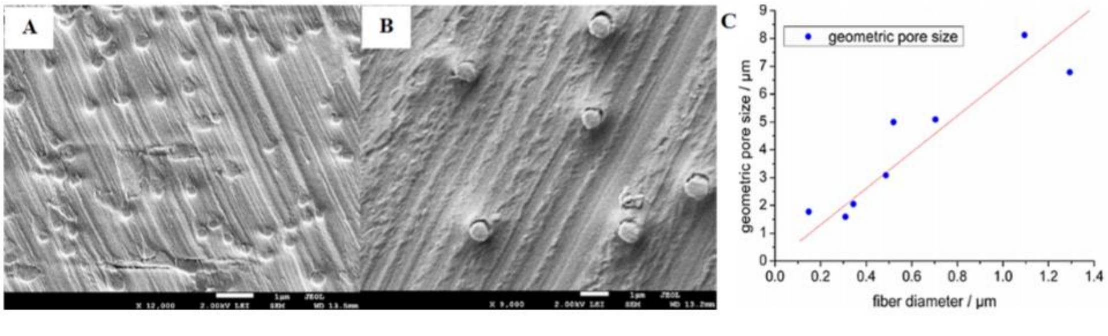

Figure 1-3 Cross-section of PAN nonwovens embedded in an epoxy matrix with fiber diameter of A) 309 nm, B) 520 nm; and C) Dependence of geometric pore size on fiber diameters for PAN based nonwovens[126].

Secondly, it is readily obvious that the specific surface area increases dramatically as the fiber diameter approached into the nanometer scale[127]. This is a key factor in improving nanofiber-matrix interface adhesion and providing effective load-transfer from the matrix to the nanofibers. In fact, the decreasing fiber diameter gives rise to significantly increasing specific surface area. **Figure 1-4** presents a survey on the increase of the specific surface as the fiber diameter decreased. It is obvious that the specific surface area increases dramatically from about 0.05 m^2/g to 100 m^2/g when the fiber diameter decreases from about 60 micrometers (diameter of a human hair) to 30 nm.

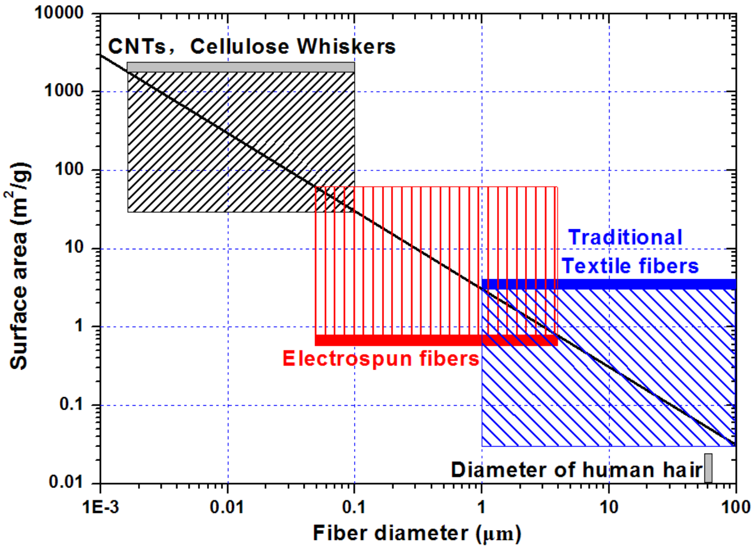

Figure 1-4 Dependence of specific surface area on fiber diameter in nonwovens.

Thirdly, the nanofiber has much higher aspect ratio (length to diameter, L/d) than that of microfiber (**Figure 1-5**). This is also one of the advantages by using nanofiber as reinforcement. It is well known that continuous fibers reinforced composites present better mechanical performance than those reinforce by particles, whiskers or short fibers, since the reinforcement effect depends on the aspect ratio. When the filler with low aspect ratio is used for reinforcement, usually a decrease of the mechanical performance of the composite can be observed. This phenomenon can be explained that[125]: (1) fiber edges result in stress concentration, which act as crack initiators; (2) no effect on matrix-to-fiber load transfer from fiber edges; (3) fillers with low aspect ratio are difficult to overlap each other in an appreciable measure, thus resulting very limited contributions to reinforce composites.

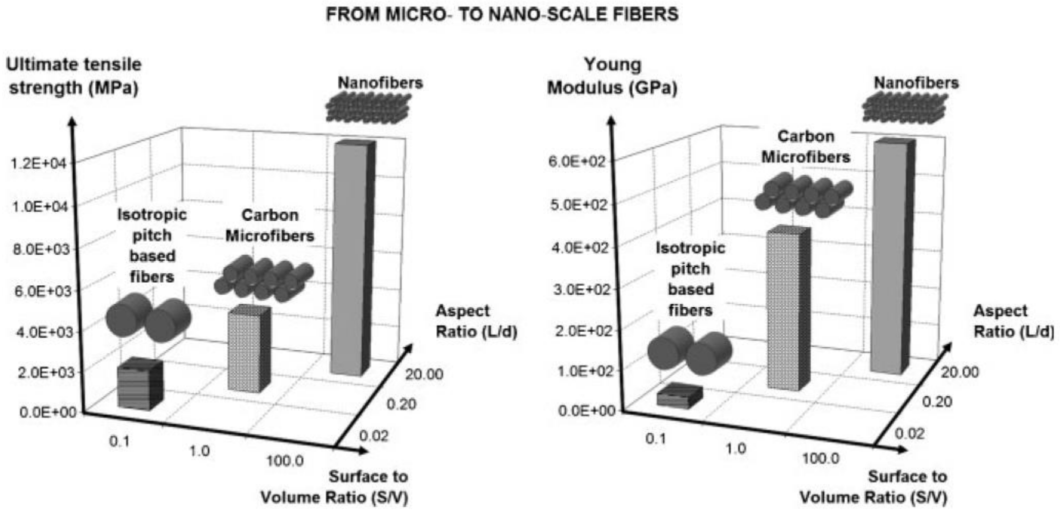

Figure 1-5 From micro- to nano-scale fibers as reinforcement of bulk composites[125].

Forth, from micro- down to nano-dimensions, the fibers are expected to show an improved mechanical properties, such as higher tensile strength, elastic modulus, toughness and strength at break[1-3, 5, 125, 128-133]. Many studies have revealed the size effect on the mechanical performance of fibers. Chew et al. showed a dramatically increasing of Young’s modulus (300 MPa to 3200 MPa) and tensile strength (20 MPa to 220 MPa) as the diameter of the PCL fibers decreased from bulk (5μm) down to the nanometer regime (200-300 nm)[134]. The similar results for PCL fibers were also obtained by Sun et al[135]. Liao et al. [136] and Papkov et al.[128] have found the size effect of polyacrylonitrile (PAN) on the elastic modulus and toughness (**Figure 1-6**). When the fiber diameter is smaller than 500 nm, the strength, modulus and toughness were observed increasing in a linear fashion. The same conclusion that dramatically increased mechanical performance come from the reduction of fiber diameter also appeared to the polyimide (PI) fibers[137], carbon fibers[138], polyamide (nylon-6) fibers[1-3] and so on. Two reasons could be explained for the improved mechanical properties[2, 125, 139]. First, during the fiber preparation, the polymer molecules would be forced oriented along the fiber axis. Stronger orientations of both chain molecules and crystals would be formed when the fiber diameter decreased. Another explanation is that, to a significant degree, the mechanical properties of a fiber is controlled by the presence of surface flaws and that the probability for the presence of surface flaws per unit fiber length decreased as the surface area per unit length of the fiber decreases.

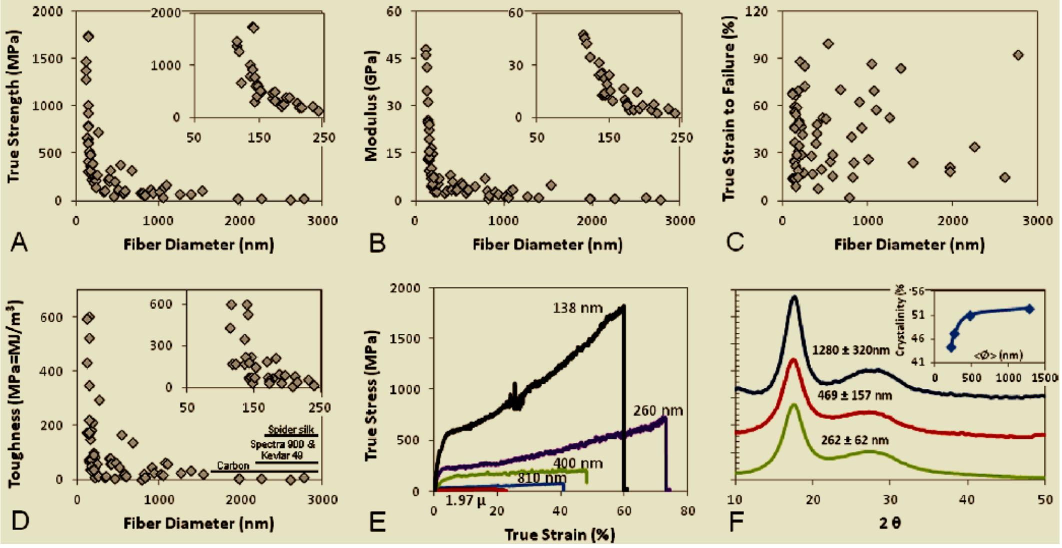

Figure 1-6 Size effects in mechanical properties and structure of as-spun PAN nanofibers. (A) true strength; (B) modulus; (C) true strain to failure; (D) toughness (lines indicate comparison values for several high-performance fibers and spider silk); (E) typical stress/strain behavior; (F) XRD patterns for nanofiber bundles with different average fiber diameters and variation of degree of crystallinity with average fiber diameter (inset)[128].

At last, fibers with diameter down to nano-scale could incorporated optical transparency into the composites[140-145]. As shown in **Figure 1-7**, when an incident light comes to an interface, it may reflect, transmit and refract. The light reflection give rise to the most of the light loss, and more light reflection will happen as the interfacial area increases. So small fiber with smaller interfacial area with matrix results in less light loss (**Figure 1-7**, more green arrows means more light loss). What's more, it is well known that light is actual a type of electromagnetic wave. It may pass an objective when its size is smaller than the light wavelength. The visible light has a wavelength arranged from 400 nm to 700 nm. Due to those nanofibers with diameter smaller than 400 nm as reinforcement, the refraction of visible light on these fiber/matrix interfaces is very minor. Thus the optical transparent composites reinforced by nanofibers could be produced.

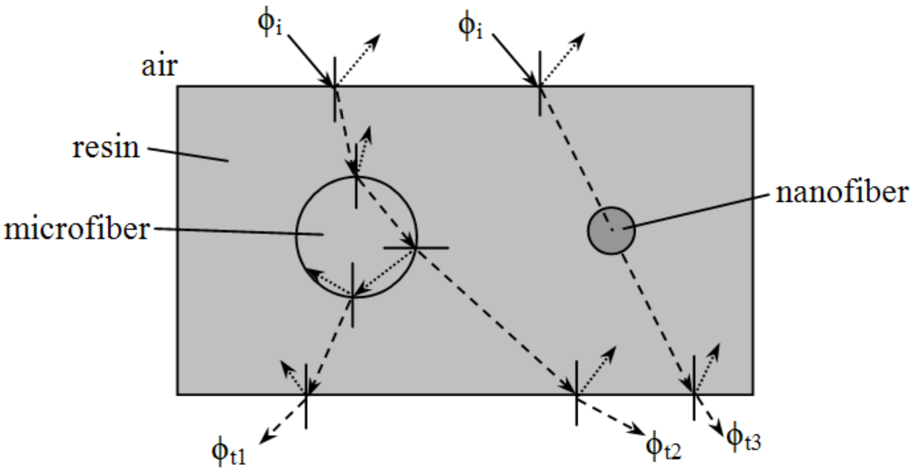

Figure 1- 7 Simplified model of light transmitted through fiber reinforced resin. Refractive indexes (RIs) of resin and fiber do not match. Φ_i is the incident light; Φ_t is the transmitted light. Green arrows mean reflected light at the air/resin and fiber/resin interfaces; Red arrows mean refracted light at the interfaces. Assuming the reflected light does not go into the other end of composite, Φ_t of transmitted light through microfiber is significantly less than Φ_i. Light would pass through nanofiber without the occurrence of reflection/refraction at the fiber/resin interfaces[140].

1.4.2. How to get nanofibers?

As described before, nanofibers have many advantages as reinforcement. Therefore it is important to learn about how to prepare nanofibers. Until now, cellulose nanofibers/nanowhiskers (CNFs/CNWs), carbon nanofibers, and synthetic polymer nanofibers are the three main classifications used as reinforcements. CNFs/CNWs usually come from the isolation of cellulose based materials[146-149]. Carbon nanofibers can be produced by a straightforward way of charring of the natural or synthetic textile fibers in the absence of air, and by pyrolysis of a hydrocarbon feedstock (natural gas, acetylene, etc.) or carbon monoxide on a metal catalyst such as iron[25, 81, 150]. Synthetic polymer nanofibers can be efficiently produced by electrospinning technology[151-155].

1.4.2.1. Isolation of Cellulose nanofibers/nanowhiskers (CNFs/CNWs)

Abundant resources like woods, plants, tunicats, algaes and bacterias could be used to fabricate cellulose nanofibers/nanowhiskers (CNFs/CNWs)[146, 148]. The isolation of CNFs/CNWs from the cellulose source usually includes two steps. The first step is a pretreatment process to produce purified cellulose so that it can be further processed. The pretreatment is dependent on the cellulose source materials. As for the woods and plants, the pretreatments is to completely or partially remove matrix materials like hemi cellulose, lignin, etc. and to isolate the individual complete fibers[156-158]. The isolation for tunicate involves the isolation of the mantel from the animal and the isolation of individual cellulose fibrils with the removal of the protein matrix[159]. For algal cellulose sources, the pretreatments typically involve culturing methods, and the purifying steps to remove algal wall matrix material[160]. As for bacterial cellulose pretreatment, it focus on culturing methods for cellulose microfibrillar growth and then washing to remove the bacteria and other media[161, 162]. The second step is to separate those purified cellulose materials into CNFs/CNWs. Three main approaches, mechanical treatment, chemical hydrolysis, and enzymatic hydrolysis, have been applied to obtain CNFs/CNWs[146, 148]. Those methods can be used separately or in sequence or in combination.

1.4.2.2. Pyrolysis to carbon nanofibers

Two methods can be applied to produce carbon nanofibers[25, 81, 150]. The most straightforward method for producing carbon nanofibers is the charring of natural of synthetic textile fibers in the absence of air. In this way, linen, cotton, nylon, polyacrylonitrile (PAN) and pitch can be processed into carbon nanofibers when the precursor fibers has diameter in the range from micro- to nano-scale. The PAN-based carbon nanofibers could be prepared in several steps including 1) stabilization in air at 200-300 ^{o}C 2) carbonization in an inert-gas atmosphere at 1200-1400 ^{o}C and 3) high-temperature annealing in vacuum or an inert-gas atmosphere at 2000-3000 ^{o}C[163]. Another important precursor for carbon fibers is pitch-based fibers, which are extruded from a dense pitch through spinnerets[164, 165]. The procedure of heat treatment from pitch-based fibers to carbon fibers is similar to the procedure from

PAN-base fibers to carbon fibers.

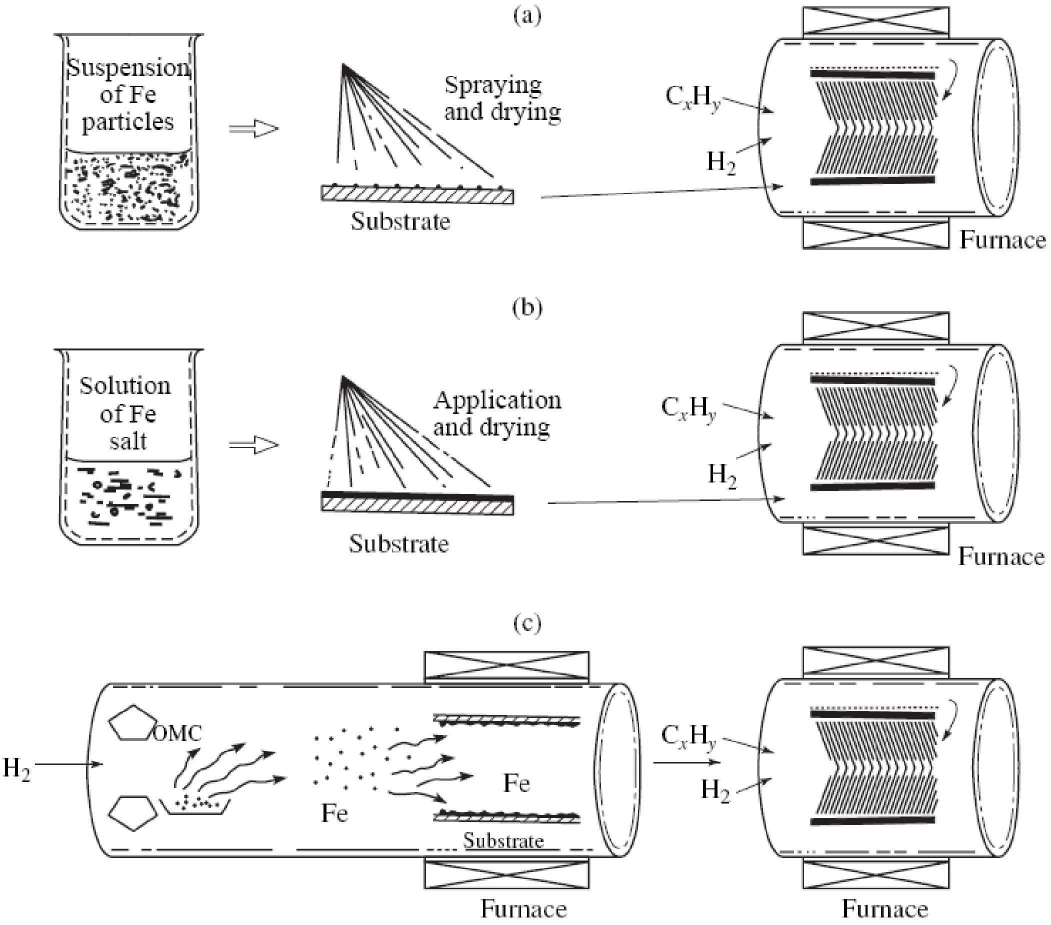

Figure 1-8 Schemes of the growth of vapor grown carbon fibers on a substrate: (a) a catalyst is applied as a suspension of a fine iron powder in a solvent, (b) a catalyst is applied as a solution of iron compounds, and (c) iron-containing organometallic compounds (OMC) are introduced immediately into the reactor[81].

Another significant way for the production of carbon nanofibers is to pyrolyze carbon gas resources (usually methane, ethylene, acetylene, carbon monoxide, etc.) on catalyst nanoparticles (Fe, Co, or Ni, most often Fe) at 500-1500 ^oC or with further high-temperature annealing at 2000-3000 ^oC in vacuum or an inert-gas atmosphere[25, 81, 150, 166]. The growing process of carbon nanofibers could be performed by two methods, whereby fibers are grown either on a substrate (**Figure 1-8**) or in a gas flow(**Figure 1-9**)[81, 166]. If the fibers are grown on a substrate, the first step is to load the catalyst on the graphite or ceramic substrate by spraying a suspension of a fine iron powder in a solvent (**Figure 1-8a**) or a solution of iron compounds (nitrates, ferrocene, etc.) with further treatment of heating in hydrogen to form metallic iron (**Figure 1-8b**). Then the iron-containing organometallic compounds are introduced into the reactor immediately (**Figure 1-8c**). In the method for growing fibers in a gas flow (**Figure 1-9**), two ways could be used to introduce metallic catalysts into the reactor. A suspension of fine iron particles in an organic solvent can be directly injected into the reaction zone during fiber growth (**Figure 1-9a**). Another method for introducing catalyst is inputting the mixtures of the volatile organometallic compounds (OMC), e.g. iron carbonyl, and carbon-containing gas together into the reactor (**Figure 1-9b**).

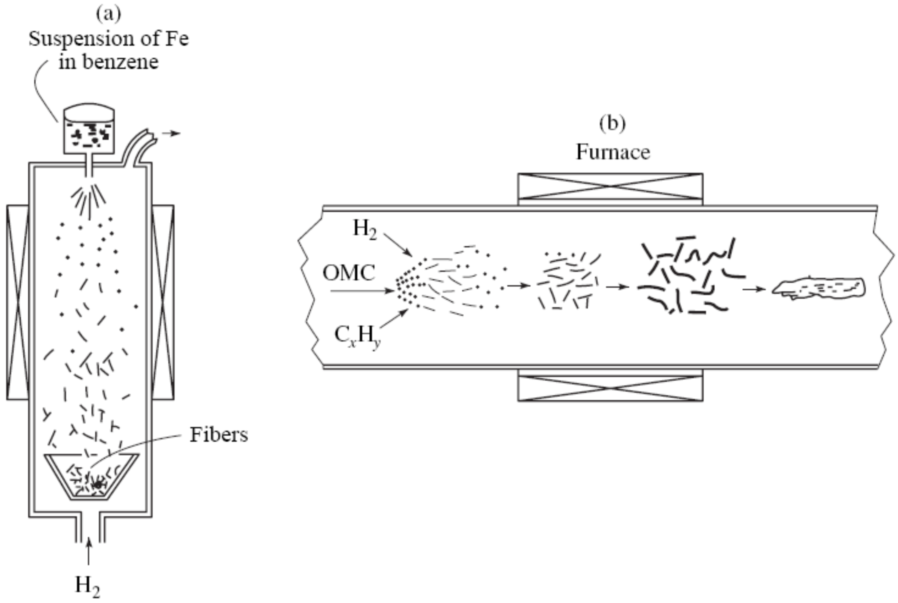

Figure 1-9 Schemes of the growth of vapor grown carbon fibers in a gas flow: (a) a catalyst is introduced into the reactor as a suspension in a liquid hydrocarbon and (b) volatile organometallic compounds (OMC) are used[81].

Two main models are used to describe the growth of vapor grown carbon nanofibers on a substrate and in a gas flow[81, 166], as schematized in **Figure 1-10**. In both models, the catalyst particle is used as seed and trapped by a growing fiber. At last, each carbon nanofiber will be covered with a metal microcrystal cap (**Figure 1-10**, inserted photo). The length of the nanofibers (up to several tens of centimeters) grown with the model (a) is much larger than the length of the fibers (several millimeters) grown from the model (b).

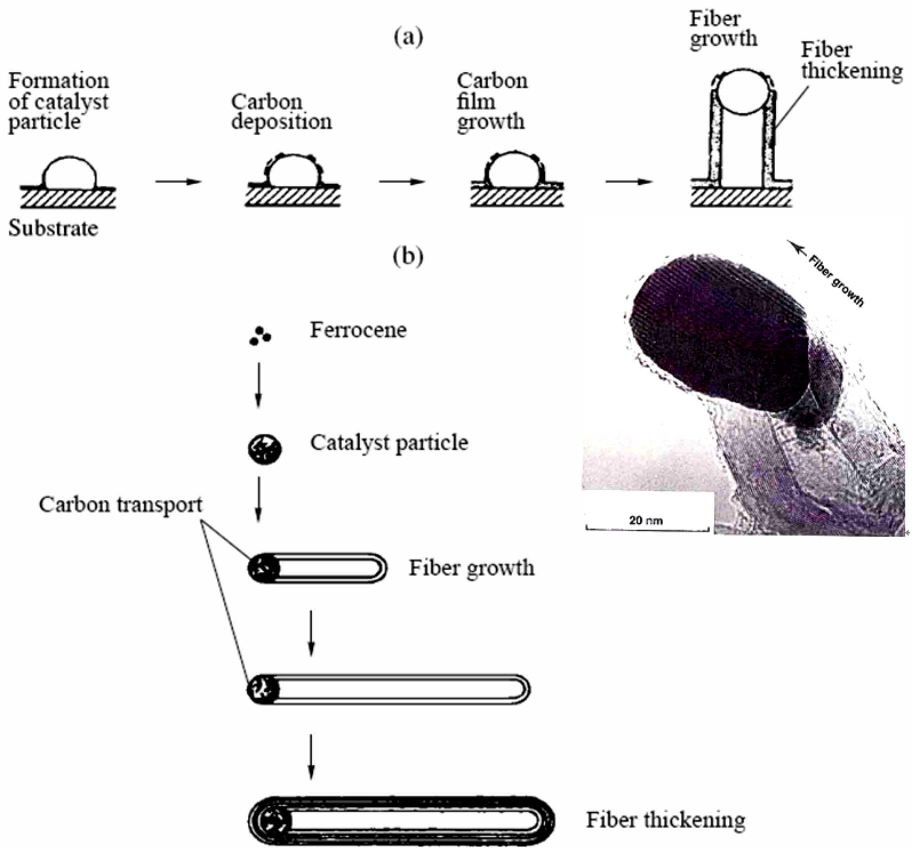

Figure 1-10 Models of the growth of vapor grown carbon nanofibers, (a) on a substrate and (b) in a gas flow. Insert: seeded metallic particle at the end of the growing carbon nanofiber[81, 166].

1.4.2.3. Electrospinning for Synthetic polymer nanofibers

Electrospinning is a versatile and fascinating technology to produce ultra-fine fibers with diameter from several micrometers to a few nanometers. So far, huge number of materials such as polymers, composite ceramics, metals, carbon nanotubes, even bacteria and virus can be fabricated/incorporated into micro/nano fibers by directly electrospinning or through post-spinning process. Many publications including reviews and research papers were focused on the process, the properties and the applications of electrospinning/electrospinning nanofibers[124, 125, 151, 153, 167-174]. Since 2000, an explosive development was taken place on electrospinning field as proved by the exponentially increasing of the publications on electrospinning in the past nearly 20 years (**Figure 1-11**).

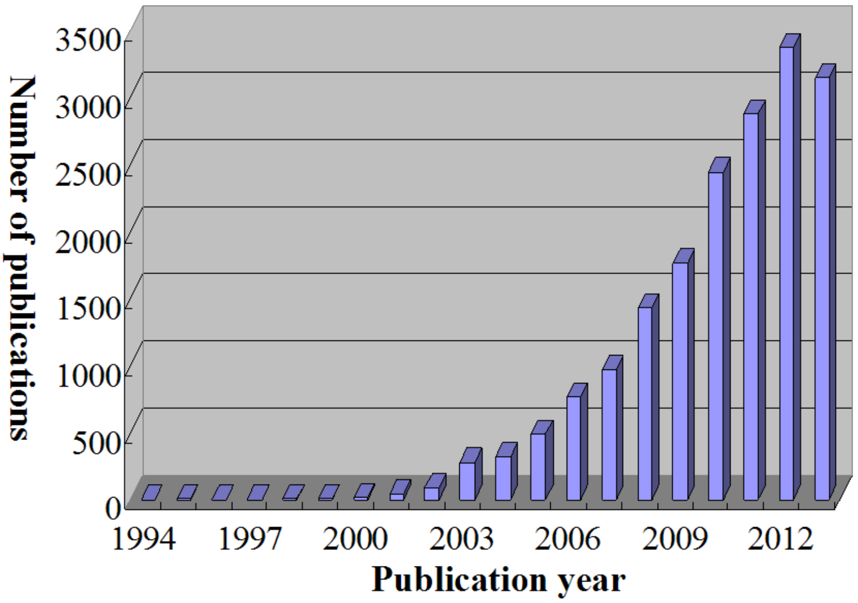

Figure 1-11 The annual number of publications on the subject of electrospinning, as provided by the search engine of SciFinder Scholar. For 2013, there are already 1317 publications before May 27.

Electrospinning can be considered as a fiber formation process driven by electrostatic field. The basic set-up for electrospinning usually consists of three parts: a high voltage power supply, a spinneret, and a collector (**Figure 1-12**).

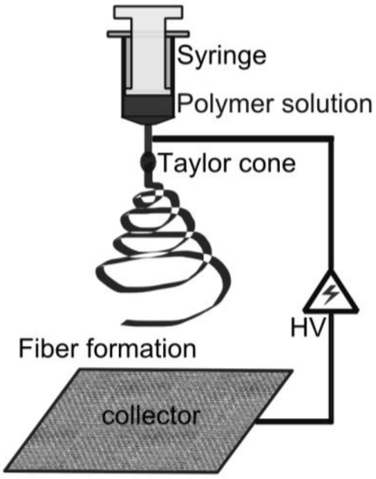

Figure 1-12 Basic set-up for electrospinning.

During the electrospinning, a polymer solution is passed through the spinneret and form a droplet at the tip of the spinneret because of the surface tension of the liquid. When the high voltage power is applied to the spinneret/droplet and continuously increased, the droplet will be charged and the shape of the droplet will start to elongate into a conical shape known as “Taylor cone”[175]. In this case, the critical applied voltage is achieved. Once the electrostatic force overcomes the surface tension of the droplet, a fine charged jet will be ejected from the bottom of the Taylor cone. Subsequently, the fine charged jet undergoes a series of whipping instabilities due to the electrostatic field and elongates into thin fibers accompanied by a fast evaporation of the solvent. In most case, stable and unstable electrospinning jet can be observed during the electrospinning process[176]. When the applied external electrostatic force is smaller than the critical voltage, the jet will be broken into droplet, which is called “Plateau-Rayleigh instability”[177-179]. If the applied external electrostatic force exceeds the critical voltage in a certain range, the stable electrospinning jet can be obtained. When much bigger external electrostatic force than the surface tension is applied, two, three and even four electrospinning jets will be formed from only one droplet (**Figure 1-13**)[180].

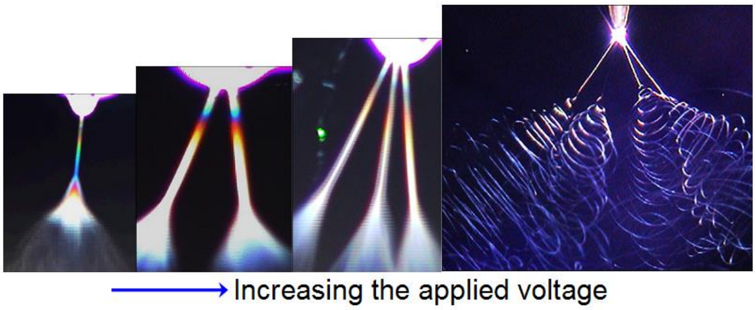

Figure 1-13 Number of electrospinning jets as increasing the applied voltage[180].

Besides the effective of the applied voltage, actually three main factors will have effects on the electrospinning process and the morphology of the resultant fibers (**Figure 1-14**)[181-186]. The first class of parameters is from the set-up of electrospinning, such as the feeding rate, the diameter and the shape of spinneret, the distance between the collector and the spinneret tip, and the shape of the collectors. The second class of parameters is from the polymer solution, such as the properties of the polymers (type, molecular weight, polymer dispersity index, etc.), the properties of the solvents (types, boiling point, dielectric constant, surface tension, etc.), the properties of the polymer solutions (concentration, viscosity, rheological behavior, electric conductivity, surface tension, etc.) and the additives (salts, surfactants). The third class of parameters is from the ambient, such as the relative humidity, temperature, and the gas velocity in electrospinning set-up. Therefore, there are no universal parameters for the electrospinning of every polymer. However, by varying the parameters mentioned above, a huge number of polymer particles/fibers with different macro or micro morphologies/structures can be fabricated through electrospinning.

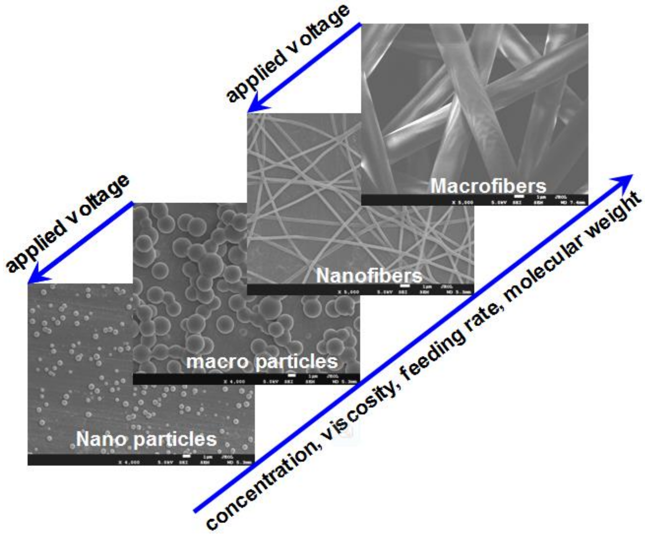

Figure 1-14 The effect of some electrospinning parameters on the formation and the morphology of the particles and fibers.

1.4.3. How strong of nanofibers?

As described in **Section 1.4.1.**, size effect of mechanical properties can be observed when the fiber diameter decreases from micro- down to nano-dimensions[1-3, 5, 125, 128-133]. As reinforcement, it is better to use stronger fibers to reinforce composites. That’s why so many studies focus on using nanofibers (cellulose nanofibers/cellulose nanowhiskers[146-148, 156], carbon nanofibers[25, 187] and electrospun nanofibers[124, 125]) to reinforced polymer matrixes. In the following, a short introduction about the mechanical properties of nanofibers and their composites will be presented.

1.4.3.1. Cellulose nanofibers/nanowhiskers (CNFs/CNWs)

The structures of cellulose nanofibers/nanowhiskers (CNFs/CNWs) determine that CNFs/CNWs have excellent mechanical properties[146-148, 188]. As shown in **Figure 1-15**, cellulose has a linear chain ringed structure with the repeat unit comprised two anhydroglucose rings joined via a β-1,4 glycosidic linkage. This special rigid structure make CNFs/CNWs high elastic modulus along the cellulose crystal axial direction and make them good candidates as reinforcement[146-148, 156, 188]. As mentioned by Moon et al., cellulose type Ⅱ has a modeling elastic modulus in axial direction of 98-109 GPa and tensile strength of 4.9-5.4 GPa, and the experimental elastic modulus in axial direction of 9-90 GPa and tensile strength of 0.2-1.0 GPa, respectively[148]. Shimazaki et al. reported an increased storage modulus of elasticity of the nanocomposites (3.7 GPa for epoxy resin and 5.0 GPa for CNF reinforced epoxy resin at 80 ^{o}C) by CNFs with diameter about 30 nm[143]. Peresin et al. studied cellulose nanocrystals as reinforcement to fabricate polyvinyl alcohol (PVA) nanofiber composites[189]. A 3-fold increase of the storage modulus of fully hydrolyzed PVA were presented by using 15 wt% of cellulose nanocrystals. Suryanegara et al. found that microfibrillated cellulose not only accelerated the crystallization of PLA, but also greatly improved the tensile modulus and strength of neat PLA[190]. 20 wt% microfibrillated cellulose in PLA could result the storage modulus of crystallized PLA at 120 ^{o}C from 293 MPa to 1034 MPa.

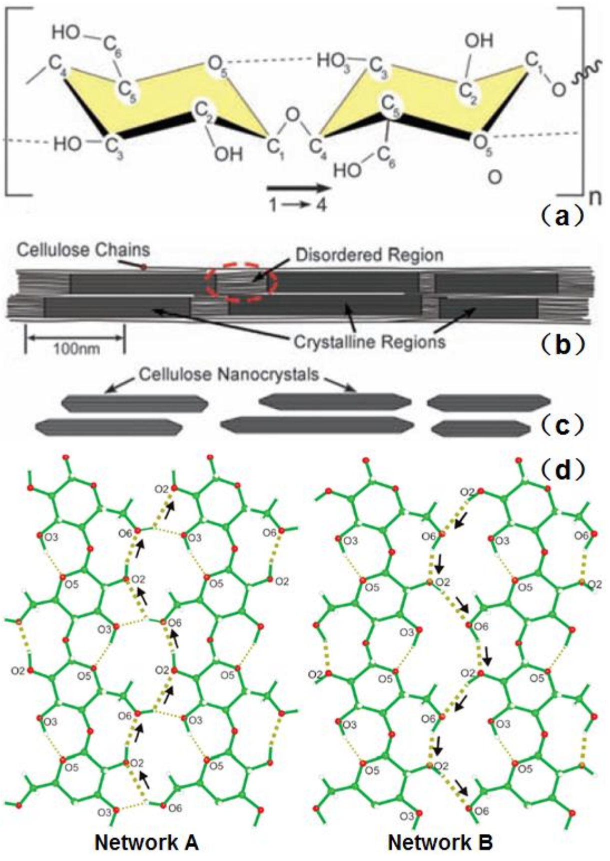

Figure 1-15 Schematics of (a) single cellulose chain repeat unit, showing the directionality of the 1 - 4 linkage and intrachain hydrogen bonding (dotted line), (b) idealized cellulose microfibril showing one of the suggested configurations of the crystalline and amorphous regions, (c) cellulose nanocrystals after acid hydrolysis dissolved the disordered regions[148], and (d) thick dotted lines indicate the proposed cooperative networks of hydrogen bonds, with arrows indicating the donor-acceptor-donor directions for the A and B schemes. Thin dotted lines indicate the O3-H···O5 hydrogen bonds, and for the A network, the O6-H···O3 linkage[191].

1.4.3.2. Carbon nanofibers

As described in **Table 1-4**, carbon fibers with several to tens of micrometers have tensile strength of 600-4000 MPa and Young's modulus of 30-300 GPa[81]. However, carbon nanofibers present simultaneously ultrahigh-strength of 12000 MPa and ultrahigh-modulus of 600 GPa[81]. Zussman et al. first presented the tensile strength and Young's modulus of the single electrospun PAN-based carbon nanofibers of

0.32-0.9 GPa and 70 GPa respectively[192]. Recently, Arshad et al. reported the individual electrospun carbon nanofibers with 3.5 ± 0.6 GPa tensile strength and 172 ± 40 GPa elastic modulus from electrospun polyacrylonitrile through optimization of electrospun parameters, stabilization and carbonization temperatures[138]. Zhou et al. firstly reported that electrospun carbon nanofiber bundles (ECNB) had a tensile strength of about 550 MPa and a Young's modulus of about 58 GPa[193]. Later, Zhou et al. further improved the tensile strength of the ECNB by using phosphoric acid (PA) as stabilization promoter[194]. As we can see from the above, the mechanical properties of carbon nanofibers are quite different from one another. Those differences maybe come from the differences of the fabrication method, the fiber structure and the diameter of the fibers. Nevertheless, all the mechanical properties of carbon nanofibers mentioned above are high enough as reinforcements. Bao and Tjong reported that the strength and Young's modulus of polypropylene (PP) were improved by adding only 0.1 wt% carbon nanofibers, and the yielding responses of the PP/carbon nanofiber nanocomposites can be described successfully by the Erying's equation and the reinforcing index[195]. Sandler et al. described the addition of CNFs could lead to a linear increase in tensile and bending stiffness and tensile yield stress and strength of poly(ether ether ketone)[196]. Ma et al. demonstrated that the compressive strength and torsional moduli of PET/CNF (5.0 wt%) composite fibers were considerably higher than those of the PET fibers[197].

1.4.3.3. Electrospun nylon-6 nanofibers

Nylon-6 is a high performance polymer. Its electrospun nanofibers exhibited excellent mechanical properties. As reported by Lin et al., single nylon-6 nanofiber had a strength of 230 MPa and Young's modulus of 4-5 GPa, which were revealed by interaction with streams of air[3]. Li et al. presented the single nylon-6 nanofiber had a high Young's modulus of about 30 GPa, which was much larger than the highest value that had been achieved for conventional nylon-6 fibers, 15 GPa[198]. Besides, nylon-6 nanofibers also exhibited excellent toughness of 22 J/g[199]. Therefore, many reports focused on using electrospun nylon-6 nanofibers as reinforcement to make composites with poly (methyl methacrylate)[144], melamine-formaldehyde[199], polycaprolactone[200], polyaniline[201], thermoplastic polyurethane[202, 203], and so on.

1.4.3.4. Electrospun polyimide (PI) nanofibers

Polyimide nanofibers are one class of high performance materials with excellent thermal stability and mechanical properties. Huang et al. first reported that aligned BPDA/PDA PI electrospun nanofiber belts possessed mechanical properties of up to 664 MPa tensile strength and 15.3 GPa tensile modulus[204]. Later, Chen et al. reported a high performance electrospun aligned copolyimide nanofiber belts with ultra-high tensile strength of 1.1 GPa[205]. Compared to the bulked PI nanofiber belts, single PI nanofiber exhibited higher tensile strength and tensile modulus[137, 206]. Single co-PI nanofibers possessed tensile strength of 1112-2387 MPa and tensile modulus of 21.35-52.31 GPa[137]. Single BPDA/PDA PI nanofibers were reported 1544-1810 MPa tensile strength and 59.6-89.3 GPa[206]. However, there are only several papers concerned using electrospun PI nanofibers as reinforcements. Chen et al. reported that 2 wt% CNT/PI aligned nanofibers could result an 138% increase of tensile strength[207]. Aligned PI nanofibers were also used as skeletal framework to reinforce polyamide 6 and the results showed that 700% and 500% improvements on tensile strength and modulus respectively were obtained compared to neat polyamide 6[206]. Another work done by our group revealed that only 2 wt% of short PI nanofibers could result in an improvements of 53% and 87% respectively in tensile strength and modulus as compared to those of neat PI film, and the strength of the composites films with only 2 wt% of short PI nanofibers was as high as that of a composite with 38 wt% of as-electrospun PI nanofiber mats[208].

1.4.3.5. Other electrospun synthetic polymer nanofibers

Except the nanofibers mentioned above, there are other electrospun synthetic polymer nanofibers used as reinforcements in composite materials. Electrospun polybenzimidazole (PBI) nanofibers could result ten times of Young’s modulus and twice of the tear strength improvement on PBI reinforced styrene-butadiene rubber (SBR) compared to the unfilled SBR, as reported by Kim et al[209]. Electrospun polyvinyl alcohol (PVA) nanofibers were used to reinforce Nafion membrane for fuel cell applications[210]. Papkov et al. reported that electrospun polyacrylonitrile (PAN) nanofibers had size effect on the elastic modulus and toughness[128]. Single PAN nanofiber with diameter of 138 nm even possessed tensile strength and tensile modulus more than 1500 MPa and 45 GPa respectively[128]. Wu et al. found that PAN nanofibers could reinforce PMMA matrix and Sun et al. reported using PAN-PMMA core-shell nanofibers to reinforce dental composites[211, 212].

1.5. Fabrication of fiber reinforced polymer composites

As for the fiber reinforced polymer composites, the fibers as reinforcement could be embedded in the polymer matrix in forms of continuous fibers (nonwovens, knitted fabrics, and aligned fiber mats), and short fibers (CNTs, short microfibers and short nanofibers) via different fabrication methods, such as dip-coating, film-stacking, solution casing, in-situ polymerization, melt blending and electrospinning.

Unlike the short fibers, the continuous fibers can’t be homogeneously dispersed into the polymer solutions or melts because of the entanglement of the long fibers. Therefore, the continuous fibers in the forms of nonwovens, knitted fabrics and aligned fiber mats could be fabricated into composites by dip-coating and film-stacking (layer-by-layer hot-pressing and layer-by-layer deposition). Dip-coating is performed by dipping the continuous fibers into the polymer matrix solutions or melts to form composites. Labronici and Ishida had a review on toughening composites via fiber coating[213]. Recently, our group studied the wetting behavior and compared the mechanical properties of nylon-6 nanofiber reinforced melamine formaldehyde (MF) with dip-coating method and the method by passing the MF solution through the nylon-6 fiber mat[199]. Film-stacking provides effective ways to prepare fiber reinforced polymer laminates. Huda et al. introduced a biocomposite with kenaf fiber reinforced polylactic acid (PLA) by compression molding using film-stacking[57]. Our group proposed a novel layer-by-layer procedure combined solution casting, electrospinning and film-stacking to produce nylon-6 nanofiber reinforced high strength, tough and transparent polyurethane composites[202]. Akangah et al. prepared sixteen-ply quasi-isotropic epoxy/carbon fiber composite laminates with nylon-66 nanofiber interleaving[214].

In order to maximize the advantages of short fibers as reinforcement, the short fibers should be well distributed in the polymer matrix to enhance the interfacial interaction with the matrix. Several processing methods including solution casting, in-situ polymerization, melt blending, electrospinning, etc., have been taken to prepare short fiber reinforced polymer composites as described in the past review articles. For example, CNTs could be incorporated into the polymer matrix by solution casting[215, 216], electrospinning[217, 218], melt mixing[219, 220], shear mixing[221, 222], melt fiber spinning[223, 224] and in-situ polymerization[225-227]. Other short traditional fibers, such as glass[111], carbon[71, 122], nature plant[47, 48], nylon[116], cellulose whisker[228] and aramid[117-120], were usually incorporated into the polymer matrix by melt mixing and solution casting. Till now, no studies have been concerned with short electrospun nanofiber reinforced composites, but we believe that the methods suitable for fabricating CNT/short fiber reinforced composites could also be applied for preparing short electrospun nanofiber reinforced composites.

1.6. Factors affecting the properties of fiber reinforced composites

Fiber reinforced composites consist of fibers, matrix and the interface between fibers and matrix. The fiber reinforcements impart their excellent properties, especially mechanical properties, to the matrix. The interface plays an important role in transferring load between fibers and matrix. The distributions of fibers in matrix affect the isotropy of anisotropy properties of the composites. Therefore there are three main factors, the original mechanical properties of fibers, the interfacial interaction between fibers and matrix and the distribution of fibers in matrix, affecting the properties of fiber reinforced composites.

1.6.1. Mechanical properties of fibers

As reinforcements, fibers often provide high strength, modulus, stiffness, hardness and excellent thermal stability to the polymer matrix. **Figure 1-16** shows the mechanical properties of common materials, like carbon, steel, nylon and so on. Stain steel has high strength and modulus. However, because of the high density, the specific strength and specific modulus are smaller than those of most of the high performance fibers, such as carbon, Zylon, Kevlar, polyimide, and glass fibers. As one kind of high performance synthetic fibers, nylon has been proved to be good reinforcement to make composites because of the good strength, toughness, and wear-resistance. Considering the cost of the materials, Zylon fibers, Kevlar fibers, and high quality carbon fibers are usually applied as reinforcements in high-tech fields, such as aerospace, military, and automobiles. Nevertheless, as the development of the manufacturing technology proceeds, more and more civil equipment have also used high performance fibers as reinforcements.

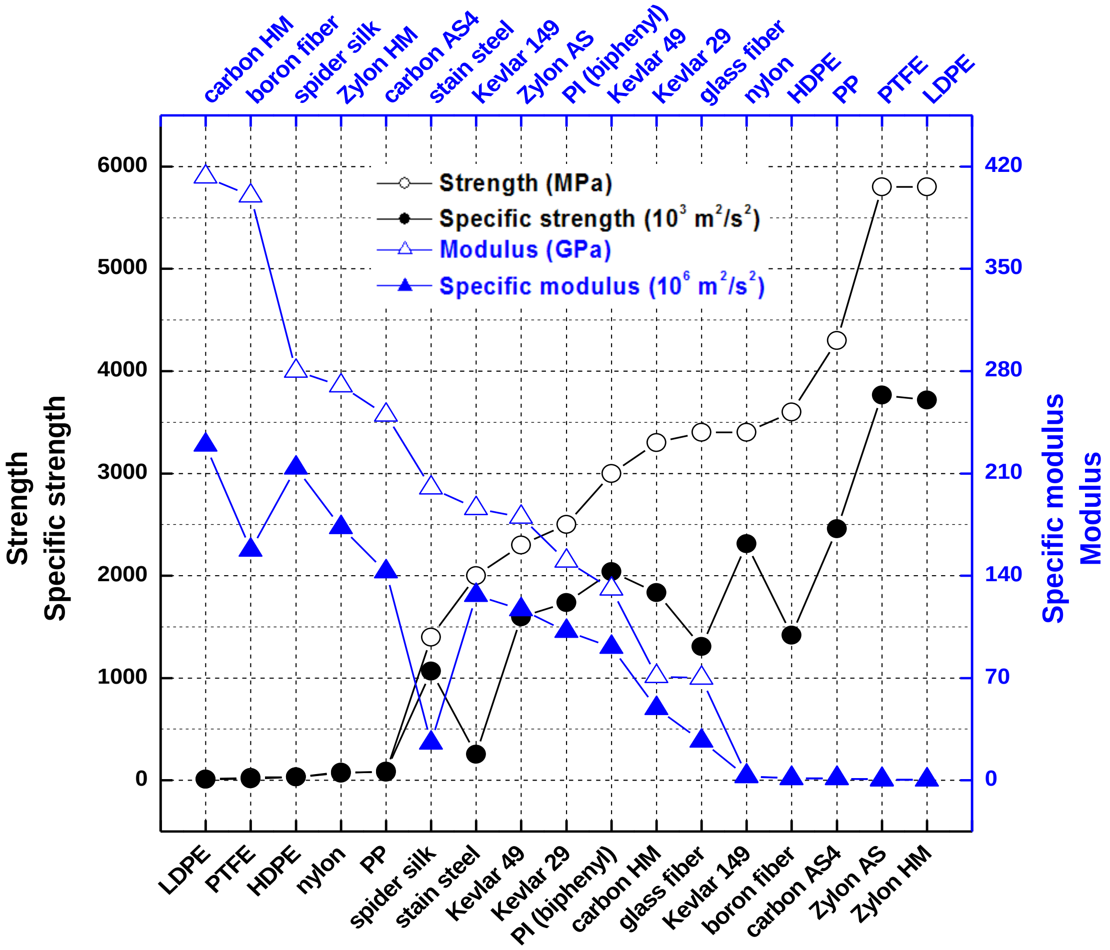

Figure 1-16 Summary of mechanical properties of various materials. (△) and (▲) for the top X axis, and (○) and (●) for the bottom X axis.

As the nanotechnology developed, nanofibers plays more and more important role in fabricating composites as reinforcements. Nanofibers have quite excellent mechanical properties compared to microfibers and films because of the stronger orientations of both chain molecules and crystals and the less flaws in nanofibers. As **Figure 1-17** presented, the mechanical properties such as tensile strength and modulus are quite different according to the formation of the materials. As compared to the nylon-6 film, nylon-6 microfiber has better mechanical properties while the best mechanical properties are exhibited by nylon-6 nanofiber[1-3]. The same trend is also happened to high performance polyimide (PI). PI film (Kapton®, DuPont™) has a tensile strength of 230 MPa and modulus of 2.5 GPa, and PI microfiber has higher tensile strength of 310 MPa and higher modulus of 15 GPa[229]. However, the best mechanical properties are found in PI single nanofiber. PI single nanofiber has a tensile strength up to 2500 MPa and modulus up to 42 GPa[5].

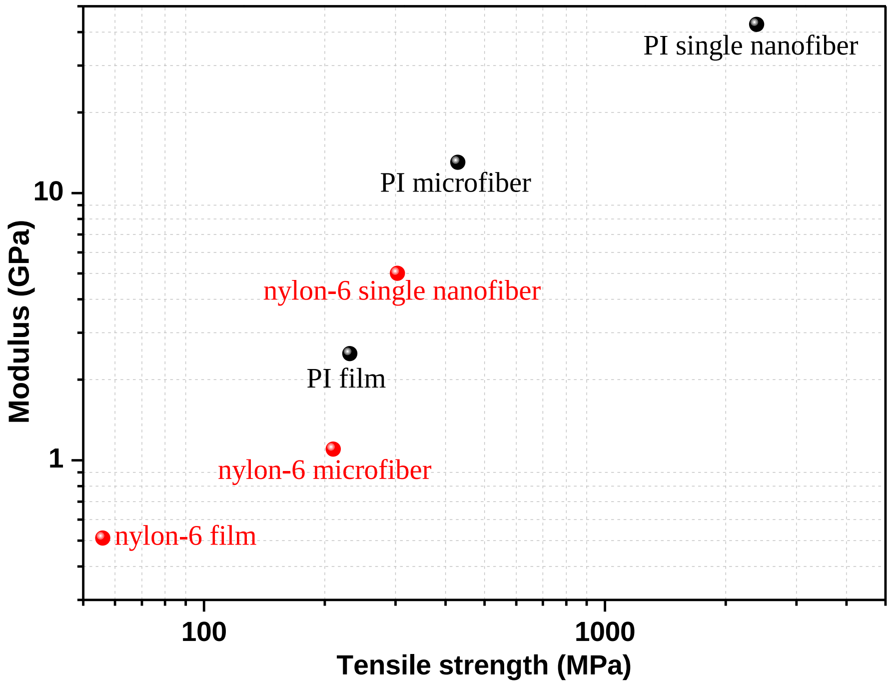

Figure 1-17 Summary of mechanical properties of single nylon-6 and polyimide (PI) electrospun nanofibers compared with other formations (nanofiber mat, film, microfiber, etc.). Nylon-6 film [5]; nylon-6 microfiber [2]; nylon-6 single nanofiber [1, 3]; PI microfiber [229]; PI single nanofiber [4, 5].

1.6.2. Fiber/matrix interfacial interaction

The fiber/matrix interface plays an important role in load transferring between fibers and matrix and determines many properties of the composites in addition to mechanical properties. The fiber/matrix interfacial interactions could be enhanced by mechanical, physical and chemical ways[25, 125, 213]. Mechanical interlocking and entanglement in the fiber/matrix interface could effectively improve the mechanical properties of composites[199]. Physical interaction mainly refers to the intermolecular forces, such as H-bonding, between the fibers and polymer matrix[202]. Chemical interaction refers to the chemical bonding between the fibers and matrix[25], which can largely increase the adhesive bond strength by preventing breakage at a sharp interface.

1.6.3. Distribution of fibers in matrix

The distribution of fibers in a matrix depends on the formation of fibers. Fibers in the forms of woven, nonwoven, and aligned fiber mats were incorporated into the polymer matrix by a lamination way. These laminated composites have anisotropic mechanical properties due to the aligned distribution of fibers. Generally, better mechanical properties are obtained in x-direction and y-direction than in z-direction because the fibers are aligned along the x-y plane and no fibers are aligned in the thickness direction (z-direction). As for the aligned fibers reinforced composites, mechanical properties are different in three dimensions and best mechanical properties would be obtained in fiber aligned direction.

As for the short fiber reinforced composites, a homogeneous distribution of fibers in matrix is necessary to obtain high performance composites. Several factors including aspect ratio (the length to diameter ratio) of fibers, fiber concentration, and fiber orientation, have effects on the distribution of fibers in matrix[109, 110, 230]. According to Agarwal and Broutmann's theoretical analysis on the mechanism of stress transfer between fibers and matrix[231], the aspect ratio of fibers are a significant parameter to control the fiber dispersion. Higher aspect ratio than the critical value results in the aggregation and entanglement of fibers during dispersing short fibers into polymer solutions. Lower aspect ratio than the critical value leads to the insufficient stress transferring between fibers and matrix. An aspect ratio of more or less 150 is suitable for traditional short fibers (micro fibers)[110, 232, 233] while bigger aspect ratio of more or less 500 is considered sufficient for the nanofibers[209]. Fiber concentration in matrix plays an important role in reinforcing the polymer matrix in many reports[33, 234, 235]. An appropriate concentration of fibers gives homogeneous distribution of fibers in matrix and good fiber/matrix interaction. A lower concentration of fibers leads to lower mechanical properties of composites while a higher concentration of fibers results in dispersion problems. Short fiber orientation is another aspect of fiber distribution in matrix[236-238]. During the processing of short fiber reinforced composites, the fibers tend to align along the flow direction, which gives different mechanical properties of composites in different directions. So short fiber reinforced composites with pre-designed properties could be fabricated by pre-designed processing methods.

1.7. References

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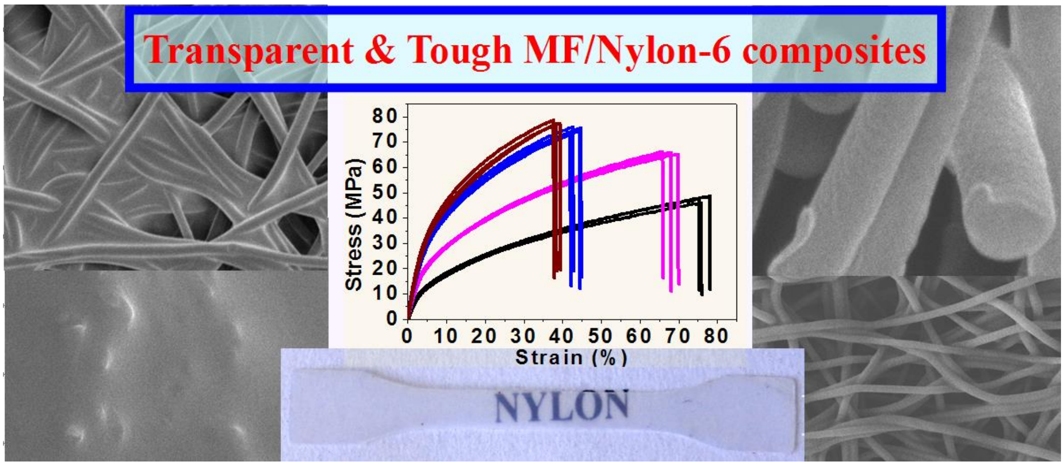
2. Cumulative part of dissertation

This dissertation contains four publications presented in **Sections 2.1** to **2.4**. This thesis is concerned with the preparation of nanofibers via electrospinning technology, the fabrication of nanofiber reinforced polymer composites and their properties including thermal stability, optical properties, and mechanical properties. My research efforts focused on new methods of composite fabrication and effects of different parameters including the length of nanofiber, the amount of nanofiber, the interface interaction and the H-bonding between nanofibers and matrix on the reinforced properties of composites. In this thesis, continuous and short nylon-6 nanofibers and polyimide nanofibers were prepared as reinforcements by electrospinning and post-cutting process. Dip-coating, filter-coating, layer-by-layer deposition combined with electrospinning and film casting, short nanofiber dispersion and film casting were adopted to fabricate nanofiber reinforced composites. The results showed that both continuous and short electrospun nanofibers could effectively reinforce polymer matrix and the same reinforcement on composites could be obtained by very small amounts of short nanofibers compared to the continuous nanofiber mats.

In the following sections, a summary of the key results obtained within the scope of this dissertation will be presented. Complete coverage of the experimental results and conclusions can be found in **Chapter 3**.

2.1. Tough and transparent nylon-6 electrospun nanofiber reinforced melamine-formaldehyde composites



This work has already been published in:

Shaohua Jiang, Haoqing Hou, Andreas Greiner, and Seema Agarwal*, "Tough and Transparent Nylon-6 Elestrospun Nanofiber Reinforced Melamine-Formaldehyde Composites", *ACS Applied Materials & Interfaces*, **2012**, *4*, 2597-2603

Specific contributions by authors:

The plan and the execution of this project was done by me. The manuscript was written by me. Many valuable suggestions and discussions for this project were proposed by Prof. Dr. Haoqing Hou and Prof. Dr. Andreas Greiner. Prof. Dr. Seema Agarwal was in charge for general guidance and supervision for this project, and helped me in final version of the manuscript.

Melamine-formaldehyde (MF) resin and its derivatives have been extensively used in furniture, construction materials, tableware, adhesives, coatings, abrasive cleaner, textile treatment and other materials requiring enhanced mechanical properties. One of the disadvantages of those materials is their brittleness. Nylon-6 electrospun nanofibers have excellent mechanical properties, such as high tensile strength and toughness, and have also been applied as reinforcements to make many composites. Therefore, in this work, nylon-6 electrospun nanofiber mats were applied to reinforce MF resin via dip-coating (**Figure 2-1**) and filter-coating (**Figure 2-2**). These two methods resulted in a drastic effect of the quite different wetting behavior of reinforcing fiber mat by the MF resin on both morphology and mechanical properties of the composites.

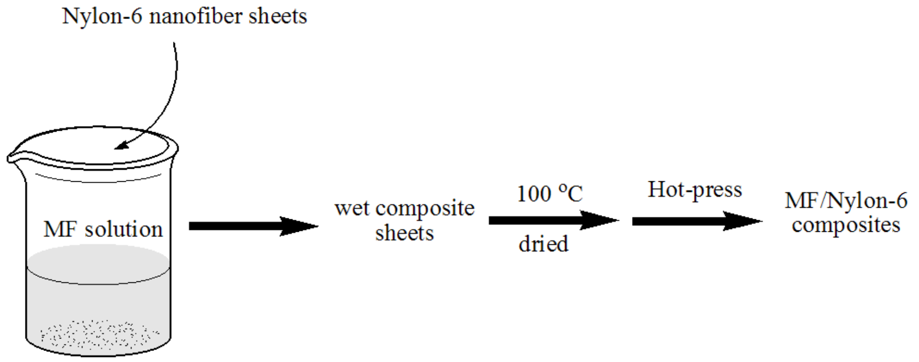


Figure 2-1 Schematic process for the preparation of the MF/nylon-6 nanocomposites by immersing and hot-pressing (method 1).

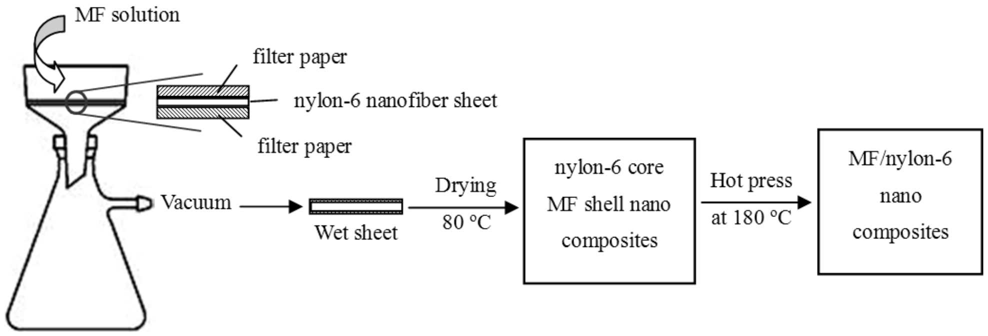


Figure 2-2 Schematic process for the preparation of the MF/nylon-6 nanocomposites by passing MF solution through the nylon-6 nanomat and followed by hot-pressing (method 2).

The resulting composites made by method 1 exhibited quite different morphologies depending on the concentration of the MF solution applied (**Figure 2-3A** and **3B**). A deposition of MF resin on nylon-6 nanofibers appeared when nylon-6 nanofibers immersed in a low concentrated MF solution (5 wt%). However, immersion in highly concentrated (15 wt%) led to the deposition of MF resin both on fibers and in-between the fibers. Compared to the morphologies led by method 1, method 2 resulted a homogenous deposition of MF resin on/around nylon-6 nanofibers, which presented a core-shell morphology as shown in **Figure 2-3C**. Both methods applied for composite fabrication needed hot-pressing. However, the morphologies of the resulted composites after hot-pressing were quite different as shown in **Figure 2-4**. Both samples exhibited a similar content of MF (38 wt% and 34 wt%). However, compared to the morphology of composite made by method 1, composite made by method 2 presented a homogenous morphology with no holes, cracks and fibers.

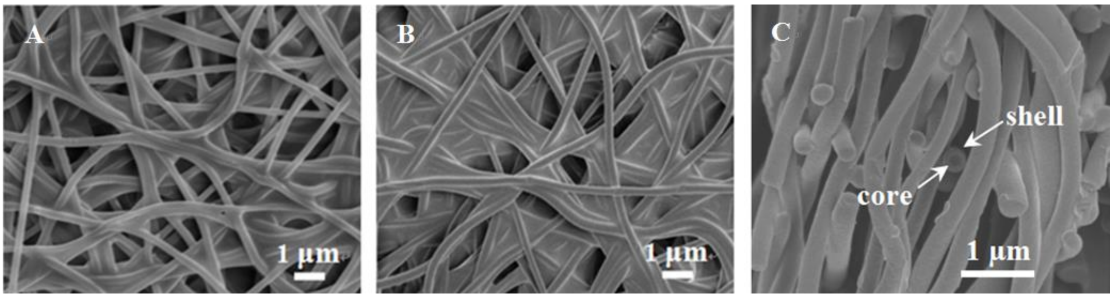


Figure 2-3 SEM images of MF/nylon-6 nanocomposite prepared by method 1 with MF concentration of 5 wt % (A) and 15 wt % (B) and SEM image of MF/nylon-6 nanocomposite prepared by method 2 (C).

The quite different wetting behavior and morphologies led to the differences of mechanical properties of the composites made by the two methods. As revealed by **Table 2-1**, due to the defects such as holes, cracks and bad interface between nylon-6 nanofibers and MF resin (**Figure 2-4A**), the nylon-6/MF composite film with 38 wt% MF made by method 1 showed a tensile strength of 54.5 MPa, elongation at break of 24.8% and toughness of 7.8 J/g. As a comparison, the homogenous nylon-6/MF composite film (**Figure 2-4B**) with 34 wt% MF made by method 2 showed a significant increase regarding tensile strength of 77.9 MPa, elongation at break of 38.5% and toughness of 17.6 J/g.

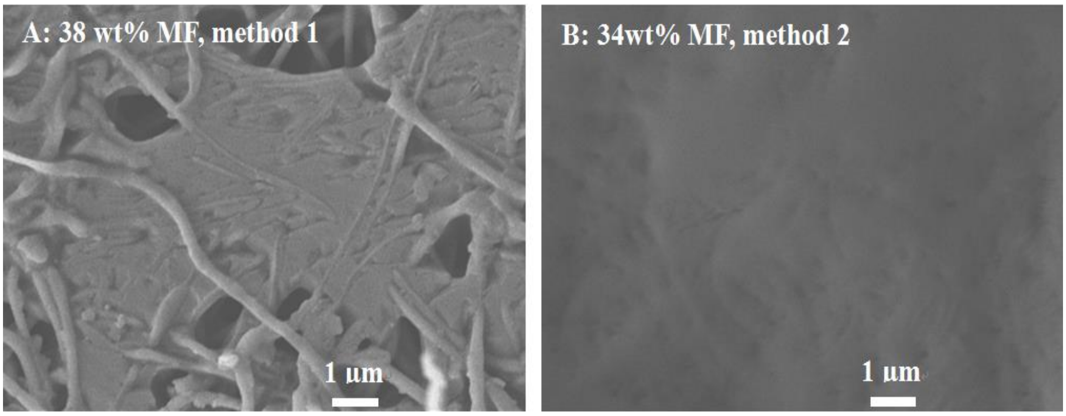


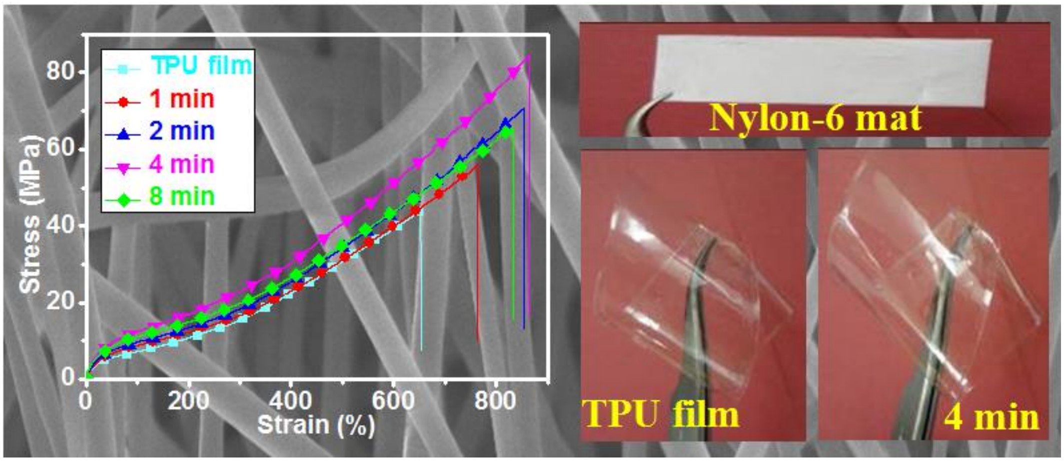
Figure 2-4 Morphology comparison of the nylon-6/MF nanocomposites after hot-pressing.

Table 2- 1 Mechanical properties of MF/nylon-6 nano composites made by method 1 and method 2* with different contents of MF resin.

MF content (wt%)	Stress (MPa)	Strain (%)	E modulus (2%) (GPa)	Toughness (J/g)
38	54.5 ± 1.4	24.8 ± 1.1	0.96 ± 0.09	7.8 ± 0.36
34*	77.9 ± 0.8	38.4 ± 0.8	0.85 ± 0.05	17.6 ± 0.45

As a conclusion, nylon-6/MF composite films were prepared by two different methods using electrospun nylon-6 nanofiber mats as reinforcement. Obvious reinforcement in mechanical properties of the MF resin was observed using electrospun nylon-6 nanofiber mats. A drastic effect of wetting behavior of the reinforcing nanofibers by the MF resin on both morphology and mechanical properties was presented. The core-shell morphology resulted from wetting nylon-6 nanofibers by passing through MF resin solution led to a significant improvement in mechanical properties as compared to the processes by immersing nylon-6 nanofiber mat in the MF resin solution for wetting of the fibers. Either fiber reinforced MF composites or MF glued nylon-6 nanofiber composites could be obtained depending on the amount of the reinforcing nylon-6 nanofiber mats.

2.2. Novel layer-by-layer procedure for making nylon-6 nanofibers reinforced thermoplastic polyurethane composites



This work has already been published in:

Shaohua Jiang, Gaigai Duan, Haoqing Hou, Andreas Greiner, and Seema Agarwal*, "Novel Layer-by-Layer Procedure for Making Nylon-6 Nanofiber Reinforced High Strength, Tough, and Transparent Thermoplastic Polyurethane Composites", *ACS Applied Materials & Interfaces*, **2012**, *4*, 4366-4372

Specific contributions by authors:

I performed the composite preparation and characterization of this work. The concept of novel layer-by-layer method was proposed by me. Gaigai Duan gave me support in interpretation of electron microscopy morphologies. The manuscript was written by me. Prof. Dr. Haoqing Hou and Prof. Dr. Andreas Greiner proposed many valuable suggestions and discussions for this project. Prof. Dr. Seema Agarwal was responsible for guidance and supervision of the project.

As for nanofiber reinforced polymer composites, wetting behavior of nanofibers by the polymer matrix is important. Complete wetted nanofibers by polymer matrix are necessary for high performance nanofiber reinforced composites with reinforced mechanical properties and high transparency. In this work, we developed a novel layer-by-layer procedure based on solution casting, electrospinning, and film stacking (**Figure 2-5**) for preparing highly transparent nylon-6 nanofiber reinforced thermoplastic polyurethane (TPU) composite films. This novel composite fabrication method greatly improved the interaction between nylon-6/TPU interface, and led to a significant improvement on mechanical properties without sacrificing optical properties like the transparency of TPU.

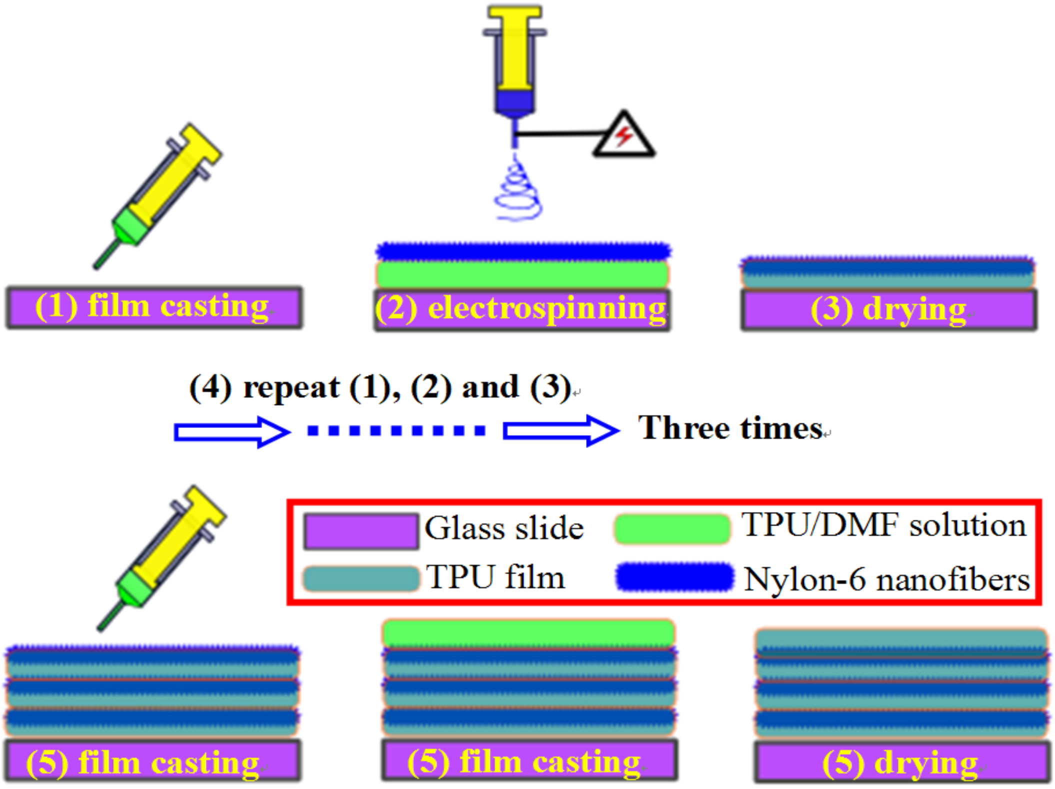


Figure 2-5 Schematic of preparation of nylon-6 nanofiber reinforced TPU composite films.

In this work, nylon-6 nanofibers were used as reinforcement due to (1) their excellent mechanical properties and (2) their insolubility in DMF but quite fast and complete wetting by DMF solvent (**Figure 2-6A**). When nylon-6 nanofibers were directly electrospun on the solid TPU film, we could found the bad contact between nanofibers and TPU resin(**Figure 2-6B**), which provided a poor interfacial interaction between fibers and matrix and led to bad quality composites. As a comparison, the direct deposition of electrospun nylon-6 nanofibers on TPU/DMF solution could achieve good wetting and embedding of reinforcing nylon-6 nanofibers in TPU matrix. The nanofibers could be completely and quickly wetted by the DMF solvent and subsequently sinked into the TPU resin while still maintaining the fiber morphology and forming tight contact with TPU resin (**Figure 2-6C**). The homogeneous distribution and nice embedding of nylon-6 nanofibers in TPU matrix also provided the chance of formation of hydrogen bonding between nylon-6 and TPU, which was proved by the FT-IR shift of carbonyl peak of nylon-6 in composite film.

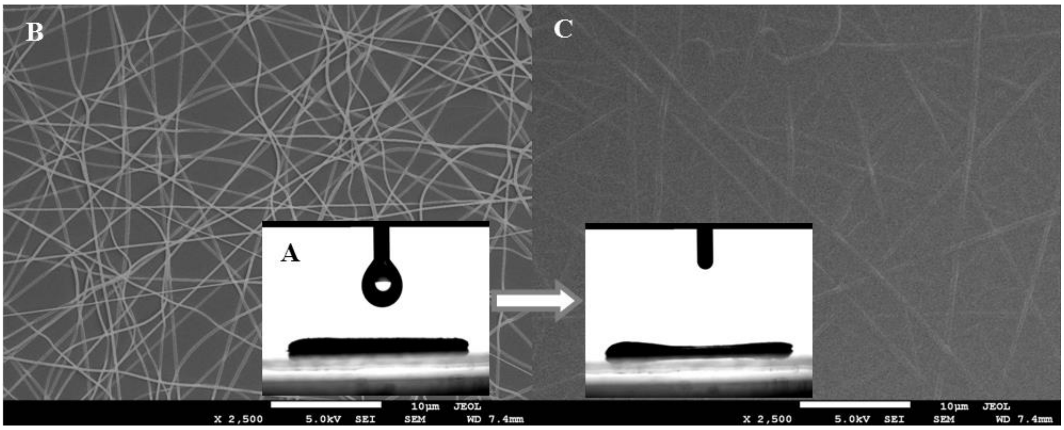


Figure 2-6 DMF wetting behavior of nylon-6 nanofiber mat (A) and surface morphologies of 2-layered TPU/nylon-6 nanofiber composites (B: nylon-6 nanofibers on TPU film; C: nylon-6 nanofibers embedded in TPU resin). Scale bar = 10 µm.

By using this novel layer-by-layer fabricating method, the resulted TPU/nylon-6 composite film presented excellent mechanical properties and transparency with very small amount of nylon-6 nanofibers. As shown in **Figure 2-7A**, only 0.4 wt% amount of the nylon-6 nanofibers (corresponding to 1 min electrospinning for each layer) already showed great reinforcing effects although the optimized improved mechanical properties were obtained with 1.7 wt% (corresponding to 4 min electrospinning for each layer) reinforcing nylon-6 nanofibers. As increasing the electrospinning time, the mechanical properties including tensile strength, elongation at break, E modulus, and toughness first increased until about 4 min electrospinning and then decreased when further increasing the electrospinning time to 8 min. Compared to the high transparency of neat TPU film (transmittance of 96%), **Figure 2-7B** and **7C** also revealed that all the nylon-6 nanofiber reinforced TPU composite films showed very high light transmittance of more than 85% although the transmittance of the composite films was dependent on the amount of nanofibers.

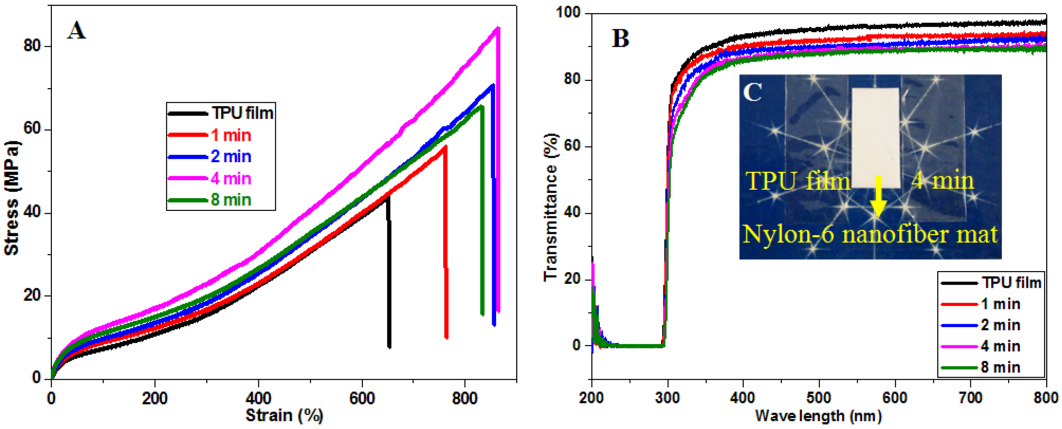


Figure 2-7 Typical stress-strain curves (A), UV-Vis spectra(B) of TPU/nylon-6 nanofiber composites with different electrospinning time for each nanofiber layer and digital photograph (C) of nylon-6 nanofiber mat, transparent neat TPU film and composite film.

To reveal the reasons for the improvement of mechanical properties and the high transparency, the cross-section morphology of the composite films was investigated (**Figure 2-8**). Compared to the smooth cross-section of pure TPU film (**Figure 2-8A**), all the composite films presented a rougher laminated morphology with 3 layers of nylon-6 nanofibers distributing in the TPU matrix (**Figure 2-8B**, **8C** and **8D**). An increasing homogeneously distributed electrospun nylon-6 nanofibers in TPU matrix without any aggregation were observed when increasing the electrospinning time from 2 min to 4 min. When further increasing the electrospinning time to 8 min, larger amount of reinforcing nylon-6 nanofibers were aggregated and formed defects like pull-out nanofibers and holes/voids around the nanofibers. This led to reduction of mechanical properties and the transparency. The reason for the high transparency of the composite films might be due to the small diameter of reinforcing nanofibers (less than 400 nm) and the quite similar refractive index of the nylon-6 (1.53) and TPU (1.51).

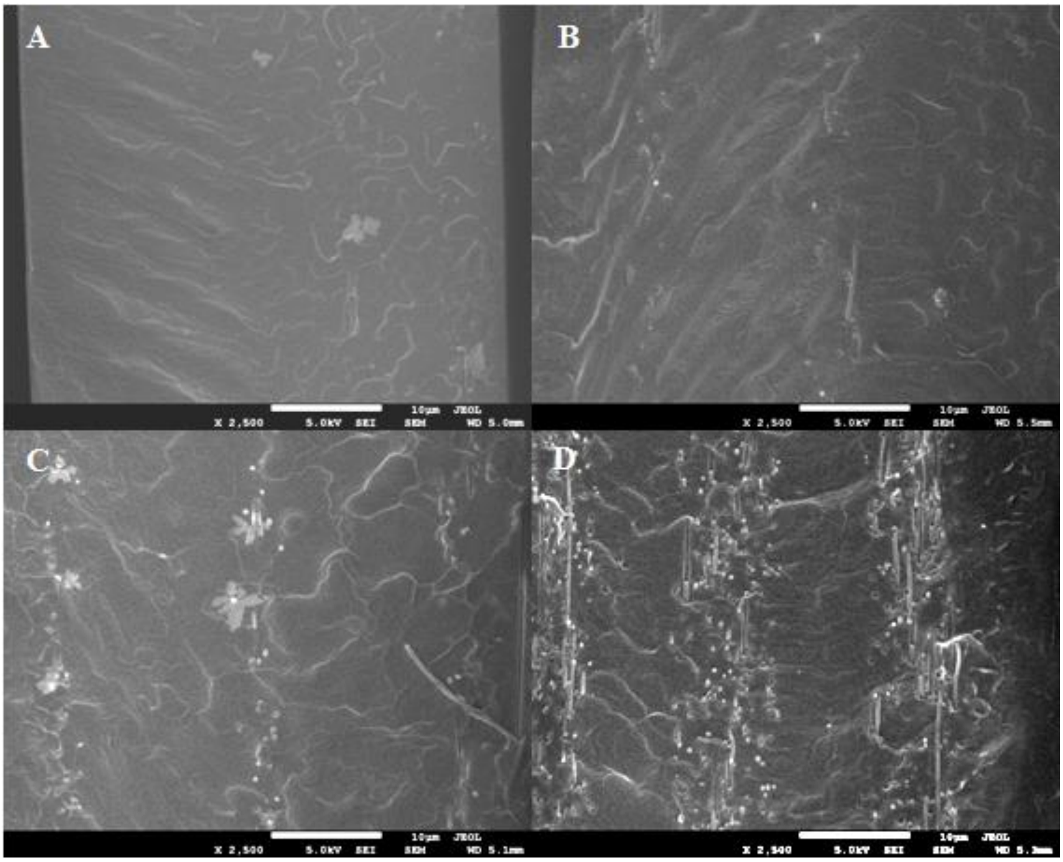
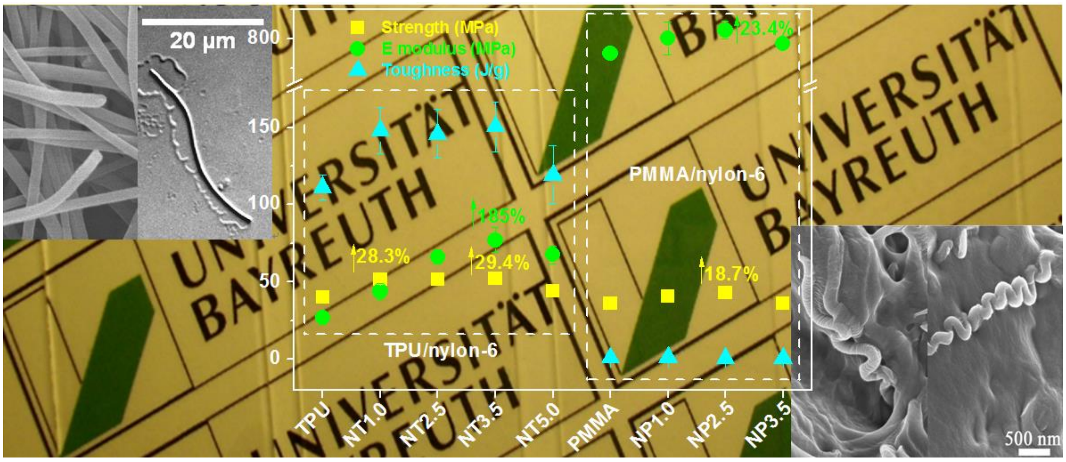


Figure 2-8 Cross-section morphologies of neat TPU film (A) and laminated TPU/nylon-6 composites with 2 min (B), 4 min (C) and 8 min (D) electrospinning time on each layer. Scale bar = 10 µm.

As a conclusion, a successful novel procedure was used to make nanofiber reinforced thermoplastic polyurethane films. This simple process can be extended to other thermoplastic polymers. With this method, very small amount of nylon-6 nanofibers, such as 3.4 wt%, 1.7 wt%, 0.9 wt%, and even 0.4 wt%, could led to significant improvement in mechanical properties. Moreover, improved mechanical properties were achieved without sacrificing high transparency of the composite films.

2.3. Short nylon-6 nanofiber reinforced transparent and high modulus thermoplastic polymeric composites



This work has already been published in:

Shaohua Jiang, Andreas Greiner, and Seema Agarwal*, "Short nylon-6 nanofiber reinforced transparent and high modulus thermoplastic polymeric composites", *Composite Science and Technology*, **2013**, *87(18)*, 164-169

Specific contributions by authors:

I performed the fabrication and the characterization of composite films. Prof. Dr. Andreas Greiner proposed the idea of applying short electrospun nanofibers in polymer composites and provided many useful suggestions for this project. The manuscript was written by me. Prof. Dr. Seema Agarwal was responsible for the general guidance and supervision of this project.

In this paper, the preparation of short electrospun nanofibers and the usage of short electrospun nanofibers as reinforcements were reported for the first time. The properties including mechanical properties and optical properties of the composite films with varying predetermined amount of short nanofibers were studied. The morphology and the interaction between fiber/matrix interface were investigated to provide evidence for the reinforcing effect of short nanofibers. The role of chemical structure of matrix polymer in enhancing fiber/matrix interface was also highlighted by using poly(methyl methacrylate) (PMMA) as matrix for comparison purposes with thermoplastic polyurethane (TPU).

The short electrospun nylon-6 nanofibers with a mean diameter of 163 nm (**Figure 2-9A**) and length from tens to hundreds micrometers (**Figure 2-9B**) were prepared by cutting off the pristine electrospun nanofiber mats. Those short nylon-6 nanofibers could be dispersed in DMF solvent, TPU/DMF and PMMA/DMF without aggregation (**Figure 2-9C**, **9E** and **9G**), which is necessary for preparing high quality composite films. After dispersion casting and drying, the resulted TPU/nylon-6 composite films showed some imprinting of short nanofibers on the surface but no pulled-out short fibers were observed on the surface (**Figure 2-9I** and **9J**), which suggested a homogeneous distribution of short nanofibers among the whole composite films. As comparison, PMMA/nylon-6 composite film presented very smooth surface and no imprints of nanofibers in/on the surface (**Figure 2-9K**), which indicated that all the short nanofibers were distributed inside the bulk of the PMMA matrix.

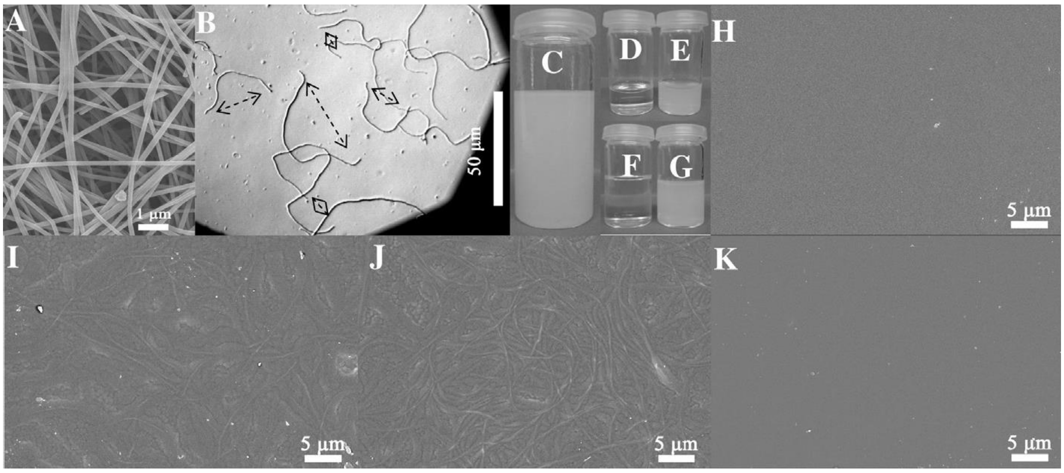


Figure 2- 9 SEM of short nylon-6 nanofibers (A); optical microscope photo of short nylon-6 nanofiber (B); digital photos of 1.0 wt% short nylon-6 nanofiber dispersion in DMF (C); pure TPU (D); nylon-6 short fiber/TPU dispersion (NT3.5) (E); PMMA solution in DMF (F); nylon-6 short fiber/PMMA dispersion (NP3.5) (G); SEM of surface morphologies of pure TPU film (H), NT2.5 (I), NT5.0 (J) and NP3.5 (K).

The distribution differences of short nylon-6 nanofibers in TPU and PMMA were also confirmed by surface analysis using ATR-IR and FT-IR with transmission mode. The ATR-IR spectra of TPU/nylon-6 composites films presented characteristic peaks of nylon-6 and the blue shift of the carbonyl peak and NH peak (**Figure 2-10A**). Those signals proved the distribution of short nanofibers on the surface of composite film and the strong hydrogen bonding between TPU and nylon-6. In comparison, the ATR-IR spectra of PMMA/nylon-6 composites films showed no characteristic signal of nylon-6 and the IR spectra with transmission mode of PMMA/nylon-6 composites films showed the IR signals from nylon-6 but no changes in the peak positions (**Figure 2-10B** and **10C**). Both of those phenomenon proved that no nanofibers were on the surface of the composite films and no hydrogen bonding existed between nylon-6 nanofibers and PMMA matrix.

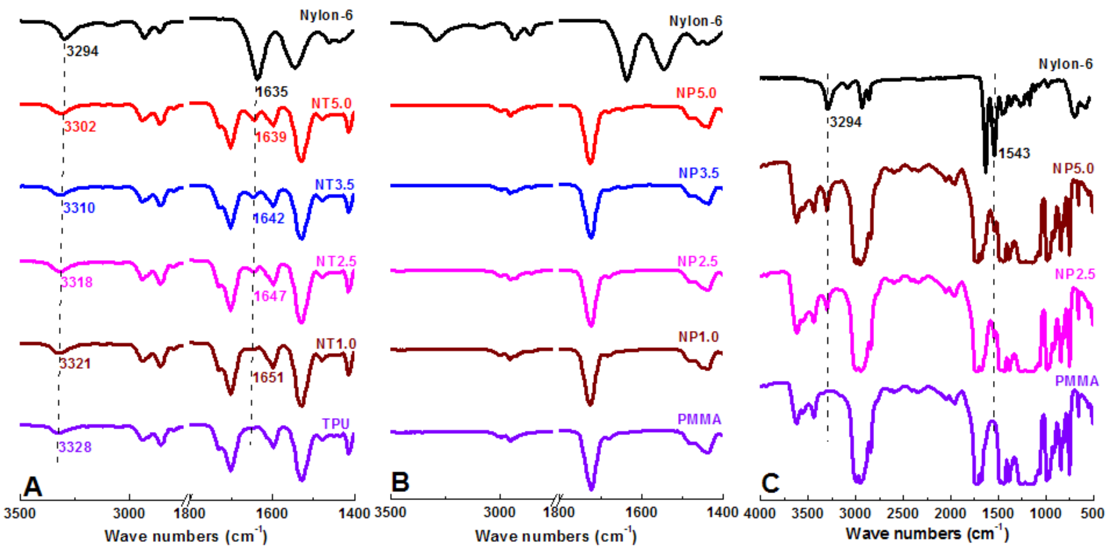


Figure 2-10 (A and B) ATR-IR spectra of pure TPU film, pure PMMA film, nylon-6 nanofiber mat and short nylon-6 nanofiber reinforced TPU and PMMA composite films. (C) FT-IR spectra with transmission mode of pure PMMA film, nylon-6 nanofibers and composite films NP2.5 and NP5.0.

Short nylon-6 nanofibers had reinforcing effect on both TPU/nylon-6 and PMMA/nylon-6 composite films. However, more significant improvement in mechanical properties was observed for TPU/nylon-6 composite film than for PMMA/nylon-6 composite films (**Figure 2-11**). When increasing the amount of short nanofibers to 3.5 wt%, a 185% enhancement in E modulus and a 30% enhancement in tensile strength were observed. As comparison, the best improvement of mechanical properties (18.7% in tensile strength and 23.4% in E modulus) were obtained when adding 2.5 wt% short nylon-6 nanofibers in PMMA matrix. The trend of the mechanical properties of short nanofiber reinforced composite film and the difference of mechanical enhancement between TPU/nylon-6 composite film and PMMA/nylon-6 composites film could be explained by the tensile failure structure of the films as shown in **Figure 2-12**. On increasing the amount of short nanofibers into PMMA/nylon-6 composite films, more defects such as aggregation of fibers and voids/cracks were observed (**Figure 2-12B** and **12C**), which led to the drop of the mechanical properties. In contrast, strong adhesion of nylon-6 nanofibers with TPU matrix without fiber aggregation and voids/cracks as presented in **Figure 2-12E** and **12F**, and the strong hydrogen bonding between nylon-6 nanofibers as proved by ATR-IR spectra, gave rise to the great improvement in mechanical properties.

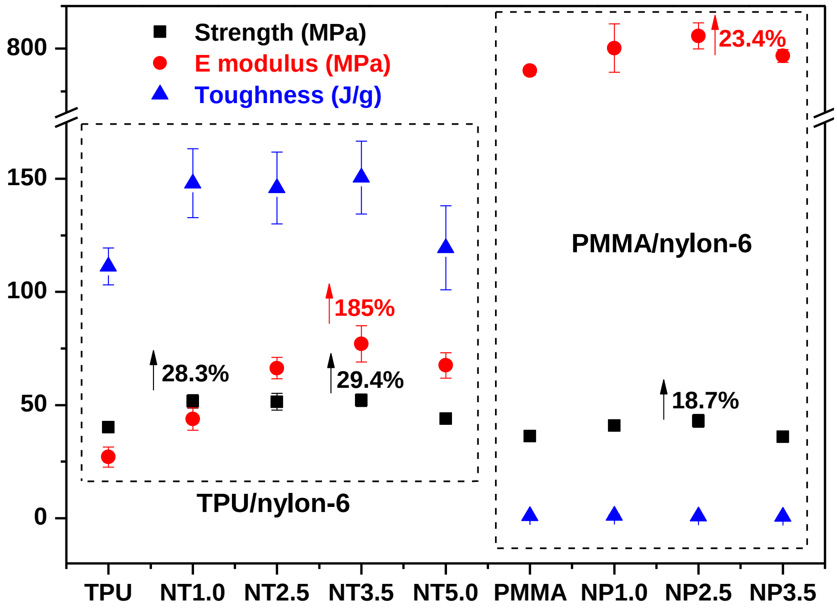


Figure 2-11 Comparison of Strength (■), E modulus (●) and toughness (▲) of pure TPU film, PMMA film and short nylon-6 nanofiber reinforced composite films.

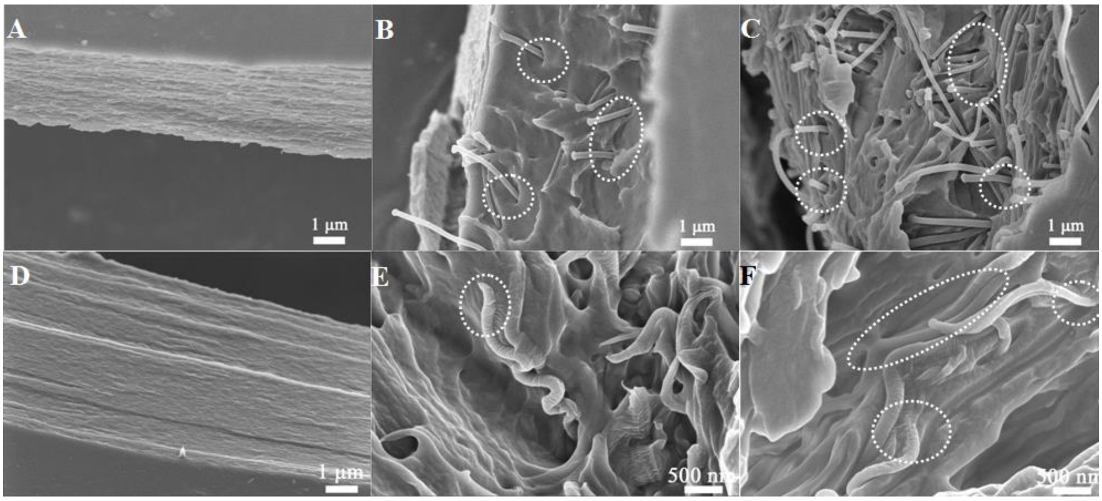


Figure 2-12 SEM pictures of the tensile failure structure of pure PMMA film (A), NP2.5 (B), NP3.5 (C), TPU film (D), NT2.5 (E) and NT5.0 (F).

The fabricated TPU/nylon-6 and PMMA/nylon-6 composite films were visible transparent as presented by the photos in **Figure 2-13**. With the same amount of short nylon-6 nanofibers such as 2.5 wt% or even higher amount such as 5.0 wt%, TPU/nylon-6 composite films showed higher transparency in the visible light range than PMMA/nylon-6 composite films. The quite small diameter (less than 200 nm) of reinforcing nylon-6 nanofibers and the small difference in refractive index between fibers and matrix resulted the transparency of the composite films. Better distribution of short nylon-6 nanofibers in TPU matrix than in PMMA matrix and better interface without voids/cracks between TPU/nylon-6 led to the higher visible light transmittance.

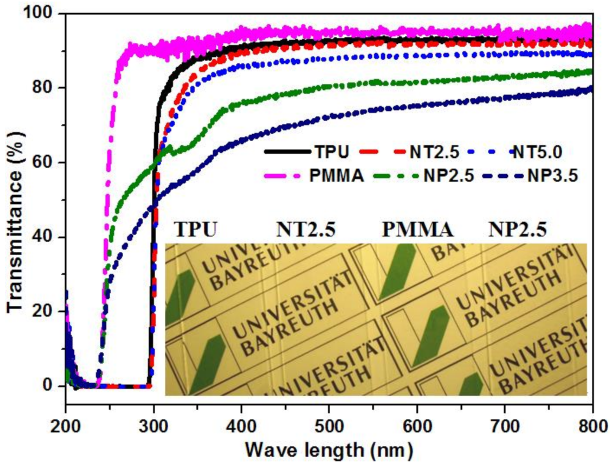
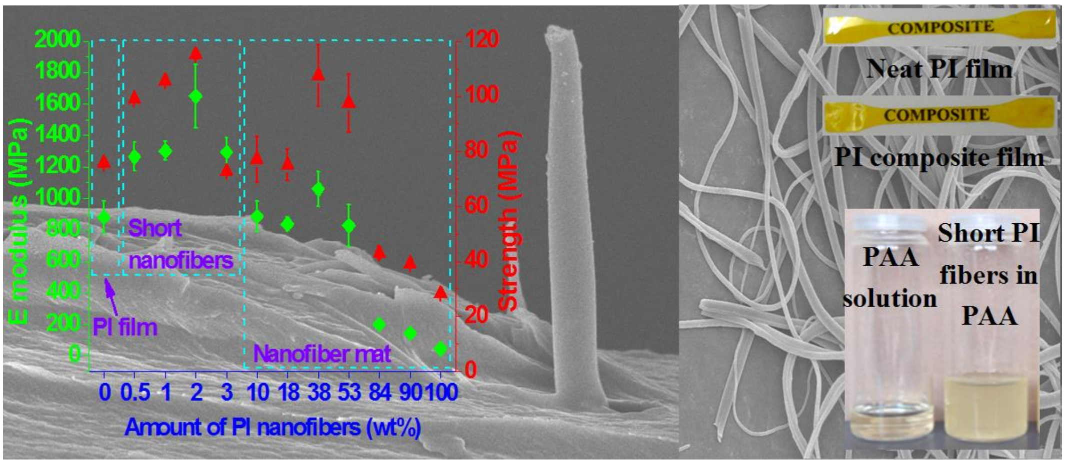


Figure 2- 13 UV-vis spectra of pure TPU film, pure PMMA film and short nylon-6 nanofiber reinforced composite films and digital photo of transparent neat films and composite films on glass slides.

In conclusion, short electrospun nanofibers were reported as reinforcement for the first time. Quite small amount (less than 5 wt%) of short electrospun nylon-6 nanofibers could significantly improve the mechanical properties like tensile strength, E modulus and toughness of polymer matrix like TPU and PMMA. The strong interaction like H-bonding between fibers and matrix could provide a homogeneous distribution of nanofibers and led to great improvement in mechanical properties (185% increase in E modulus) as compared by using TPU and PMMA as matrix polymers. The reinforcement by using short nylon-6 nanofibers could be obtained with high transparency of the composite films. Advantages of using short electrospun nanofibers like use of predetermined amount of nanofibers, mixing in solution and homogeneous distribution in the whole bulk of matrix polymers were revealed to lead to significant improvement of mechanical properties.

2.4. Short electrospun polymeric nanofibers reinforced polyimide nanocomposites



This work has already been published in:

Shaohua Jiang, Gaigai Duan, Judith Schöbel, Seema Agarwal* and Andreas Greiner*, "Short electrospun polymeric nanofibers reinforced polyimide Nanocomposites", *Composite Science and Technology*, **2013**, *88(14)*, 57-61

Specific contributions by authors:

I performed the fabrication of short PI nanofiber reinforced PI composites. Gaigai Duan gave me support on the imidization of polyamic acid. Judith Schöbel carried out a research practical project with me and made some of the composite films under my guidance. The manuscript was written by me. Prof. Dr. Andreas Greiner help me with many useful suggestions for this project. Prof. Dr. Seema Agarwal was responsible for the general guidance and supervision of this project.

This paper highlighted a novel process for nanofiber nonwovens by liquid processing techniques. This nanofiber nonwovens made up with short electrospun nanofibers is similar to electrospun nonwovens but is independent from the demands of the electrospinning process. The short electrospun nanofibers provided completely new opportunities for the application of electrospun nanofibers. In this paper, self-reinforced polyimide (PI) composite films reinforced by short electrospun PI nanofibers were selected as representative examples for showing the versatility of short electrospun nanofibers. Significant enhancement of 53% and 87% in mechanical properties like tensile strength and E modulus were achieved by using only 2 wt% of short PI nanofibers. Parallel experiments by using long and continuous electrospun PI nanofiber mats as reinforcements revealed amazing difference. To achieve the same improvement in tensile strength, 38 wt% of continuously long fibers were required in comparison to only 2 wt% of short fibers required.

The short PI nanofiber dispersions (**Figure 2-14A**) could be prepared by cutting the PI nanofiber mat in the cooled isopropanol/water (30/70 w/w) by a high rotated blade. After filtration, the resulted short nanofiber exhibited a fiber length arranged from 50 to 500 µm and diameter of 0.2-0.5 µm (**Figure 2-14B**). As compared to the nanofiber deposition by standard electrospinning process, improved adhesion of short PI nanofibers on the filter paper substrate could be observed by filtration the short nanofiber dispersion (**Figure 2-14C**). Moreover, by filtration of the dispersion of short nanofibers and adjusting the amount of dispersions, nanofiber nonwovens with different homogeneous thickness could be easily achieved.

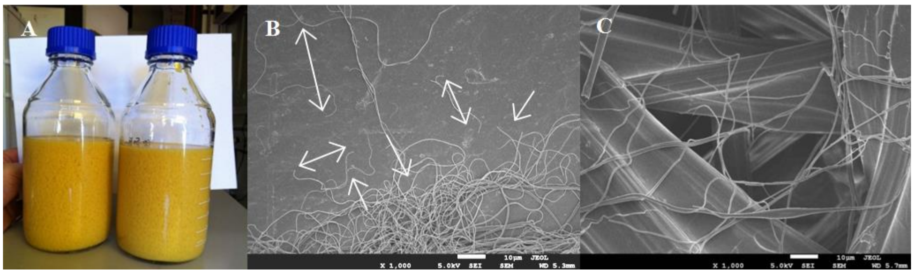


Figure 2-14 Photograph of dispersions of electrospun fibers after cutting (A); SEM micrograph of short PI nanofibers (B) and SEM micrograph of short PI nanofibers deposited from dispersion on filter paper (C). Scale bar of (B) and (C) = 10 µm.

The insolubility or no swelling of PI in DMF solvent provided the opportunity of applying short PI nanofibers as reinforcement to make self-reinforce PI composite films. Different amount of short PI nanofibers were redispersed in PAA precursor solution (10 wt% in DMF). After the same imidization process as for the electrospun PI nanofiber nonwovens, the resulting PI/PI nanofiber composite films were obtained, which were referred as PIPICOF. In order to compare the effect of short PI nanofibers on the mechanical properties of PIPICOF, the PIPICOF were also prepared by using PI nanofiber mat with long and continuous nanofibers. The comparison of mechanical properties like tensile strength and E modulus of those two kinds of PIPICOF were presented in **Figure 2-15**. As for PIPICOF reinforced by short PI nanofibers, the mechanical properties showed first increasing and then decreasing as increasing the amount of short nanofibers. The highest improvement of 53% and 87% in tensile strength and E modulus were obtained for the sample with only 2 wt% of short PI nanofibers as compared to the pure PI films. Those mechanical properties achieved by adding only 2 wt% short PI nanofibers was significantly higher than any of the PIPICOF with as-electrospun. What’s more, due to lack in homogeneity, it was impossible to prepare nanofiber composites with less than 10 wt% of as-electrospun long PI nanofibers.

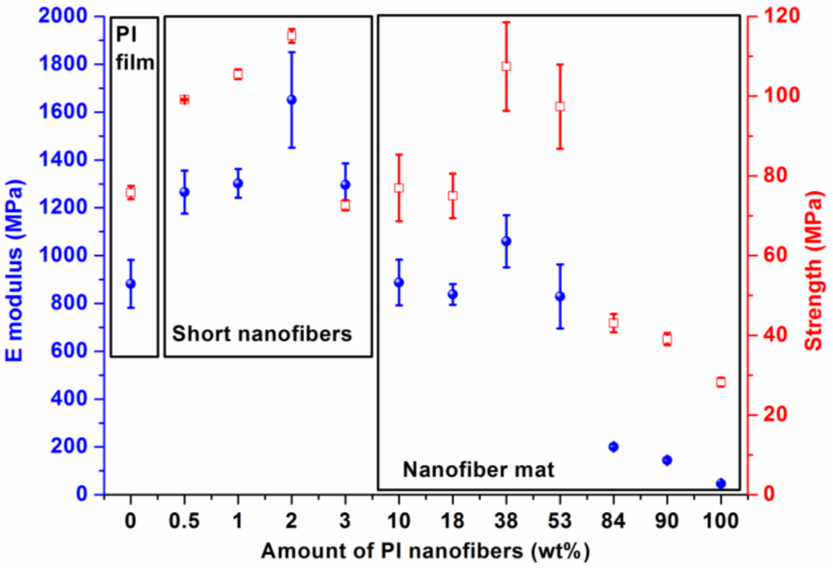


Figure 2-15 Comparison of E modulus (●) and strength (□) of PIPICOF and PI self-reinforced nanofiber composite with as-electrospun PI nanofibers and a pure PI film.

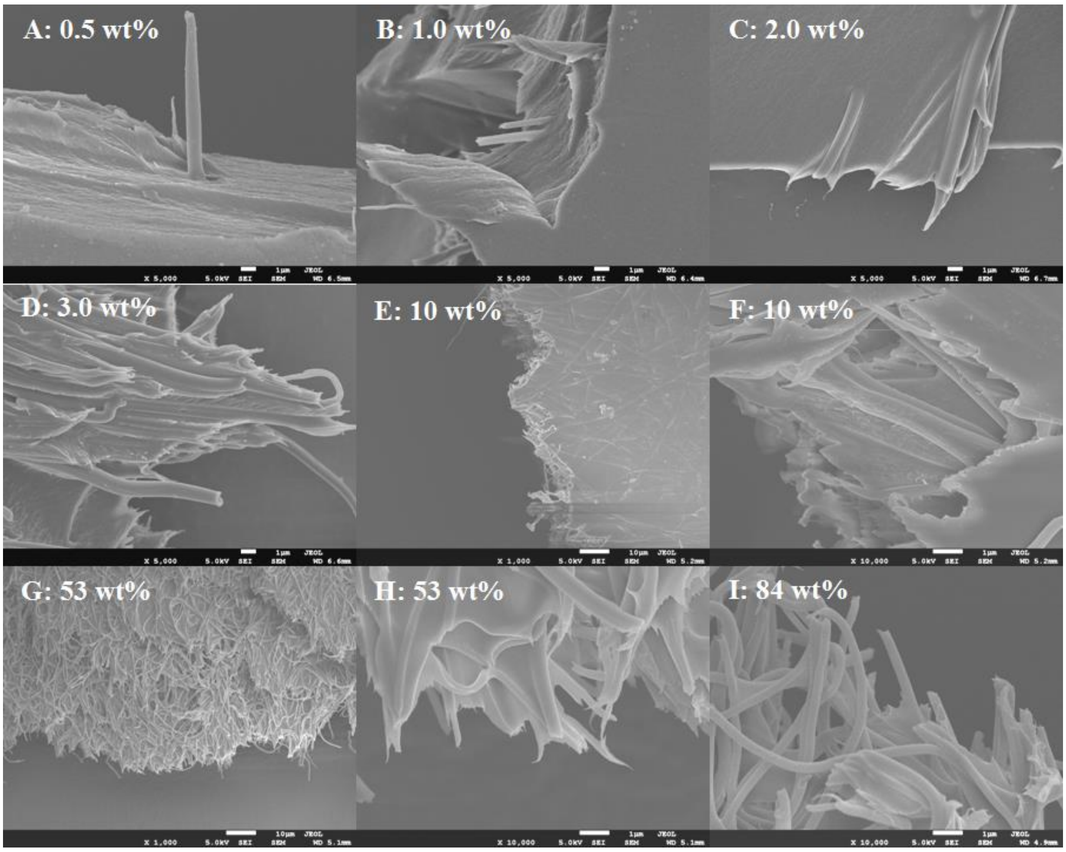


Figure 2-16 Fractured surface morphologies of PIPICOF with different amount of short PI nanofibers (A, B, C, and D) and as-electrospun long PI nanofibers (E, F, G, H, and I). Scale bar of (A), (B), (C), (D), (F), (H) and (I) = 1µm and scale bar of (E) and (G) = 10 µm.

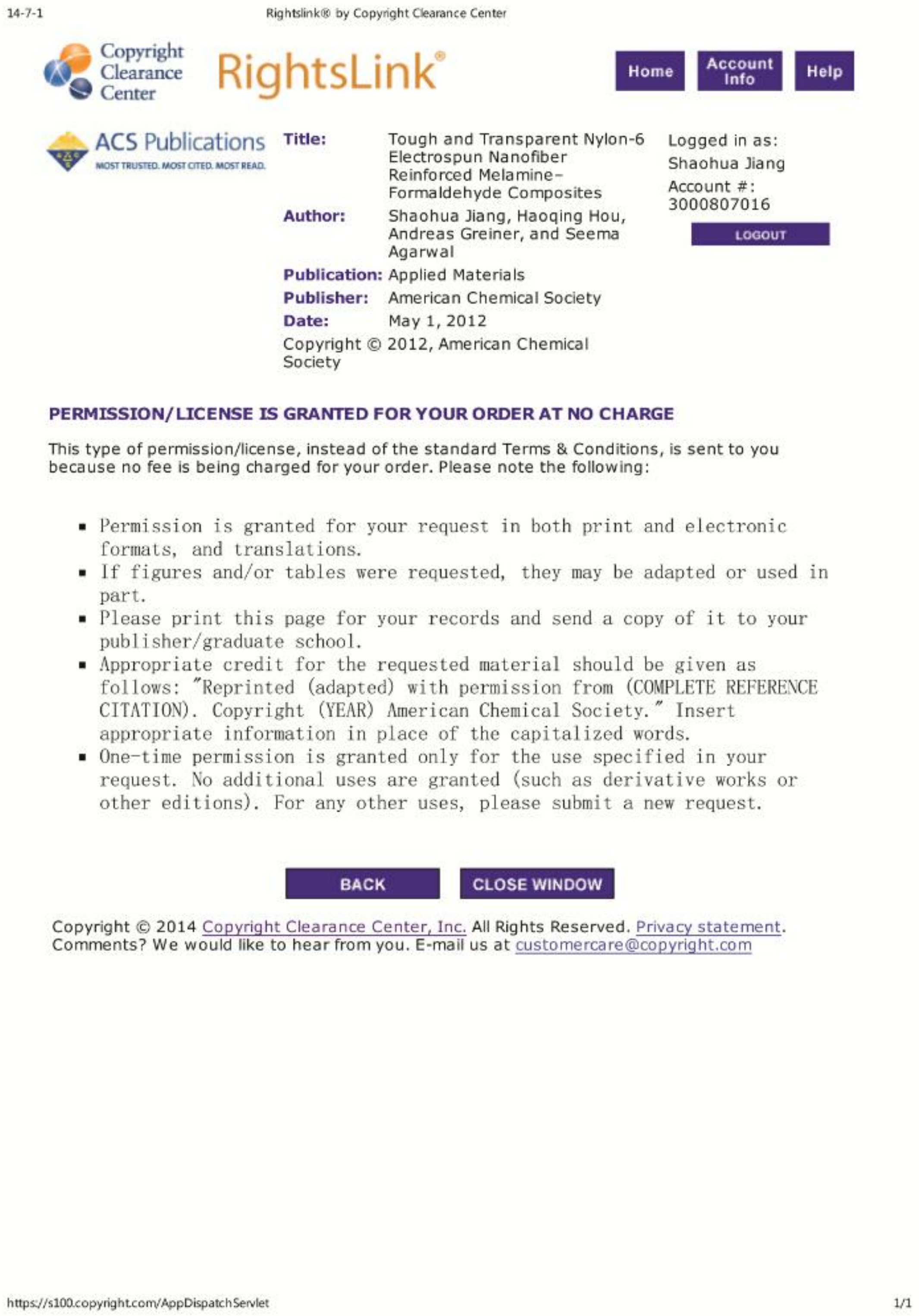
To reveal the reasons for the trend of mechanical properties of PIPICOF, the fractured surface morphologies of PIPICOF with different amount of PI nanofibers were investigated as shown in **Figure 2-16**. When small amount of short PI nanofibers such as 0.5 wt%, 1.0 wt% and 2.0 wt% were applied, the short fibers were isolated from each other, which suggested a homogeneous distribution of nanofibers in the PI matrix. No defects such as holes or cracks were observed at the interface between fibers and matrix, and the fibers were intimately embedded in PI matrix. Further increasing the amount of short PI nanofibers into 3 wt% led to the aggregation of fibers, which resulted in the decreasing in mechanical properties. As comparison, the disadvantages of using as-electrospun PI nanofibers as reinforcements were obvious. First it was impossible to prepare PIPICOF with less than 10 wt% PI nanofiber mat and with predicted amount of PI nanofibers. Second, the wetting of PI nanofiber mat by PAA precursor solution was not complete due to the high amount of nanofibers. Thirdly, the high amount of as-electrospun PI nanofibers led to the aggregation of fibers, large amount of holes and pull-out fibers. Fourth, high amount of as-electrospun PI nanofibers as reinforcements could not result PI composite films but only PI matrix coated PI nanofibers.

In conclusion, short electrospun nanofibers provided completely new fields for the application of electrospun nanofibers. This technique for short electrospun nanofibers could be extended to other polymers with different structures and properties. The use of short nanofibers does not only offers advantages of processing process but also provides opportunities for significant property improvements as shown in this paper as an example for self-reinforced PIPICOF. It is obvious that better improvement of mechanical properties were obtained by using short PI nanofibers than using as-electrospun PI nanofiber mat as reinforcements. The main reason for superior mechanical properties with short nanofibers is the quite better distribution of the short nanofibers in polymer matrix. The application of short nanofibers is not limited to fiber reinforced composites. We can expect that the short nanofibers can be broadly applied in many other fields.

3. Publications

3.1. Tough and Transparent Nylon-6 Electrospun Nanofiber Reinforced Melamine-Formaldehyde Composites

Shaohua Jiang, Haoqing Hou, Andreas Greiner, and Seema Agarwal*, “Tough and Transparent Nylon-6 Elestrospun Nanofiber Reinforced Melamine-Formaldehyde Composites”, *ACS Applied Materials & Interfaces*, **2012**, *4*, 2597-2603



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Title: Tough and Transparent Nylon-6 Electrospun Nanofiber Reinforced Melamine–Formaldehyde Composites

Author: Shaohua Jiang, Haoqing Hou, Andreas Greiner, and Seema Agarwal

Publication: Applied Materials

Publisher: American Chemical Society

Date: May 1, 2012

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Tough and Transparent Nylon-6 Electrospun Nanofiber Reinforced Melamine–Formaldehyde Composites

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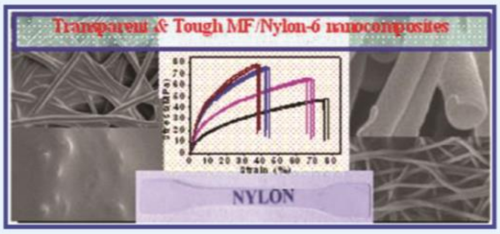
ABSTRACT: The use of nylon-6 electrospun nanofiber mats as reinforcement with synergistic effect in tensile strength and toughness for melamine–formaldehyde (MF) resin is highlighted in this article. Interestingly, there was a drastic effect of the wetting procedure of reinforcing fiber mat by the MF resin on the morphology and mechanical properties of the composites. The wetting of nylon fibers by passing through a solution of MF resin showed a core–shell morphology and a significant improvement in properties as compared to the dip-coating procedure for wetting of the fibers. Depending on the wt% of reinforcing nylon fiber mats, the composites could be considered as either fiber reinforced MF composites or MF glued nylon fibers.



KEYWORDS: *nanocomposites, mechanical properties, electrospinning, heat treatment, nanofibers*

■ INTRODUCTION

Melamine–formaldehyde (MF) resin and its derivatives are well-known for stiffness, hardness, strong adhesion to cellulose, and easy processing and are therefore widely applied in furniture, construction materials, tableware, adhesives, coatings, abrasive cleaner, textile treatment, and other materials requiring enhanced mechanical properties.[1−6] Pure MF resin is easily prepared from water-based melamine and formaldehyde solution by polycondensation and cross-linking during the compression molding or heating procedure,[7] but it is difficult to get the mechanical properties data of neat MF resin as it is brittle and develops extensive microcracks during sample preparation. The only data available indicated the mechanical properties of neat MF as a tensile strength of about 40 MPa and a stiffness of approximately 8−9 GPa, which implies a very low strain of less than 0.5%.[8] Different additives have been used in the past to improve the mechanical properties of MF resin, such as carbon fibers,[8] cellulose,[9] flax fibers,[10] pulp fibers,[11] carbon nanotubes,[12] and MWNT (multiwalled carbon nanotubes).[13] The resulting composites showed a higher tensile strength and modulus but nearly no increase in the elongation at break. Recently, polymer nanofibers produced by electrospinning have been attracting more and more attention for the preparation of composites. The continuous long fibers produced by electrospinning do not exhibit fiber edges (ends) and therefore lack stress concentration points in composites. During the electrospinning, the polymer molecular chains tend to align along the fiber axis as the polymer jet is drawn up to 100 000 times in less than 0.1 s. These highly molecular oriented nanofibers can provide a mechanically strong fiber for the preparation of fiber reinforced composites. Also, in most cases, electrospun nanofibers are collected in the form of a random aligned nonwoven mat with high porosity and large specific surface area. Therefore, the nanomat can be more feasibly impregnated with the resin solution and could make a remarkable improvement regarding the fracture toughness compared to the bulk film counterpart. Ramakrishna et al. pointed out in their review article that the incorporation of entangled nanofiber layers, characterized by a combination of interlocked in-plane and out-of-plane nanofibers, might contribute to improve interlaminar fracture resistance.[14] In addition, the diameters of electrospun nanofibers ranging from several to hundreds of nanometers can decrease the refractive index difference between the resin and reinforcing nanofibers, which is a significant advantage in producing transparent composites. Early reports of reinforcing effects of nanofibers in an epoxy and a rubber matrix (styrene–butadiene rubber) were contributed by Kim et al.[15] They showed an increase in Young's modulus, fracture toughness, and fracture energy of the epoxy matrix. Bergshoef et al. showed the formation of transparent epoxy composites using 4 wt % nylon-4, 6 electrospun nanofibers (30−200 nm in diameter).[16] Nylon-6 nanofibers produced by electrospinning exhibit excellent mechanical properties, such as toughness and high tensile strength,[17,18] and have also been adopted to make composites with poly (methyl methacrylate),[19] poylaniline,[20] polycaprolactone,[21] and with bis-glycidyl methacrylate/tetraglycidylmthacrylate ((BIS-GMA/TEGDMA) as dental restorative composites.[22] The field of applying electrospun nanofibers as reinforcement is still in its infancy with just a few countable reports in the literature. A recent review article[14] is a good refrence supporting this fact. In this work, we highlight the use of nylon-6 nanofibers for

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preparing very tough and transparent composites with MF resin. The importance of the fiber wetting procedure for the preparation of the corresponding composites is also emphasized. A change of the wetting method could bring about a drastic change in the morphology (from film to core−shell) of the wet fibers. Different composites with varied amounts of nylon-6 fibers generated a profile of properties. Even composites with very high amounts of fibers (nylon-6 mats) with high strength could be prepared from core−shell fiber composites. FT-IR, SEM, TGA, tensile testing, and UV−vis spectroscopy techniques were applied to determine the structure and properties of the MF/nylon-6 nanofiber composites.

■ EXPERIMENTAL SECTION

Materials. Nylon-6 (Ultramid B24) was kindly supplied by BASF. Melamine−formaldehyde−water solution (Madurit SMW818 75% WA) was supplied by INEOS Melamines GmbH, Germany. The solvents, formic acid (FA, ≥98 wt %) and acetic acid (AcOH, ≥98 wt %), were acquired by Sigma-Aldrich. All materials were used as received without further purification.

Electrospinning and Composite Preparation. Nylon-6 was dissolved in FA/AcOH (40/60, w/w) to form an electrospinning solution with a concentration of 20 wt %. During the electrospinning process, a high voltage electric field of 100 kV/m, by imposing a 25 kV electrical potential to a 25 cm gap between a spinneret and a rotating cylinder, was applied on the flat tip of a needle. The polymer solution was delivered by a syringe pump at a feeding rate of 0.3 mL/h, and the nylon-6 nanofibers were collected on a cylinder, which rotated at 30 rpm. The resulting nanofiber mat was cut into small samples exhibiting a size of 4.5 × 5.0 cm and dried in a vacuum oven at 80 °C for 12 h. Two different methods were used for making composites, and their respective advantages and disadvatges are discussed in the Results and Discussion section. In method 1, the dried nanofiber mats were immersed into the melamine−formaldehyde−water solutions of different concentrations (i.e., 5 wt %, 10 wt %, and 15 wt % MF in water) (method 1; dip-coating; Figure 1) which were diluted from a 75 wt % MF solution, or alternatively, MF solutions were passed through the fiber mats; i.e., a process similar to liquid filtration (method 2; Figure 2). The electrospun nanomat is kept between two Whatman qualitative filter papers (Grade 1, 11 μm) in a suction filtration flask, and MF solutions of different concentrations were passed under vacuum (about 20 bar) in different experiments.

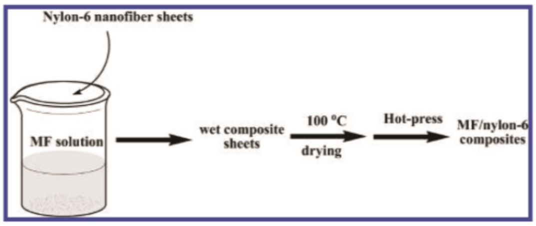


Figure 1. Schematic process for the preparation of the MF/nylon-6 nanocomposites by immersing and hot-pressing (method 1).

After wetting of the fibers (either method 1 or method 2), the sheets were dried at at 100 °C for 12 h and subsequently two impregnated and dried sheets were hot pressed at 180 °C for 10 min at a pressure of 20 MPa.[23] During the hot-pressing, the MF was polymerized and cross-linked around the nylon-6 nanofibers, resulting in composites with varying compositions. Two electrospun nylon-6 mats were also hot-pressed under similar conditions as applied for the formation of the composites and used as blank for properties comparison.

Characterization. A JSM-7500 scanning electronic microscope (SEM) was applied to investigate the morphology and structure of nylon-6 nanofibers and MF/nylon-6 nanocomposites. Prior to scanning, the specimens were sputter-coated with gold to avoid charge accumulations. Diameter distribution of the nylon-6 nanofibers was obtained by analysis of the SEM images via the ImageJ software. Mechanical properties were measured by means of a Zwick/Roell BT1-FR 0.5TN-D14 machine equipped with a 200 N KAF-TC load sensor using a stretching rate of 5 mm/min at room temperature. Dog-bone-shaped specimens were cut with a length of 3.0 cm and a width of 0.2 cm. FT-IR spectra were recorded on a Digilab Excalibur Series with an ATR unit MIRacle by Pike Technology. Transparency in the range of visible light was investigated by a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer operating in transmittance mode (200−800 nm). Thermal properties of the composites were evaluated on Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C/min in N_2 from 50 to 800 °C.

■ RESULTS AND DISCUSSION

Electrospinning is a fast and effective technology to prepare nanofibers with a diameter distribution from several to hundreds of nanometers.[24] In this work, nylon-6 nanofibers were electrospun from 20 wt % nylon FA/AcOH solutions. They comprised a smooth surface, a random alignment, and a centralized diameter distribution. As shown in Figure 3A,B, the diameter of nanofibers is mainly distributed from 186 to 221 nm and no defects such as beads, pores, or ribbons were found. For the preparation of the composites, nylon-6 nanofiber mats were impregnated with the MF water solution. This was due to (1) the high porosity and low water contact angle of nylon-6 nanofiber mats, which can be as low as 12 degrees after a contact time of 10 s^{25} and (2) an improvement in wetting behavior relative to nylon-6 bulk.[26] Two different methods were used to wet the nylon fibers. The first method made use of immersing the nylon fibers in MF solutions of different

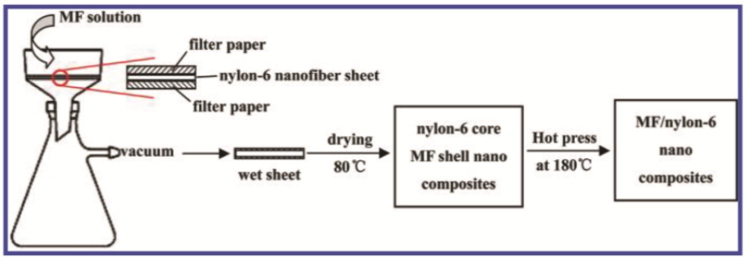


Figure 2. Schematic process for the preparation of the MF/nylon-6 nanocomposites by passing a MF solution through the nylon-6 nanomat and followed by hot-pressing (method 2).

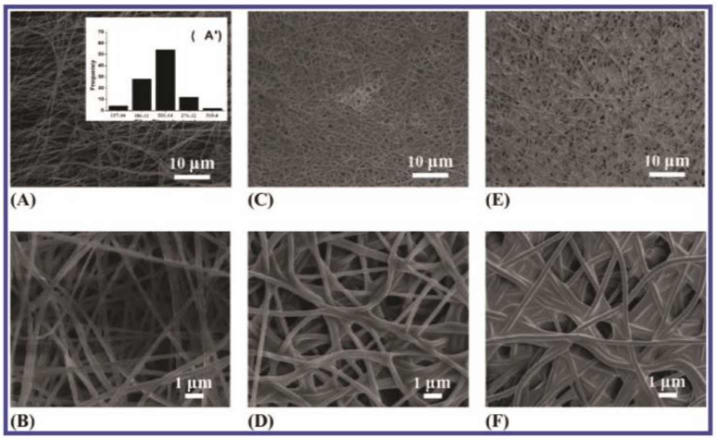


Figure 3. SEM images of (A) and (B) nylon-6 nanofibers, (C) and (D) MF/nylon-6 nanocomposite prepared by immersion into a MF solution of a concentration of 5 wt %, and (E) and (F) MF/nylon-6 nanocomposite made by immersion into a MF solution of a concentration of 15 wt %. (A′) column diagram of the diameter distribution of nylon-6 nanofibers.

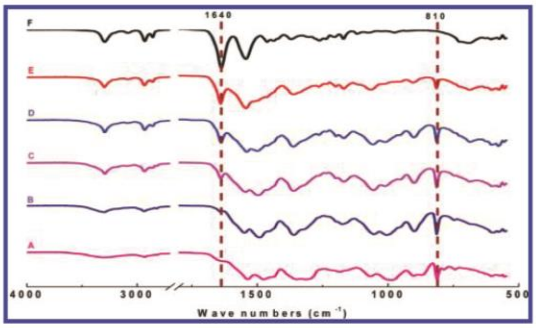


Figure 4. FT-IR spectra of composites with different contents of nylon-6 nanomat: A, 0 wt % (neat MF); B, 13 wt %; C, 26 wt %; D, 30 wt %; E, 62 wt %; F, 100 wt % (nylon-6 nanofibers).

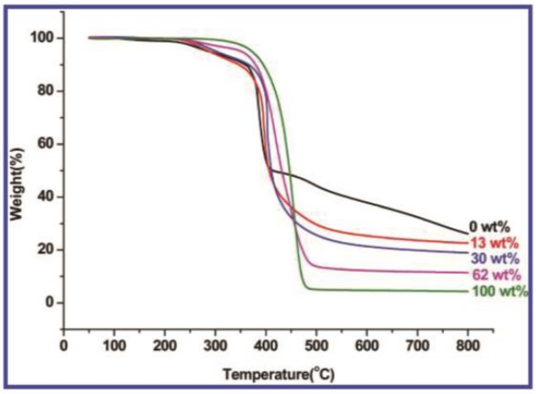


Figure 5. Thermal stabilities of pure MF resin, nylon-6 nanofiber sheets, and MF/nylon-6 nanocomposites with different amounts of nylon-6 nanofibers.

Table 1. Thermal Properties of MF/Nylon-6 Composites with Different Contents of Nylon-6 Nanomats

content (wt %)	0	13	30	62	100
$T_{5\%}$ (°C)	288	289	302	352	372
T_d (°C)	386	395	403	418	450
char yield (%)	26	23	19	11	4

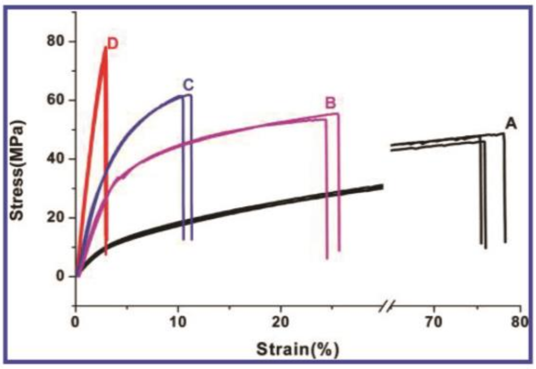


Figure 6. Typical stress−strain curves of MF/nylon-6 nanocomposites (method 1) with a content of nylon-6 in composites of (A) 100 wt %; (B) 62 wt %; (C) 30 wt %; (D) 13 wt %.

concentrations. To make composites with high amounts of MF resin, a more concentrated solution of MF was required. Different MF/nylon-6 composites with varied amounts of nylon-6 in the composite (13 wt %, 30 wt %, and 62 wt %) were prepared as determined by gravimetry.

The resulting composites depicted in Figure 3C,D exhibited quite different morphologies depending on the concentration of the respective MF solution applied. Immersion in low concentrated (5 wt %) MF solution led to deposition of MF resin on fibers. However, immersion into highly concentrated MF solutions (15 wt %) led to the deposition of MF resin both on fibers and in-between the fibers in the form of films between fibers. A small coiling of MF coated nylon fibers in composites was observed after drying at 100 °C for 12 h (Figure 3). This could be due to the different coefficient of thermal expansion between nylon-6 and MF resin.

Table 2. Mechanical Properties of MF/Nylon-6 Nanocomposites Made by Method 1 and Method 2* with Different Contents of Nylon-6 Nanofibers

nylon-6 content (wt %)	stress (MPa)	strain (%)	E modulus (2%) (GPa)	integration of stress−strain curves (MJ/m^3)	toughness (J/g)
100	47.5 ± 1.4	76.2 ± 1.6	0.37 ± 0.02	24.7 ± 0.85	21.8 ± 0.75
62	54.5 ± 1.4	24.8 ± 1.1	0.96 ± 0.09	10.7 ± 0.49	7.8 ± 0.36
30	61.7 ± 0.3	10.6 ± 0.5	1.34 ± 0.04	4.8 ± 0.33	3.6 ± 0.25
13	74.5 ± 2.9	2.85 ± 0.1	2.88 ± 0.08	1.2 ± 0.07	1.0 ± 0.05
82*	65.2 ± 1.3	67.9 ± 2.0	0.59 ± 0.23	31.6 ± 1.00	27.0 ± 0.85
72*	75.1 ± 1.0	43.4 ± 1.4	0.79 ± 0.07	23.4 ± 0.88	19.6 ± 0.74
66*	77.9 ± 0.8	38.4 ± 0.8	0.85 ± 0.05	21.3 ± 0.55	17.6 ± 0.45

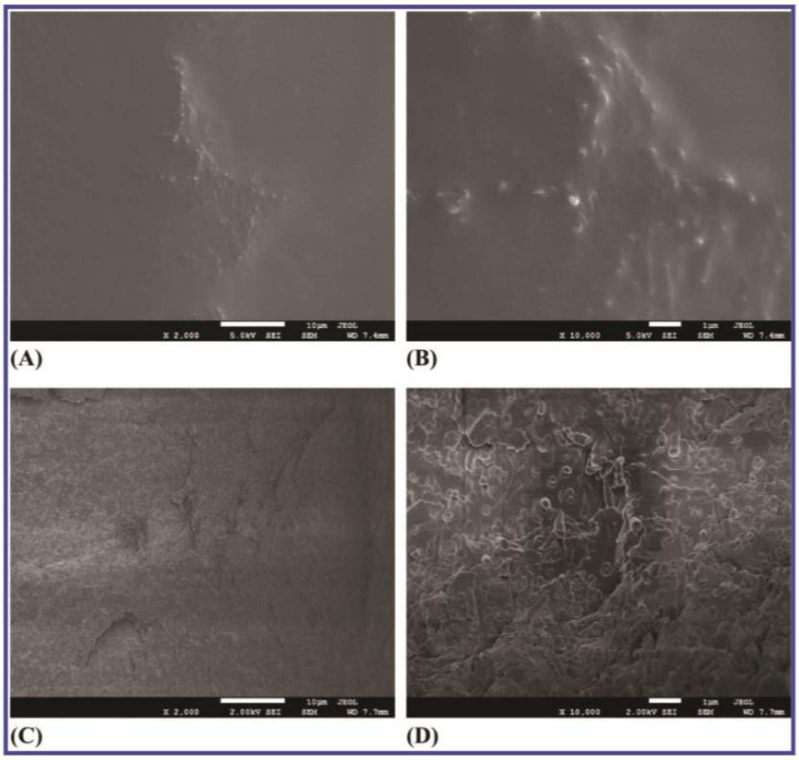


Figure 7. SEM images of fracture cross-section of composites (method 1) with a content of nylon-6 nanofibers of (A) and (B) 13 wt % and (C) and (D) 62 wt %. Scale bar: (A) and (C), 10 μm; (B) and (D), 1 μm.

FT-IR spectra of neat MF, nylon-6 nanofibers, and the MF/nylon-6 nanofiber composites are shown in Figure 4. The pure MF resin exhibited a strong and sharp peak at 810 cm^{-1}, which is characteristic for the triazine ring, while nylon-6 nanofiber sheets showed a strong band at 1640 cm^{-1}, which was due to the vibration of amide (Figure 4A,F).[27,28] Regarding MF/nylon-6 nanocomposites, according to Figure 4B−E, the characteristic peaks shown in the spectra of neat MF and nylon-6 also appeared in the spectra of MF/nylon-6 nanocomposites. The intensity of the peak at 1640 cm^{-1} became weaker, whereas the intensity of the peak at 810 cm^{-1} increased, as the content of nylon-6 nanofibers was raised in the composites. This confirmed that the integrated chemical behavior of both materials was present in the composites.

The resulting composites were investigated for their thermal stability by thermogravimetry in N_2 at a heating rate of 10 °C/min. As shown in Figure 5, all the samples exhibited an excellent heat-resistance up to at least 200 °C. As for nylon-6 nanofibers, a single step of thermal degradation was observed, while the TGA curve of the pure MF resin showed three stages of degradation. The first step of weight loss started at 210 °C and could be due to the dehydration of the uncross-linked methylol in MF resin; the second obvious degradation from 350 to 400 °C might have resulted from a decomposition of aliphatic ether group; the last slow weight loss may be due to a decomposition of the triazine. This decomposition behavior is similar to the literature for MF resins.[27] Similar trends could be found among the TGA curves of MF/nylon-6 composites. The further results are summarized in Table 1, in which $T_{5\%}$ temperature at which 5% weight loss took place, the decomposition temperature (T_d), and char yield at 800 °C are compared. As the content of nylon-6 nanofibers increased,

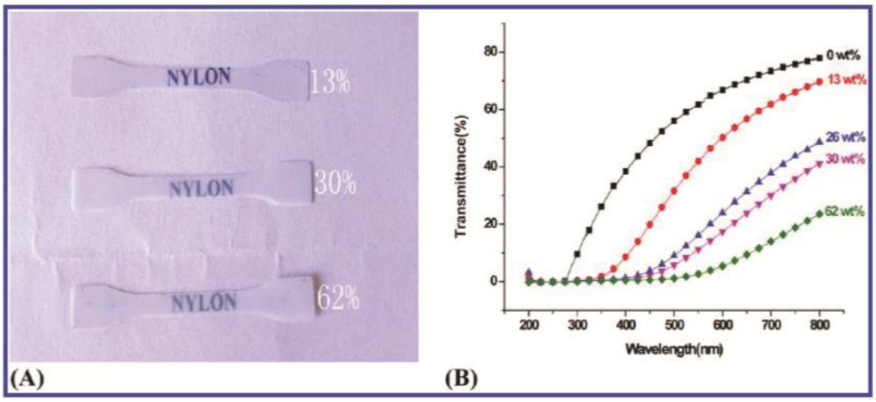
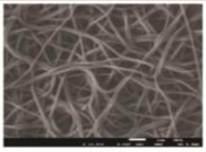
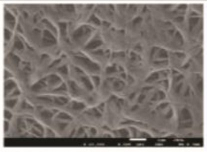
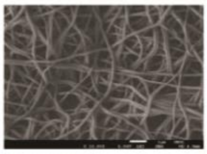
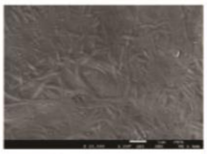
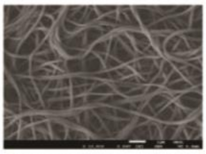
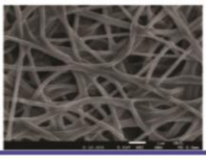
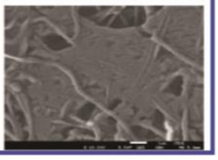


Figure 8. (A) Photographs of semitransparent composites. (B) Transmission spectra of composites with varying content of nylon-6 nanofibers.

Table 3. Morphology Comparison of the Nanocomposites with Different Content of MF before and after Hot-Pressing[a]

Composite	Before hot-pressing	After hot-pressing
1: 18 wt% MF		
2: 28 wt% MF		
3: 34 wt% MF		
4: 38 wt% MF		

[a] Scale bar = 1 μm.

$T_{5\%}$ of the composite increased from 289 to 330 °C, while T_d increased from 396 to 418 °C. However, the char yield at 800 °C showed a decrease from 23% to 12% as the amount of nylon-6 nanofibers increased and the lowest char yield for nylon-6 nanofiber mat was seen. The char yield is one of the measures of thermal stability. The thermal degradation behavior of MF resin is well-known in the literature. The degradation products are water, formaldehyde, hydrogen cyanide, carbon monoxide, and melamine. The melamine can undergo further condensation to give high molecular weight solid degradation products. According to the literature, the C−N bonds in MF char do not undergo further combustion and the composites with more MF content show, in general, more char yield.[29,30]

The mechanical properties of MF/nylon-6 nanofiber composites reinforced with different amounts of nylon-6 made by method 1 were measured. Typical stress−strain curves and the tensile properties are presented in Figure 6 and Table 2 respectively. The electrospun nylon-6 mats alone (two mats without impregnation with MF)) were also hot-pressed under similar conditions as applied for the formation of the composites and tested for mechanical properties. The compressed nylon-6 nanomat (blank) exhibited a tensile strength of 47 MPa strain at break of around 76% and toughness of around 21.8 J/g. The MF/nylon-6 composite with 13 wt % of nylon-6 comprised a very high tensile strength of 74.5 MPa and strain at break of about 3%. The reinforcement with nylon-6 nanofibers showed a synergistic effect regarding the tensile strength of the resulting composites with a value higher than those of nylon-6 nanofiber mats or MF resin. This value was nearly 2 times the strength and 6 times the strain of the pure MF resin. Further, a decrease in tensile strength and an increase in strain at break on increasing the nylon-6 content in the composites was detected, but the tensile strength is always higher compared to that of pure MF resin or nylon-6 nanofiber mats. The nylon-6 nanofibers were nonaligned and randomly distributed in the composites as shown in the Figure 3. During tensile testing, the stretching force was taken by reinforcing nylon-6 fibers and the fricton between fibers helped in delaying composite failure. Therefore, more fibers resulted in a higher strain, as shown in the tensile testing results of the composites.

Generally, cracking is one of the most important factors to affect the strength of materials.[31] Figure 7 shows SEM micrographs of the fracture cross-section of the composites with different contents of nylon-6 nanofibers. Samples with 13 wt % nanofibers comprised a smooth cross-section, and the interfaces between fibers and matrix were integrated closely. Nevertheless, a rougher morphology appeared when the content of nanofibers was increased, and many cracks could be detected (Figure 7C,D). When cracks appear, the strain energy was released in a material volume adjacent to the crack. Thus, a smaller strength was obtained upon increasing the content of fibers.

The composites prepared from MF and nylon-6 nanofibers were semitransparent as shown in Figure 8A. This appearance of the nanocomposite might be the result of the small diameter

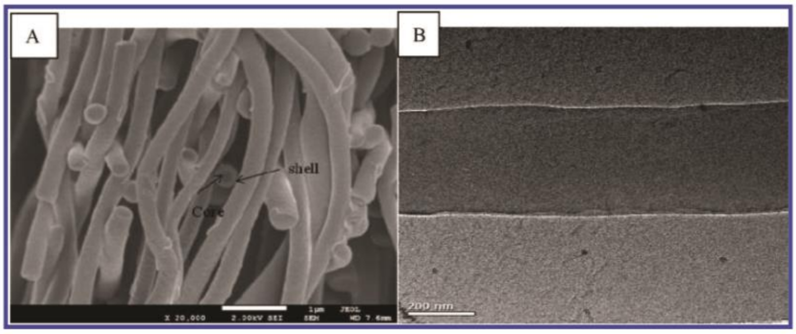


Figure 9. Core−shell structure of the nanocomposites with 66 wt % nylon fibers before hot-pressing (A) SEM (scale bar = 1 μm); (B) TEM.

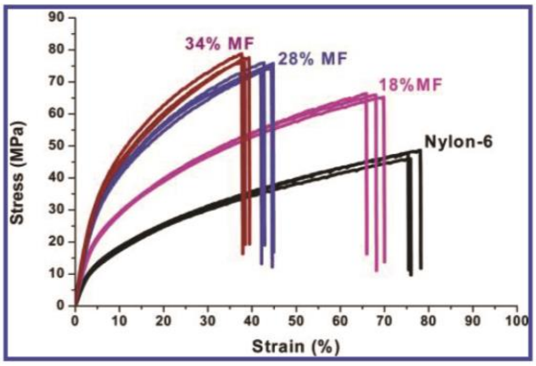


Figure 10. Typical stress−strain curves of MF/nylon-6 nanocomposites (method 2) with different contents of MF.

of nylon-6 nanofibers and nearly the same refractive index of the nylon-6 and the MF resin, 1.53 and 1.52, respectively.[32,33] However, the transparency decreased as the content of fibers was increased, which can be proved by the transmission spectra shown in Figure 8B. When the nylon-6 nanofiber content increased from 13 wt % to 62 wt %, the transmittance decreased dramatically from 70% to 24% at a wavelength of 800 nm. A higher content of nanofibers in the composite shielded the transmittance of visible light. Therefore, the composite with 13 wt % fibers, which showed a smooth cross-section, exhibited the highest transmittance of 70% (800 nm), which is only 8% less than the transmittance of pure MF, and was found to be best in terms of mechanical properties also.

As described above, the comparison of SEM pictures of composites with different amounts of nylon-6 fibers before and after hot-pressing revealed an irregular and incomplete wetting/covering of nylon-6 fibers for very high amounts of nylon-6 fibers, i.e., 62 wt %. Therefore, an attempt was also made to modify the wetting procedure of nylon-6 nanomats with MF resin for composite formation. Instead of immersing the nylon-6 nanofiber mat into the MF solution, MF solutions with different concentrations were passed through nylon-6 nanofiber mats in a process similar to liquid filtration, as depicted in Figure 2 (method 2). Afterward, two impregnated nanomats were hot-pressed together as described in the experimental part. This resulted in the generation of composites with different amounts of nylon fibers as determined by gravimetry.

The morphologies of the resulting composites are listed in Table 3. A good comparison can be found among composites 3 and 4 in Table 3. Composite 3 was prepared by passing MF solution through the nylon-6 fiber mat (method 2) whereas composite 4 was made by immersing nylon-6 fiber mat in a dilute solution of MF (method 1). Both exhibited a similar content of nylon-6, i.e., 66% and 62 wt %, respectively, as determined by gravimetry. The comparison of the respective SEM pictures clearly showed the advantage of passing MF solution through the nylon-6 mat (method 2) as the wetting procedure. In this case, the whole nylon-6 mat was completey wetted without cracks and inhomogeneous wetting. The resulting composite fibers had a core−shell morphology, as shown in Figure 9. In comparison to this, immersion of nylon-6 mat in MF solution provided an incompletely wetted mat (composite 4). This was reflected in the properties of composites as well (Figure 10 and Table 2). Composite 3 showed a significant increase regarding tensile stress (78 MPa vs 54 MPa) and elongation at break (38% vs 25%) as compared to composite 4 prepared by method 1. In addition, the composites with extremely high amounts of nylon-6 fibers (around 82 wt %) prepared by method 2 showed a significant improvement of the mechanical properties. The shell of MF resin glued the fibers together and strengthened the interface bewteen matrix (MF resin) and the reinforcing fiber (nylon-6) in composites made by method 2.

The toughness of composites is a measure of work done per unit mass to break the sample. It was determined by dividing the area under stress−strain curves with density of the composites in a similar way as reported in literature for other systems.[34] The values are tabulated in Table 2. There was a small decrease in toughness from 27 J/g (31.5 MJ/m^3) to 18 J/g (21.3 MJ/m^3) on reducing the amount of reinforcing nylon fibers from 82 to 66 wt %, but still, the values are very high in the range of elastomeric materials. For example, toughness of about 25 MJ/m^3 was reported in the literature for elastomeric polyurethane membranes.[34] The toughness values for carbon nanotubes (CNT) reinforced poly(vinyl alcohol), kevlar, and spider dragline silk are 16, 33, and 165 J/g, respectively.[35] The effect of irregular and incomplete wetting/covering of nylon-6 fibers in composites made using method 1 was also reflected in toughness values. Another good comparison between the efficiency of two wetting procedures used in this work could be entries 2 and 7 of Table 2. They both had almost the same fiber content but drastically different toughness values. The composite made by method 1 (entry 2, Table 2) was tougher than many thermoplastics (PVA = 3−4 J/g) but showed significantly less toughness as compared to the composite made using method 2.

■ CONCLUSIONS

MF/nylon-6 composites were prepared using electrospun nylon-6 mats as reinforcement. The reinforcement in mechanical properties of the MF resin could be seen using nylon nanofiber mats. The fiber reinforced composites showed enhanced mechanical properties in comparison to those of pure nylon-6 nanomats and the MF resin. Interestingly, there was a drastic effect of the wetting procedure of the reinforcing fiber mat by the MF resin on both morphology and mechanical properties of the composites. The wetting of nylon-6 nanofibers by passing through a solution of MF resin resulted in a core–shell morphology and a significant improvement in properties as compared to the immersion procedure for wetting of the fibers. Depending upon the wt% of reinforcing nylon nanofiber mats, the composites can be considered as either fiber reinforced MF composites or MF glued nylon fibers.

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Notes

The authors declare no competing financial interest.

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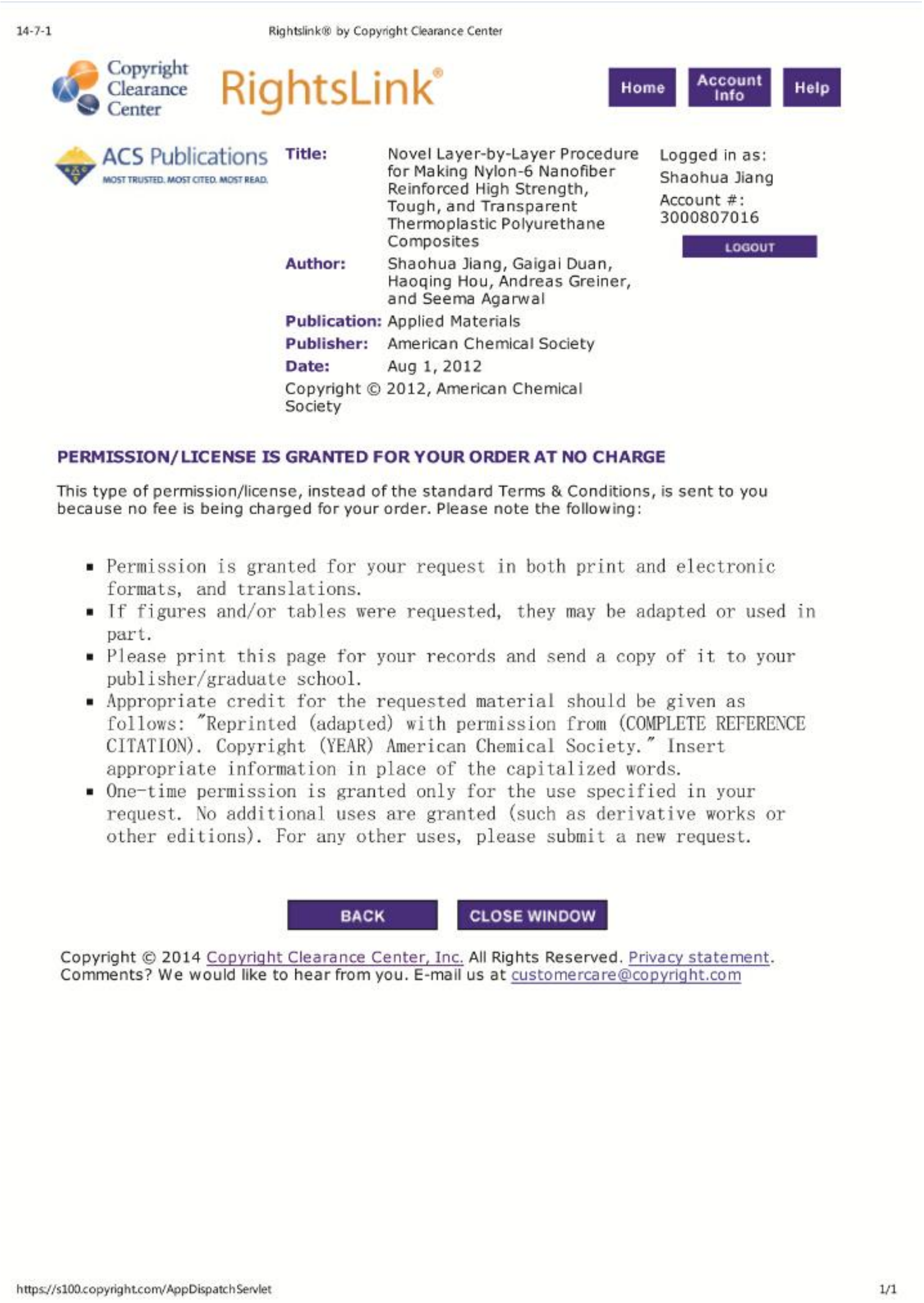
3.2. Novel layer-by-layer procedure for making nylon-6 nanofibers reinforced thermoplastic polyurethane composites

Shaohua Jiang, Gaigai Duan, Haoqing Hou, Andreas Greiner, and Seema Agarwal*, “Novel Layer-by-Layer Procedure for Making Nylon-6 Nanofiber Reinforced High Strength, Tough, and Transparent Thermoplastic Polyurethane Composites”, *ACS Applied Materials & Interfaces*, **2012**, *4*, 4366-4372



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Novel Layer-by-Layer Procedure for Making Nylon-6 Nanofiber Reinforced High Strength, Tough, and Transparent Thermoplastic Polyurethane Composites

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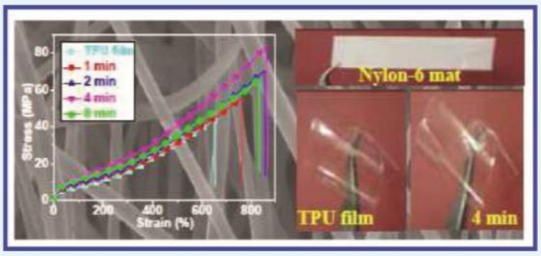
ABSTRACT: We highlight a novel composite fabrication method based on solution casting, electrospinning, and film stacking for preparing highly transparent nylon-6 nanofiber reinforced thermoplastic polyurethane (TPU) composite films. The procedure is simple and can be extended to the other thermoplastics. The morphology of fiber/matrix interface and the properties of composite films were also investigated. The method led to a significant reinforcement in mechanical properties of TPU like tensile strength, E modulus, strain, and toughness just using very small amounts of nylon fibers (about 0.4−1.7 wt %; 150−300 nm diameter). The enhanced mechanical properties were achieved without sacrificing optical properties like transparency of TPU.



KEYWORDS: *electrospinning, nanocomposites, mechanical properties, transparency, nanofibers*

1. INTRODUCTION

Thermoplastic polyurethanes (TPUs) are a special class of polymers widely used in different industries for varied applications like textile, footwear industry, tubings, biomaterials, and adhesives, to name a few.[1−6] TPUs with different material property profiles are required for these applications and can easily be made by changing the chemical structure of the starting materials like diisocyanate, polyol, and the chain extender.[7] Another easy and cost-effective method of changing properties of TPUs is using reinforcement fillers. Nanoparticles (nanoclay particles, silica nanoparticles)[8,9] and fibers (aramid fibers, carbon fibers, glass fibers, etc.)[10−12] have been used in the literature for improving the mechanical properties of TPUs.

In general, the key issues for producing high performance fiber reinforced polymer composites are the use of high strength fibers, large length/diameter ratio of fibers, good wetting procedure of fibers by matrix solution, homogeneous dispersion of fibers in matrix, and strong interfacial interaction between fibers and matrix. Polymer nanofibers produced by electrospinning have been attracting more and more attention for the preparation of composites. The continuous long fibers produced by electrospinning lack fiber edges (ends) and therefore do not have stress concentration points in composites. During the electrospinning, the polymer molecular chains tend to align along the fiber axis as the polymer jet is drawn up to 100 000 times in less than 0.1 s.[13] These highly molecular oriented nanofibers can provide a mechanically strong fiber for the preparation of fiber reinforced composites. Also, electrospun nanofiber mats have high porosity and large specific surface area. Therefore, nanofibers produced by electrospinning could be highly promising candidates for reinforcement purposes. Moreover, the diameters of electrospun nanofibers are usually less than the wavelength of visible light and expected to give transparent composites.[14−16]

Despite so many advantages of nanofibers, only countable studies are available in the literature regarding the electrospun nanofiber reinforced composites. A recent review article[17] is a good refrence supporting this fact. Early reports of reinforcing effects of nanofibers in an epoxy and a rubber matrix (styrene-butadiene rubber) were contributed by Kim et al.[18] They showed an increase in Young's modulus, fracture toughness, and fracture energy of the epoxy matrix. Bergshoef et al. showed the formation of transparent epoxy composites using 4 wt % nylon-4, 6 electrospun nanofibers (30−200 nm in diameter).[14] Nylon-6 nanofibers produced by electrospinning exhibit excellent mechanical properties, such as toughness and high tensile strength,[19,20] and have also been adopted to make composites with poly (methyl methacrylate),[21] polyaniline,[22] and polycaprolactone[23] and with bis-glycidyl methacrylate/tetraglycidylmthacrylate (BIS-GMA/TEGDMA) as dental restorative composites.[24,25] Subsequently, cellulose,[26] polyvinyl alcohol (PVA),[27] polyacrylonitrile (PAN),[28,29] polyimide,[30] and nylon-66[31] nanofibers were reported to make nanofiber reinforced composites.

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Recently, we highlighted the importance of the nanofiber wetting procedure for the preparation of highly tough and transparent composites using nylon-6 as reinforcing fibers for Melamine formaldehyde.[32] A change of the wetting method could bring about a drastic change in the morphology of the wet fibers. The wetting of nylon fibers by passing through a solution of MF resin showed a core−shell morphology and a significant improvement in properties as compared to the dip-coating procedure for wetting of the fibers. Different composites with varied amounts of nylon-6 fibers generated a profile of properties.

There are several conventional ways to fabricate fiber reinforced composites such as solution mixing and casting, melt mixing, and wetting of fibers by polymer matrix and subsequent stacking by hot-press. The method chosen should show uniform distribution and good wetting of the reinforcing material. In the present study, we highlight a novel composite fabrication method based on solution casting, electrospinning, and film stacking for preparing highly transparent nylon-6 nanofiber reinforced thermoplastic polyurethane composite films. The effect of this novel and quick wetting procedure on the morphology of fiber/matrix interface and on the properties of composite films were investigated using scanning electronic microscopy (SEM), attenuated total reflectance spectroscopy (ATR-IR), thermo gravimetric analysis (TGA), tensile testing, and UV−vis spectroscopy. A very small amount of nylon fibers could enhance the mechanical properties significantly without sacrificing optical properties like transparency of TPU. The results are presented here.

2. EXPERIMENTAL SECTION

2.1. Materials. Nylon-6 (Ultramid B24 NSD05, pellet size: 2.0−2.0 mm) was kindly supplied by BASF while thermoplastic polyurethane (TPU, Desmopan DP 2590A) was purchased from Bayer Materials Science. The solvents, formic acid (FA, ⩾98%), acetic acid (AcOH, ⩾98%), and anhydrous dimethyl formamide (DMF, 99.8%), were acquired from Sigma-Aldrich. All materials were used as received without further purification.

2.2. Electrospinning and Composite Fabrication. The fabrication of nylon-6 nanofiber reinforced TPU composites consists of solution casting, electrospinning, and film stacking. TPU (2.5 wt %) solution in DMF and 20 wt % nylon-6 solution in FA/AcOH (40/60, w/w) were used for film casting and electrospinning, respectively. The detailed composite preparation process is shown in Figure 1. It contains the following steps: (1) 1 mL of 2.5 wt % TPU solution in DMF was casted on a glass slide; (2) electrospinning of one thin layer of nylon-6 nanofibers on the wet TPU solution; (3) drying at 100 °C to obtain composite with one layer of TPU film and one layer of nylon-6 nanofibers; (4) repeat the above 3 steps (casting TPU solution, electrospinning nylon-6 nanofibers, and drying) for another 3 times; (5) casting the last layer of TPU solution and drying to gain a laminated composite with alternate layers of TPU and nylon-6 nanofibers (in total 3 layers of nylon-6 nanofibers sandwiched by 4 layers of TPU films). During the electrospinning, a 20 kV electrical potential was applied on the flat tip of the needle (diameter of 0.8 mm) while the distance between the needle tip and the glass slide was 20 cm.

Many different composites were made by keeping the amount of TPU constant but varying the amount of nylon-6 reinforcing fibers. The amount of nylon-6 fibers in composites was varied by carrying out electrospinning for different intervals of time, i.e., each layer of nylon-6 was spun for 1, 2, 4, or 8 min. The concentration of nylon-6 solution used for electrospinning was kept constant. The content of nylon-6 nanofibers in the composites was measured by gravimetry. All the composites had 4 layers of TPU (1 mL, 2.5 wt % in DMF) and 3 layers of nylon-6 nanofibers (each layer was electrospun for 1, 2, 4, or 8 min). The content of nylon-6 by weight ($C_{\text{nylon-6}}$) was calculated by the following equation:

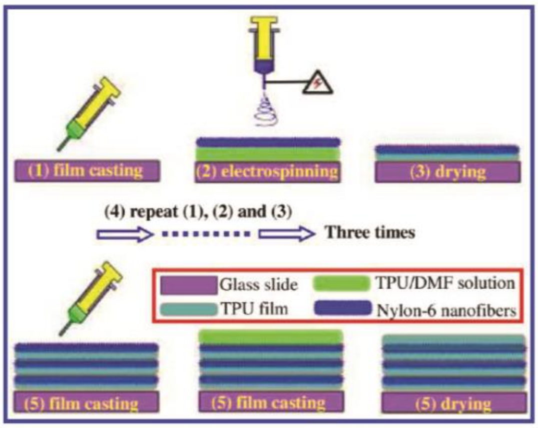

Figure 1. Schematic of the preparation of nylon-6 nanofiber reinforced TPU composite films.

$$C_{\text{nylon-6}} = \frac{3 \times m_{\text{nylon-6}}}{4 \times m_{\text{TPU}} + 3 \times m_{\text{nylon-6}}} \times 100\%$$

where m_{TPU} and $m_{\text{nylon-6}}$ stand for the weight of 1 layer of TPU and nylon-6 nanofibers, respectively. The electrospinning time of 1, 2, 4, and 8 min for each layer corresponded to 0.4, 0.9, 1.7, and 3.4 wt % of nylon-6 nanofibers in the laminated composites (4 layers of TPU films and 3 layers of nylon-6 nanofibers). As blanks, neat TPU films were made by casting 4 mL of (2.5 wt %) TPU/DMF solution, and nonwoven nylon-6 nanofiber mat was made by electrospinning 20 wt % nylon-6 in FA/AcOH (40/60, w/w).

2.3. Characterizations. The G10 contact angle analysis system (Kreuess, Hamburg, Germany) was used to test the wetting of the nylon-6 nanofiber mat with DMF. The surface morphology and the cross-section morphology of the TPU/nylon-6 nanofiber composites were observed by the JSM-7500 scanning electronic microscopy (SEM). Prior to scanning, the specimens were sputter-coated with gold for 120 s to avoid charge accumulations. Cross-section samples were prepared by breaking the frozen films in liquid nitrogen. Image J software was used to measure the diameter of nylon-6 nanofibers and to make a diameter distribution. ATR-IR spectra were recorded on a Digilab Excalibur Series with an ATR unit MIRacle from the company Pike Technology. The Zwick/Roell BT1-FR 0.5TN-D14 machine, equipped with a 200 N KAF-TC load sensor using a stretching rate of 50 mm/min, was applied to measure the mechanical properties. All the specimens were cut into dog-bone-shape with an average length of 3.0 cm and a central width of 0.2 cm. The Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer operating in transmittance mode (200−800 nm) was used to characterize the optical properties. The Mettler Toledo TGA/SDTA 851e was carried to study the thermal properties at a heating rate of 10 °C/min in N_2 from 50 to 800 °C.

3. RESULTS AND DISCUSSION

3.1. Fabrication of TPU/Nylon-6 Nanofiber Composites. The long continuous nylon-6 nanofibers were fabricated by the process of electrospinning in this study. The resulted nylon-6 nanofibers were collected as nonwoven mat and had a smooth surface morphology as seen in Figure 2A. No defects such as beads, pores, or ribbons were found in/on the nanofibers. The ultrafine nylon-6 nanofibers displayed a centralized diameter distribution ranging from 150 to 300 nm (Figure 2B).

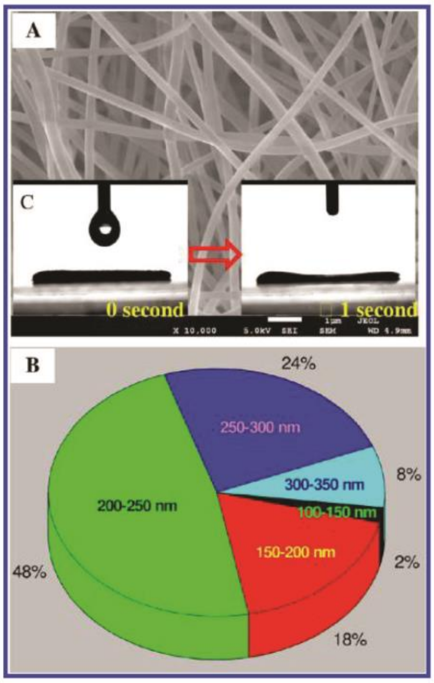

Figure 2. SEM image (A), pie chart of the diameter distribution (B), and DMF wetting behavior (C) of nylon-6 nanofiber mat. Scale bar of (A) = 1 μm.

For the fiber reinforced composites, it is important to embed the fibers into the polymer matrix. This in turn depends on the dispersion of fibers and good wetting between fibers and matrix. In one experiment, the nylon-6 nanofibers were collected on the dried TPU film. Because of the multilayered morphology of nanofiber mat and the cylinder/ellipsoid structure of nanofibers, only a part of the fibers was in contact with the TPU film (Figure 3A). This kind of nanofiber/matrix morphology (Figure 3A) provides a poor interfacial interaction between fibers and matrix, which would not be useful to fabricate high quality composites.

To achieve good wetting and embedding of reinforcing nylon-6 fibers in TPU matrix, the nylon-6 nanofibers were directly electrospun on the TPU/DMF solution in a layer-by-layer process. This procedure was adopted because of ultrafast wetting of nylon-6 nanofibers by DMF. Nylon-6 is not soluble in DMF but undergoes very fast wetting (in less than 1 s; Figure 2C). Therefore, the randomly deposited nanofibers on TPU/DMF solution ensured nice dispersion and homogeneous wetting of reinforcing nylon-6 nanofibers with TPU matrix. The nanofibers could be completely wetted quickly by the DMF solvent, subsequently sinked into the TPU resin while maintaining the morphology and formed tight contact with the resin (Figure 3B). Further, different experiments were carried out with varied amounts of nylon-6 nanofibers in the first layer. The amount of nanofibers was regulated by the time of electrospinning as described in the experimental part. The wetting behavior of nylon-6 nanofibers by DMF made the fibers completely embedded in the TPU matrix for low amounts of nylon fibers, i.e., electrospinning until about 4 min (Figure 3B,C); the increased thickness of the nanofiber layer with increased spinning time (8 min) led to wetting of underneath layers, but top layers could not be impregnated completely (Figure 3D). Therefore, the layer-by-layer process of wetting reinforcing nylon fibers was used and another layer of TPU/DMF solution was casted on the surface of the 2-layered composites described above followed by electrospinning of nylon-6 again for the same time intervals, i.e., 1, 2, 4, and 8 min on different samples. The procedure was continued to make a TPU/nylon-6 composite film with 4 TPU layers sandwiching 3 layers of randomly oriented nylon fibers.

The resulted composite films revealed a smooth surface as shown in Figure 4B and had almost the same morphology as the neat TPU film (Figure 4A). The absence of nylon-6 nanofibers both on the surface of TPU/nylon-6 nanofiber composite film and on edges as pulled-out structures suggested a good dispersion of nanofibers in the TPU matrix.

The uniform dispersion of reinforcing nylon fibers could also be proved by the ATR-IR spectroscopy. There was no difference observed in spectra of neat TPU (Figure 5A), 2 layer composite film with ATR measured on TPU side (Figure 5G) and multilayered composite film (Figure 5H) with both sides (top and bottom) TPU layers. This confirmed the homogeneous distribution of fibers in bulk and no fibers on the surface. The ATR-IR was also recorded on 2-layer composite samples with the incident light directed from nylon-6 nanofiber side to TPU side (Figure 5B,C,D,E). The intensity of the characteristic peak of nylon-6 (carbonyl stretching, indicated with black arrow) increased from spectra (C) to (E) showing increased amount of the nylon-6 nanofiber in the 2 layered composites. Further, the carbonyl peak of nylon-6 in composites had a small red shift (1643 cm^{-1} for (C), (D), and (E); 1639 cm^{-1} for pure nylon-6 mat), which might be the result of hydrogen bonding between nylon-6 and TPU. Spectrum (B) did not show any characteristic peaks of nylon-6, and the ATR-IR spectrum was nearly the same as that of neat TPU (Figure 5A). This is due to the deposition of an extremely thin layer of nylon-6 nanofibers (electrospinning time of 1 min) in TPU, and all the nanofibers were embedded into the TPU matrix.

TPU and nylon-6 nanofiber mat showed a good resistance to heat. A 5% weight loss as determined by thermogravimetric analysis (TGA) was observed at 316 and 390 °C for TPU and nylon-6 nanofiber mat, respectively (TGA thermogram not shown here). After incorporating nylon-6 nanofibers into TPU matrix, the composites presented almost similar thermal behavior as that of neat TPU.

3.2. Mechanical Properties. Figure 6 shows the typical stress−strain curves of neat TPU film and TPU/nylon-6 nanofiber composite films. The average tensile properties such as tensile strength, elongation at break, and E modulus are summarized in Table 1. It can be seen that the neat TPU film revealed an avearge tensile strength of 42 MPa, E modulus of 27 MPa, and elongation at break of 673%. The TPU/nylon-6 nanofiber composite films displayed significantly high mechanical properties with even very small amounts of nylon fibers. The tensile strength and E modulus increased with an increase in the amount of reinforcing nylon-6 nanofibers until about 1.7 wt %. The tensile strength and E modulus were almost doubled with 1.7 wt % of reinforcing fibers with a significant increase in elongation at break. Although, further increase in the amount of nylon fibers to 3.4 wt % led to a drop in mechanical properties, but still, the mechanical properties were significantly higher than the neat TPU film. A similar trend was also observed for

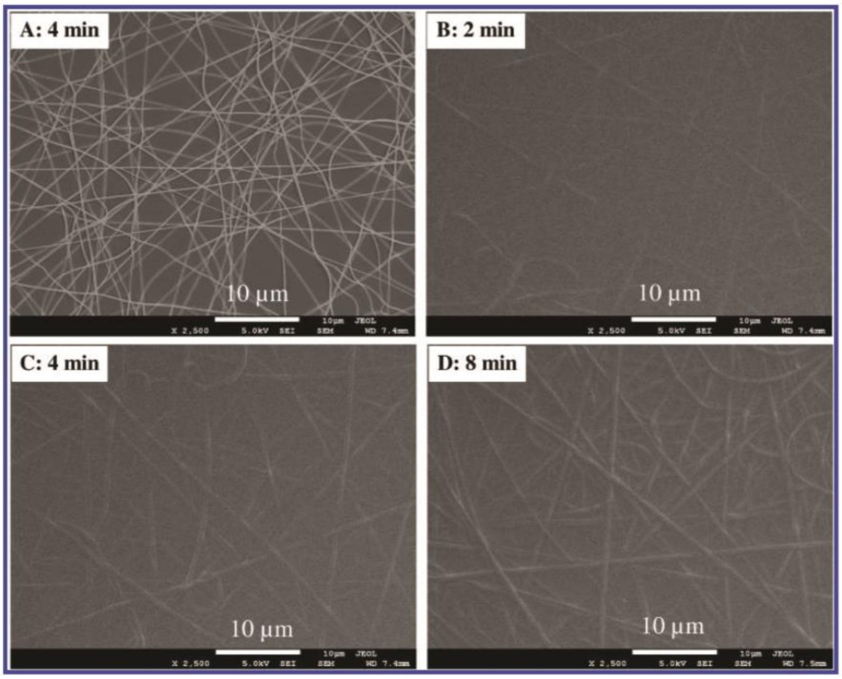

Figure 3. Surface morphologies of 2-layered TPU/nylon-6 nanofiber composite films (A: nylon-6 nanofibers on TPU film; B, C, and D: nylon-6 nanofibers embedded in TPU resin). The electrospinning time of A, B, C, and D were 4 min, 2 min, 4 min, and 8 min, respectively. Scale bar = 10 *µ*m.

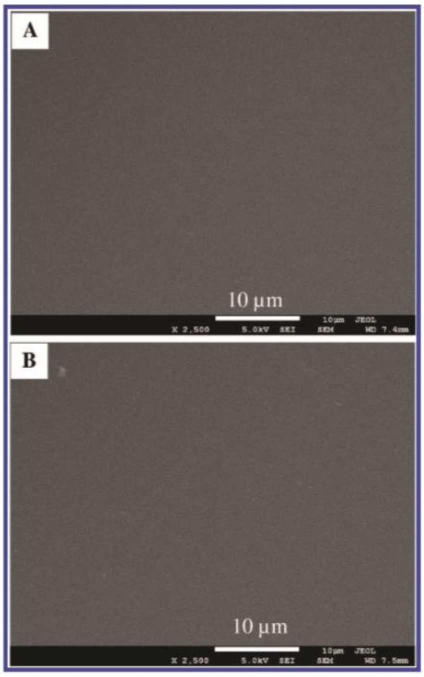

Figure 4. Surface morphologies of neat TPU film (A) and laminated TPU/nylon-6 nanofiber composite (B). Scale bar = 10 *µ*m.

toughness. The toughness of composites is a measure of work done per unit mass to break the sample. It was determined by dividing the area under stress−strain curves with the density of the composites in a similar way as reported in the literature for other systems.[33] There was a significant increase in toughness of composite films (108 J/g for TPU; 274 J/g for reinforced TPU with 1.7 wt % of reinforcing fibers), and highly flexible films were obtained.

Generally, several factors will influence the mechanical properties of fiber reinforced composites: the original mechanical properties of the fibers, the dispersion of fibers in matrix, and the fiber/matrix interfacial interaction. In the present work, nylon-6 nanofibers were chosen as reinforcing fibers as they are already proved to be excellent reinforcing material in previous reports.[21,23−25] The layer-by-layer (LBL) process used for making composites provided homogeneous dispersion of randomly deposited nylon-6 nanofibers in the TPU/DMF solution, as evidenced by the SEM images in Figure 3B,C,D. Also, due to the quick wetting process of nylon-6 nanofibers by DMF, as described before, the nylon-6 nanofibers were completely impregnated in the TPU matrix. This resulted in a strong interfacial morphology with no obvious edges between nanofibers and TPU matrix. The nanofibers were entirely embedded into the TPU matrix with no voids around the fibers as evidenced by the cross-section morphologies of the composites (Figure 7B,C,D). Additionally, the intermolecular interaction between nylon-6 and TPU, such as the hydrogen bonding as proved by FT-IR, could also be responsible for a strong interface. Therefore, during the tensile test, the load could be effectively transferred from the nylon-6 nanofibers to the TPU matrix, which resulted in the significant improvement

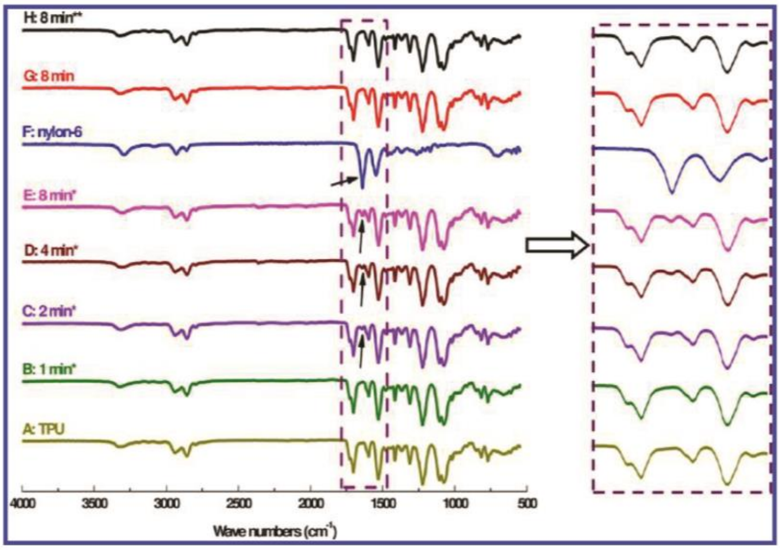

Figure 5. ATR-IR spectra of pure TPU film (A), neat PA-6 nanofiber mat (F), 2 layered TPU/nylon-6 nanofiber composite (B, C, D, E, and G), and laminated composite with 3 layers of nylon-6 nanofibers and 4 layers of TPU films (H).

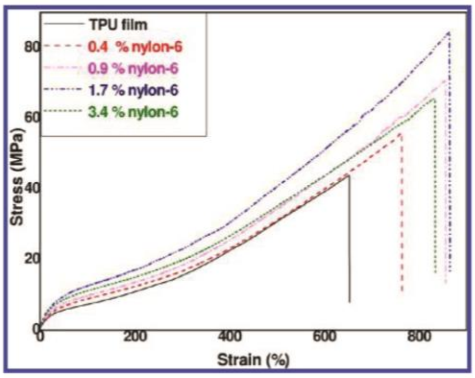

Figure 6. Typical stress−strain curves of TPU/nylon-6 nanofiber composite films with different amounts of reinforcing nylon-6 nanofibers.

of mechanical properties of the composites even with very small amount of nylon fibers. The small amounts of nylon fibers (0.4 wt %) already showed reinforcing effects although the optimum properties were achieved at 1.7 wt % of the reinforcing nylon fibers.

Figure 6 and Table 1 revealed that the electrospinning time (or the amount of nylon-6 nanofibers) had a significant effect on the mechanical properties of the TPU/nylon-6 nanofiber composite films. On increasing the electrospinning time, the mechanical properties, including tensile strength, elongation at break, and E modulus first increased until about 4 min of electrospinning time (each layer was electrospun for 4 min and corresponded to about 1.7 wt % of nylon fibers) and then decreased on increasing the electrospinning time to 8 min.

To reveal the reasons for the mechanical properties trend, cross-section morphology of the composite films was investigated. This helped in commenting about the fiber distribution, the fiber amount in matrix, and the interaction between nanofibers and matrix. In order to obtain the original morphology without damage by the external forces, all the samples were first frozen in liquid nitrogen and then broken. As shown in Figure 7A,B,C,D, the neat TPU film presented a smooth cross-section while the composites revealed a rougher laminated morphology where 3 layers of nylon-6 nanofibers (white dots) were distributed in the TPU matrix (gray area). On increasing the electrospinning time from 2 to 4 min, there was an increase in the amount of homogeneously distributed load bearing reinforcing nanofibers in TPU matrix but importantly without any aggregation. When the electrospinning time was further increased to 8 min, there was an increase in the amount of nanofibers (Figure 7D) but they aggregated (Figure 7D, a) and formed defects, such as pulled-out nanofibers (Figure 7D, b), and holes/voids around the

Table 1. Summary of Mechanical Properties of the Neat TPU Film and TPU/Nylon-6 Nanofiber Composite Films with Varied Electrospinning Time (Nylon-6 Content) for Each Nanofiber Layer

nylon-6 content (%)	stress (MPa)	strain (%)	E modulus (2%) (MPa)	integration of stress−strain curves (MJ/m^3)	toughness (J/g)
0	42.27 ± 2.36	672.9 ± 40.3	27.1 ± 1.5	131.25 ± 11.21	108.47 ± 9.27
0.4	53.70 ± 3.67	753.4 ± 59.4	34.2 ± 1.9	183.92 ± 23.19	152.04 ± 19.17
0.9	64.82 ± 4.12	867.7 ± 52.6	35.9 ± 3.4	254.40 ± 22.95	210.39 ± 18.98
1.7	82.98 ± 6.19	876.0 ± 72.5	51.9 ± 6.7	332.14 ± 48.32	274.83 ± 39.98
3.4	60.32 ± 5.93	812.3 ± 70.5	49.0 ± 2.8	233.91 ± 38.85	193.78 ± 32.18

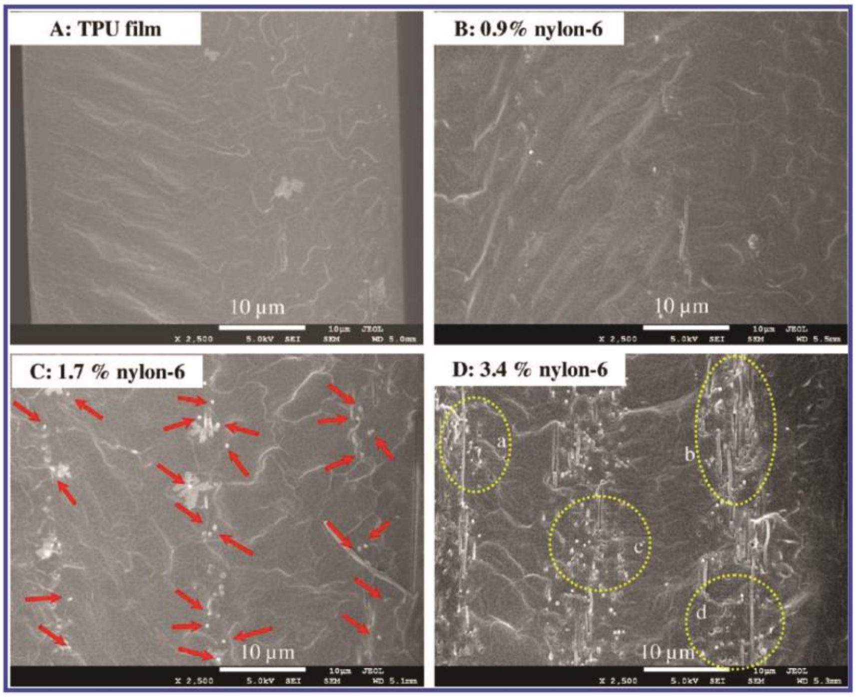

Figure 7. Cross-section morphologies of neat TPU film and laminated TPU/nylon-6 composites with varied electrospinning time on each layer. Scale bar = 10 μm.

nanofibers (Figure 7D, c and d). This led to reduction in mechanical properties.

The neat TPU film was transparent with light transmittance of 96% in the visible light range. In contrast, the nylon-6 nanofiber mat is opaque with no visible light transmittance (Figure 8). The nylon-6 nanofibers reinforced TPU composite films showed very high light transmittance and were transparent. The high transmittance of composite films might be the result of the small diameter of nylon-6 nanofibers and nearly the same refractive index of the nylon-6 (1.53) and TPU (1.51).[34,35] Although, the transmittance of the composites was dependent upon the amount of nylon fibers, but all composite films showed more than 85% light transmittance. The composite film with about 1.7 wt % of the reinforcing nylon-6 nanofibers showed the highest improvement in mechanical properties with very high (89%) light transmittance.

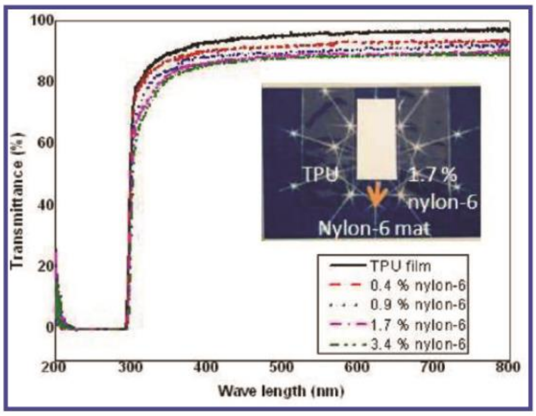

Figure 8. UV–vis spectra of TPU/nylon-6 nanofiber composite films (A) and digital photograph of transparent neat TPU film, nylon-6 nanofiber mat, and composite film (B).

4. CONCLUSION

A novel procedure of making nanofiber reinforced thermoplastic films is successfully shown by taking nylon-6 nanofibers and thermoplastic polyurethane (TPU) as an example. The procedure is simple and can be extended to other thermoplastics. The significant reinforcement in mechanical properties of TPU like tensile strength, E modulus, elongation at break, and toughness could be seen just using very small amounts of nylon fibers. Even as small as 0.4 wt % of nylon fibers could improve mechanical properties significantly and increase further with an increase in the amount of fibers until an optimum amount was reached (1.7 wt % in this case). The mechanical properties were almost doubled at this amount. The enhanced mechanical properties were achieved without sacrificing optical properties like transparency of TPU.

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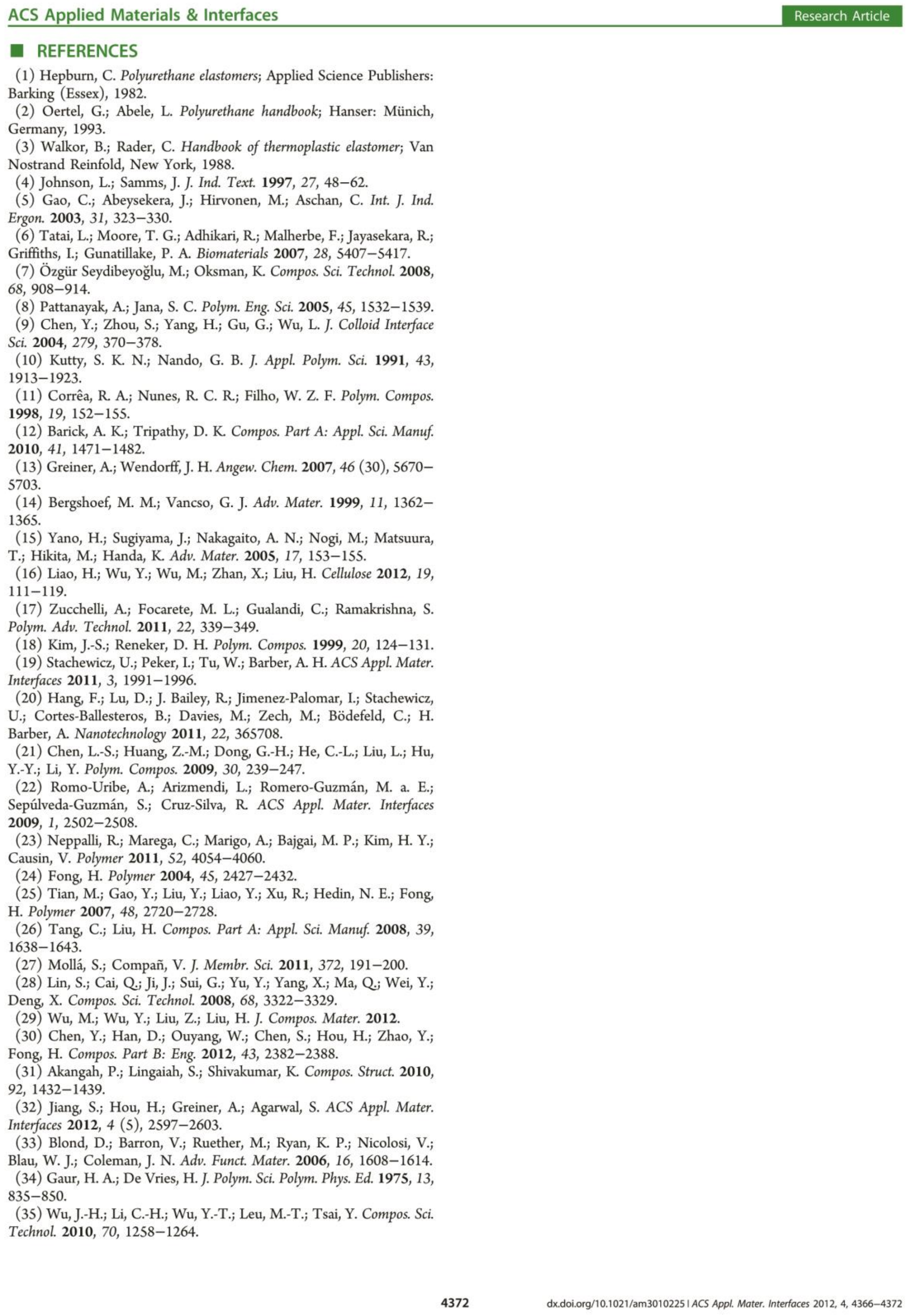
Notes

The authors declare no competing financial interest.



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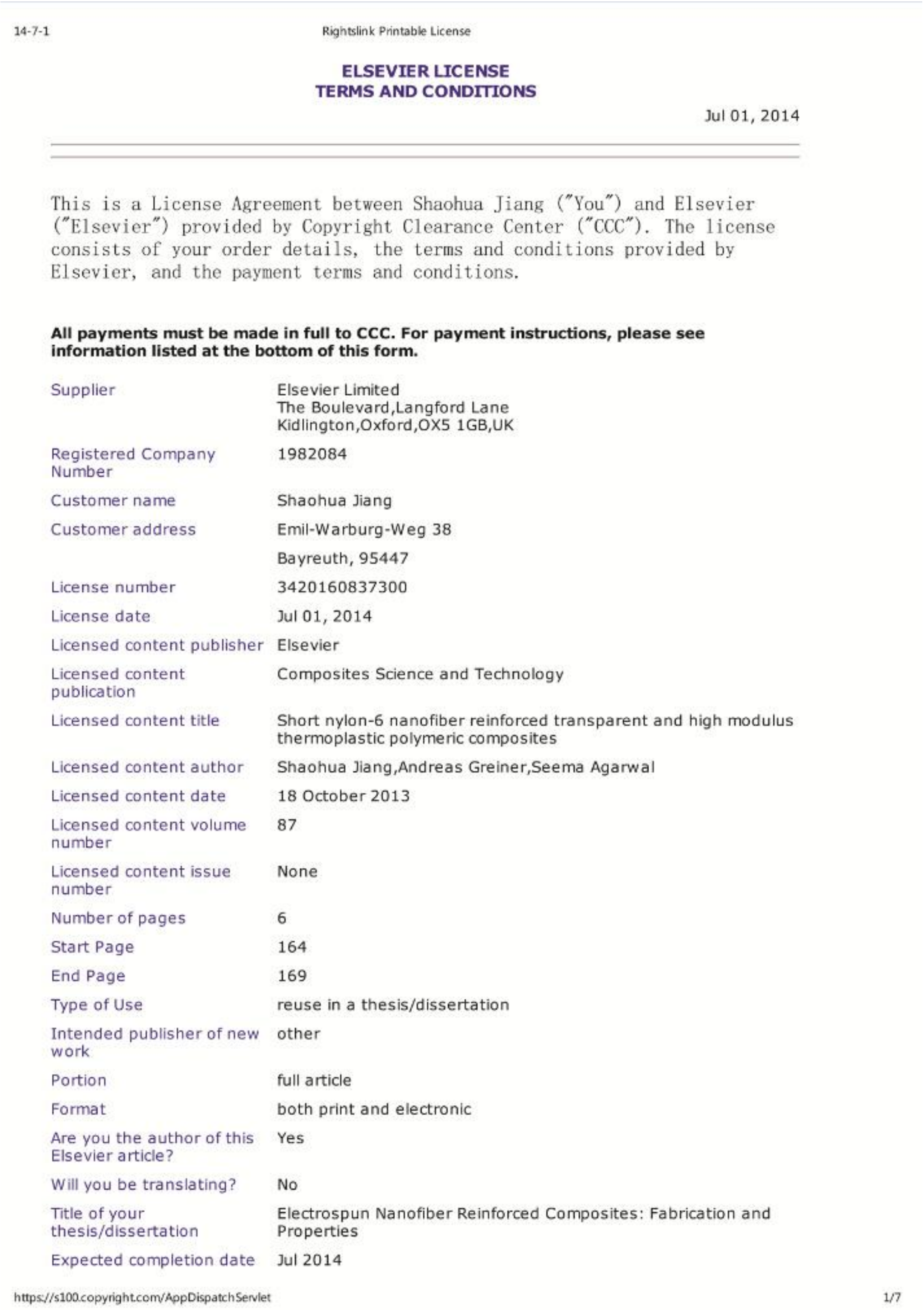
3.3. Short nylon-6 nanofiber reinforced transparent and high modulus thermoplastic polymeric composites

Shaohua Jiang, Andreas Greiner, and Seema Agarwal*, "Short nylon-6 nanofiber reinforced transparent and high modulus thermoplastic polymeric composites", *Composite Science and Technology*, **2013**, *87(18)*, 164-169



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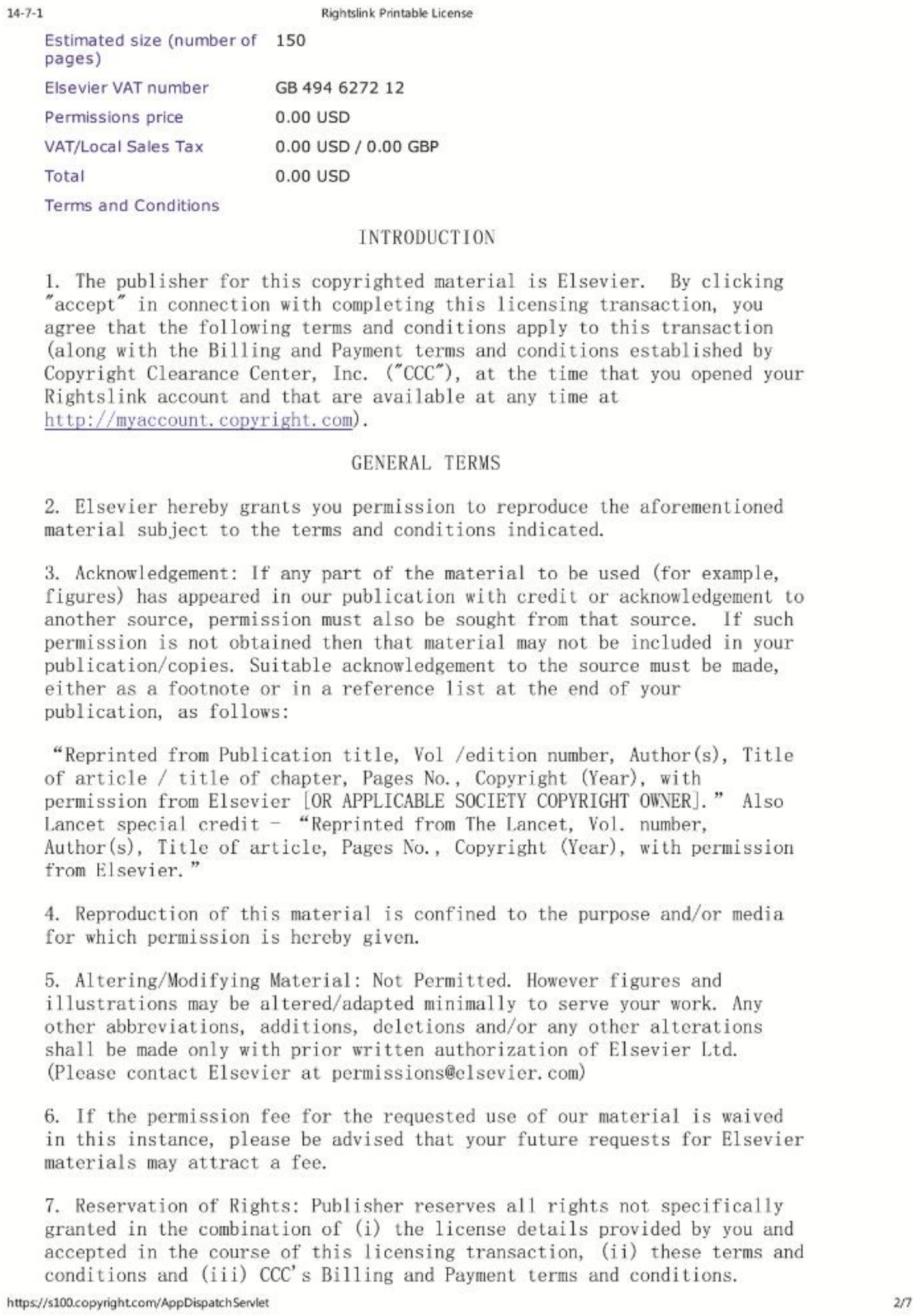

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INTRODUCTION

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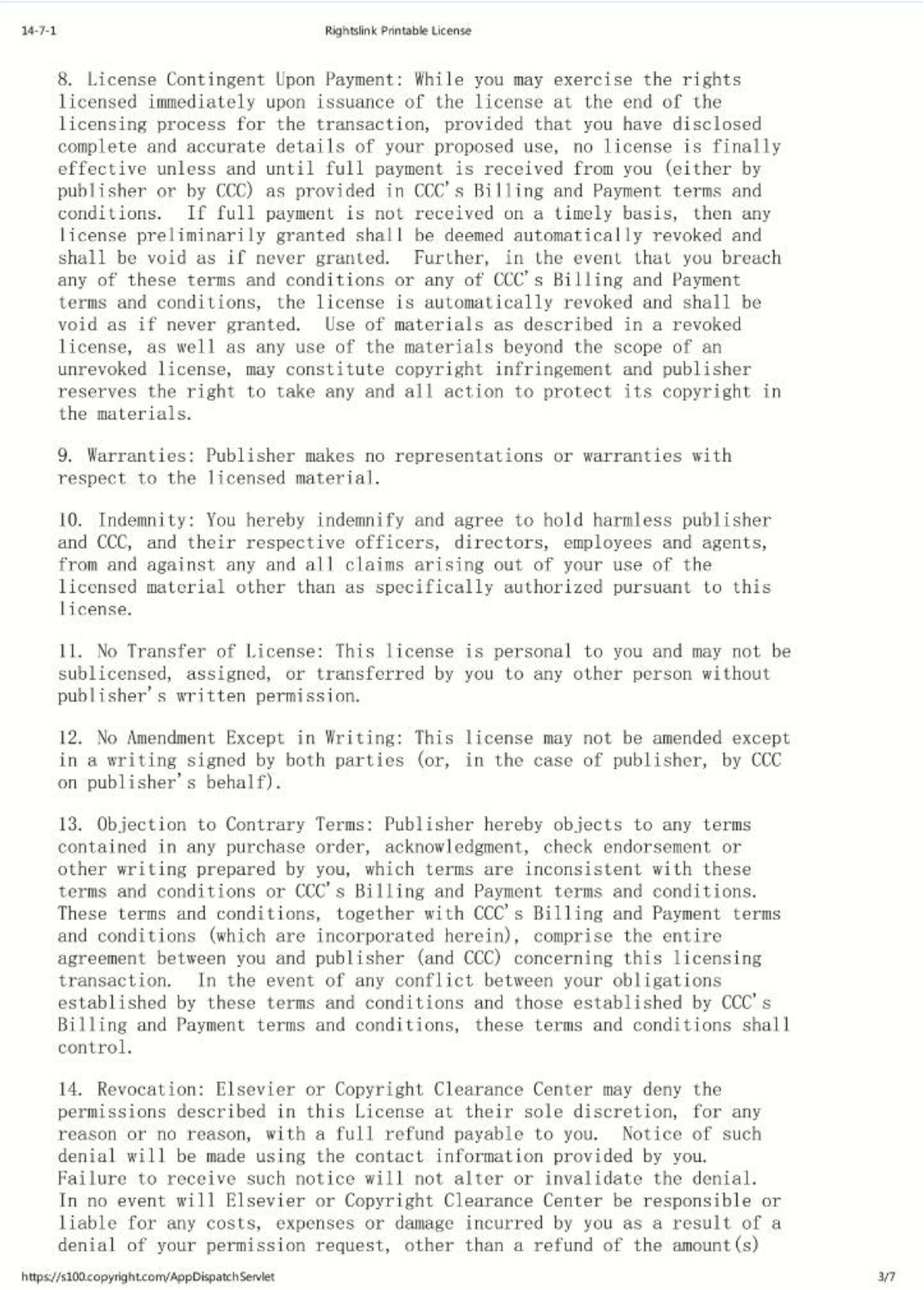

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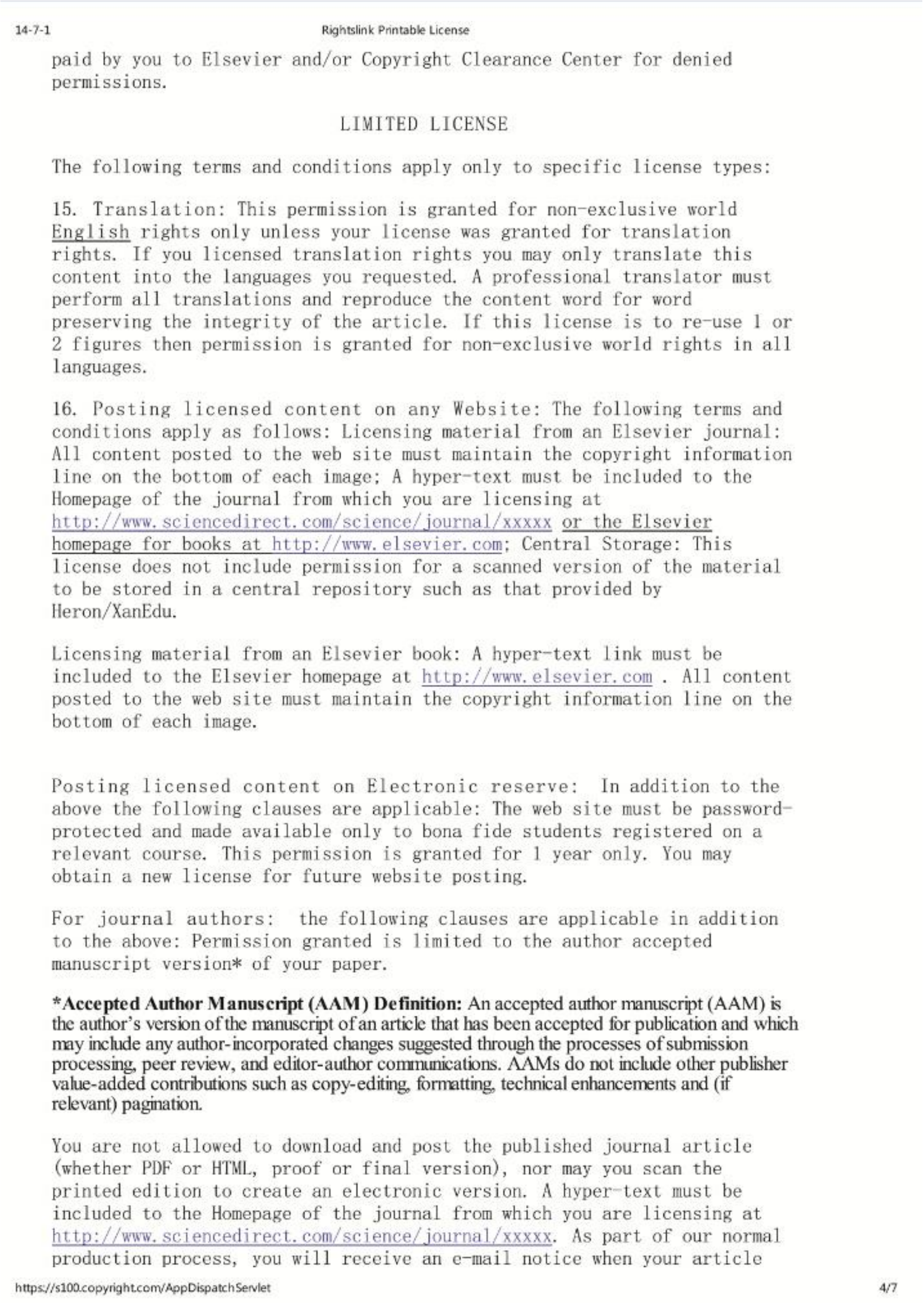

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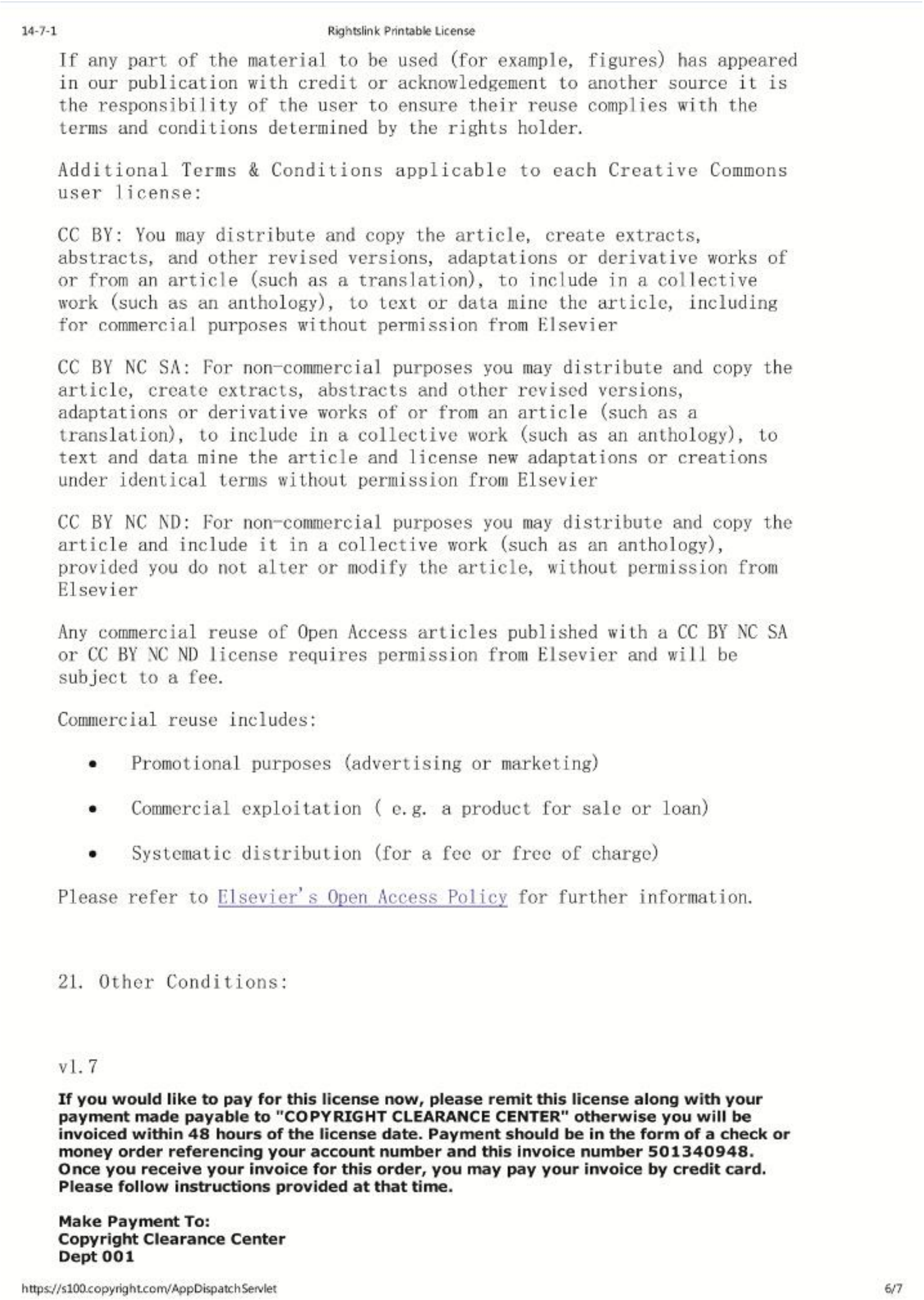

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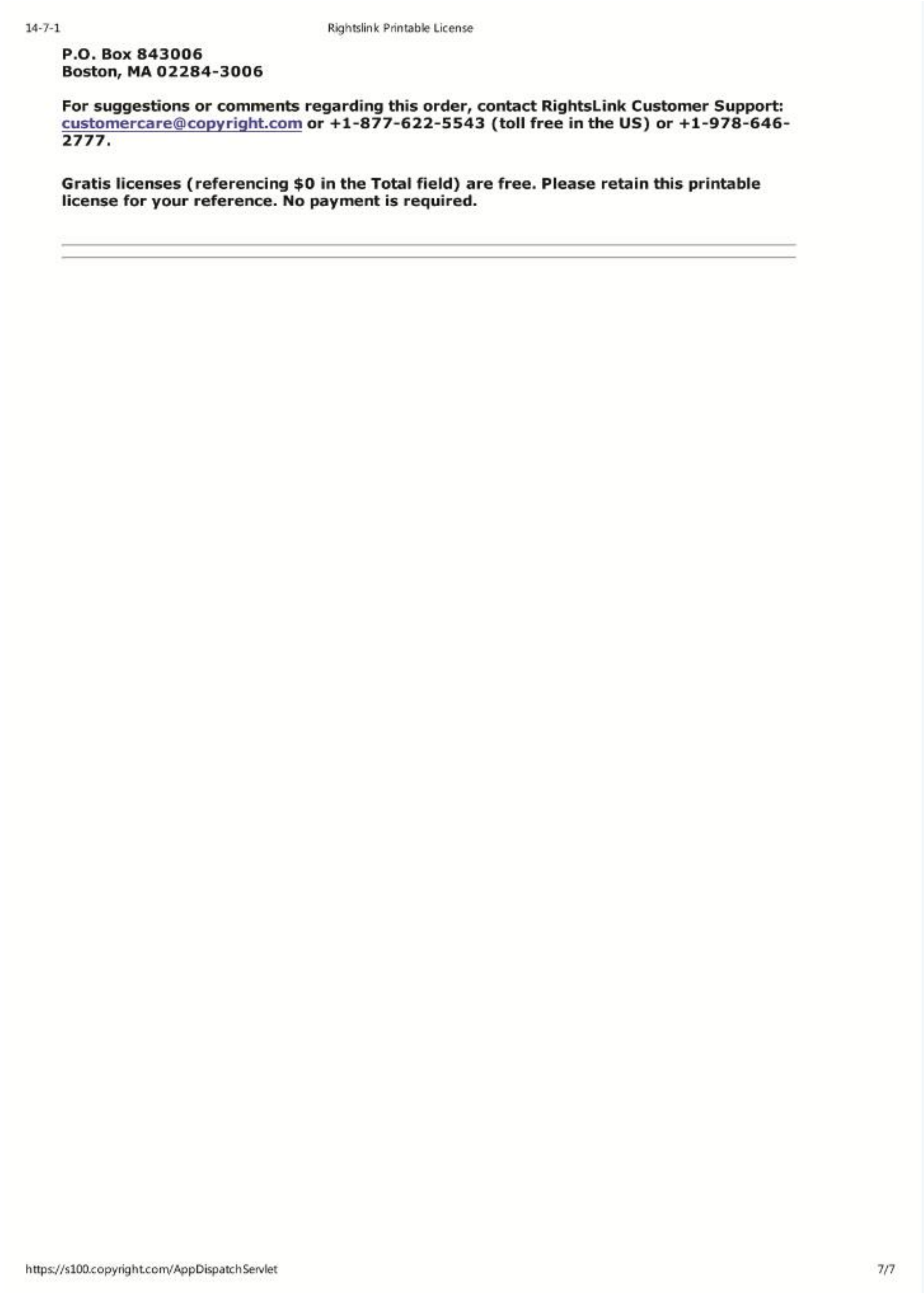

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Short nylon-6 nanofiber reinforced transparent and high modulus thermoplastic polymeric composites

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ABSTRACT

The use of small amounts (<5 wt%) of short nylon-6 nanofibers (diameter less than 200 nm) for reinforcing mechanical properties of TPU without losing its optical properties is highlighted in this work. The interaction of H-bonding type between the reinforcing fibers and the matrix polymer could provide a homogenous distribution of fibers and a strong interface leading to significant enhancement in mechanical properties (185% increase in *E* modulus) as shown by comparative use of TPU and PMMA as matrix polymers. The reinforcing effect of short fibers was attained without sacrificing transparency (>90% transparency in 400–800 nm range) of TPU. The effective use of short nylon-6 fibers in comparison to the long and continuous fibers is also discussed.

1. Introduction

Fiber reinforced polymeric composites make use of fibers like glass, ceramic, carbon, jute and cellulose for reinforcing mechanical, optical and thermal properties of thermoplastics and thermosets [1,2]. The key issues for producing high performance fiber reinforced polymer composites are the use of high strength fibers, large length/diameter ratio of fibers, good wetting procedure of fibers by matrix solution, homogeneous dispersion of fibers in matrix, and strong interfacial interaction between fibers and matrix [3,4]. The state-of-the-art reinforcing fibers are in general few micrometers in diameter and till date, the research efforts on nanofiber reinforced polymer composites are mainly focused on the use of carbon fibers (CNFs) or vapor-grown carbon nanotubes (CNTs) [5–9] and cellulose whiskers [10,11].

One of the fiber processing techniques called electrospinning provides continuous, highly molecularly oriented fibers with varied diameters (in nanometer range), morphologies and types in a simple way [12]. Although the use of polymer nanofibers produced by electrospinning for reinforcing purposes is still in its infancy but is attracting more and more attention for the preparation of composites. After the early work of Kim et al. of using polybenzimidazole nanofibers for reinforcing epoxy and a rubber matrix (styrene–butadiene rubber) [13] many more scattered studies were carried out in the literature regarding use of various polymeric nanofibers, most commonly nylon-6 made by electrospinning for improving polymer matrix properties [14]. Other polymeric electrospun nanofibers like cellulose, polyacrylonitrile (PAN), polyimide and nylon-66 have also been used as reinforcement for composites [15–17]. The continuous long fibers produced by electrospinning lack fiber edges (ends) and therefore do not have stress concentration points in composites. Also, they have high porosity and large specific surface area (about 100 times more than that of conventional reinforcing micro fibers like carbon and glass). Besides these advantages, any polymer that is either soluble in water/organic solvents or meltable can be spun into nanofibers by electrospinning. This widens the horizon of choosing appropriate fibers depending upon the functionality required in the reinforced composites. The technical developments made in the last few years in the method of electrospinning have enhanced the production capacities from few grams to many kilograms of nanofibers or nanofiber nonwovens in short time. With such developments many new application areas of nanofiber nonwovens would pick-up pace and one such area is fiber reinforced composites.

The individual and scattered studies of using polymeric nanofibers for reinforcement purposes as highlighted above does not help in making any sound conclusions regarding the effect of fiber properties and/or processing method on the final composite properties. Recently, we highlighted the importance of the composite preparation method (nanofiber wetting procedure) using electrospun long and continuous nylon-6 as reinforcing fibers for melamine–formaldehyde as thermoset [18]. Since long and continuous nanofiber nonwovens were utilized in these methods it was not possible to make composites with less than 13 wt% of the reinforcing fibers. Further, we highlighted a novel Layer-by-

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Layer (LBL) composite fabrication method based on solution casting, electrospinning and film stacking for preparing highly transparent nylon-6 nanofiber reinforced thermoplastic composite films with less amounts of reinforcing fibers [4]. Thermoplastic polyurethane was chosen as the example and the reinforcing nanofibers were directly spun on the thermoplastic solutions for different time intervals to control its amount. Very small amount of nylon fibers (<4 wt%) could enhance the mechanical properties significantly without sacrificing optical properties like transparency of TPU. However, it is very difficult to make homogenous composites with predetermined amounts of nanofibers in all these methods described above. The exact amount of fibers was determined after composites were made using different analytical techniques.

Here we report our findings regarding use of short nylon-6 nanofibers in reinforcing mechanical properties of TPU. The morphology of fiber/matrix interface and the properties of composite films were investigated using various analytical methods. The mechanical properties could be significantly enhanced without sacrificing optical properties like transparency of TPU by using very small amounts of reinforcing fibers. The role of the chemical structure of matrix polymer in enhancing fiber–matrix interface is also highlighted using PMMA as matrix for comparison purposes with TPU.

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA, Mw = 120,000), N,N'-dimethylformamide (DMF, 99.8%), formic acid (FA, ⩾98%) and acetic acid (AcOH, ⩾98%) were purchased from Sigma–Aldrich. Thermoplastic polyurethane (TPU, Desmopan DP 2590A) and nylon-6 (Ultramid B24) were kindly supplied by Bayer Materials Science and BASF respectively. All the materials were used as received without further purification.

2.2. Electrospinning and composite fabrication

The use of short electrospun nanofibers can provide the opportunity of making composites with predetermined amounts of nanofibers by mixing with matrix polymer either in solution or in melt besides ease of the processing method and good dispersability. The technique of electrospinning was used for making nylon-6 nanofiber mat with long and continuous fibers as described in the literature [18]. Short nylon-6 electrospun fibers (mean diameter of 163 nm; a standard deviation of 2.9% (Fig. 1A) and length from tens to hundreds micrometers (Fig. 1B)) dispersion in DMF with a concentration of 0.1 wt% was prepared by cutting of 0.5 g of nylon-6 mat (25 cm × 20 cm × 0.038 mm) at −13 °C in DMF by use of rotation blades as reported previously [19], but with reduced rotating speed (about 1500 rpm) for 5 min. The short fibers (Different amounts of TPU were dissolved into 10 g of the above short nylon-6 dispersion. After film casting and drying, the short nylon-6 nanofiber reinforced TPU composite films with 1.0, 2.5, 3.5 and 5.0 wt% of short nanofibers were prepared. Using similar procedure, nylon-6/PMMA composite films were also made for comparison purposes. The resulting composites for nylon-6/TPU and nylon-6/PMMA with 1.0, 2.5, 3.5 and 5.0 wt% of short nanofibers were denoted as NT1.0, NT2.5, NT3.5, NT5.0 and NP1.0, NP2.5, NP3.5, NP5.0 respectively in the following text. Characterization techniques are described in supporting information.

3. Results and discussion

3.1. Fabrication of short nylon-6 nanofiber reinforced composite films

Short nylon-6 nanofibers prepared by cutting off the pristine electrospun nylon-6 mats had very homogeneous fiber morphology with a mean diameter of 163 nm (a standard deviation of 2.9%) (Fig. 1A) and length from tens to hundreds micrometers (Fig. 1B). They could be dispersed in DMF solvent without aggregation/precipitation for at least one month (this is the time for which we observed dispersion before submitting this article, stability studies are being continued). Different amounts of TPU and PMMA were dissolved into 10 g of the short nanofiber dispersion (0.1 wt%) separately for the preparation of the composite films (Fig. 1.) After casting and drying of dispersions, the short nylon-6 nanofiber reinforced composite films were prepared. For comparison, the pure TPU and PMMA films were also fabricated. The surface morphology of the films as observed by SEM showed some imprinting of short nylon-6 nanofibers on the surface of 2.5 wt% and 5.0 wt% short nanofiber reinforced TPU films but without pull out nanofibers (samples NT2.5 and NT5.0; Fig. 1I and J). This shows a homogeneous distribution of the short nanofibers within TPU in NT composite films. In comparison, the surfaces of the pure TPU film and short nylon-6 nanofiber reinforced PMMA films were very smooth. The absence of the short nylon-6 nanofibers on the surface of PMMA (NP) composite films and no short nanofibers pulled-out structures suggested that all the short nanofibers were only dispersed in the bulk of the PMMA matrix.

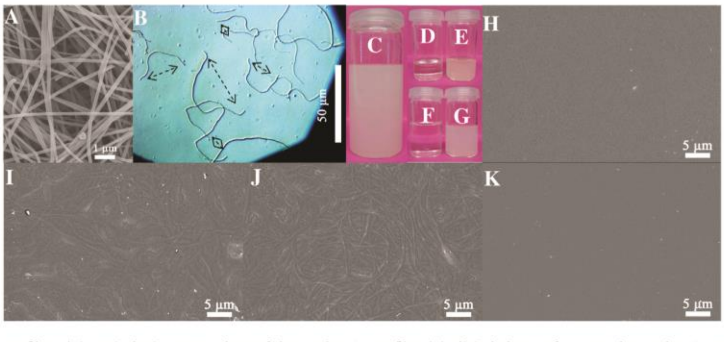


Fig. 1. SEM of short nylon-6 nanofibers (A); optical microscope photo of short nylon-6 nanofiber (B); digital photos of 0.1 wt% short nylon-6 nanofiber dispersion in DMF (C); pure TPU (D); nylon-6 short fiber/TPU dispersion (NT3.5) (E); PMMA solution in DMF (F); nylon-6 short fiber/PMMA dispersion (NP3.5) (G); SEM of surface morphologies of pure TPU film (H), NT2.5 (I), NT5.0 (J) and NP3.5 (K).

The difference in distribution of short nylon-6 nanofibers in TPU and PMMA matrix was also confirmed by surface analysis of composite films using ATR-IR and transmission IR. PMMA composite films (Fig. 2B NP1.0 to NP5.0) showed no obvious characteristic peaks of nylon-6 at the surface and the ATR-IR spectra of PMMA and composite films were very similar. This confirmed the distribution of the short nanofibers in the bulk of the nylon-6/PMMA (NP) composite films and no fibers on the surface. Further studies regarding the interaction between nylon-6 fibers and PMMA matrix were carried out by transmission IR (Fig. 2C). Characteristic peaks of nylon-6 at 3294 cm^{-1} (NH) and 1543 cm^{-1} (amide II) also appeared in the spectra of the composite films (NP2.5 and NP5.0) but there was no change in the peak positions confirming the absence of H-bonding type interactions between nylon-6 fibers and PMMA matrix.

In contrast, the ATR-IR spectra of short nylon-6 nanofiber reinforced TPU composite films (Fig. 2A) showed characteristic peak of nylon-6 (carbonyl stretching) proving their surface morphology. Further, two trends were obvious from the ATR-IR spectra of NT composite films: 1) the increase in intensity of the carbonyl peak of nylon-6 on increasing its amount in the composite films (i.e. on going from NT1.0 to NT5.0 2) the blue shifts of the carbonyl peak (from 1635 cm^{-1} for nylon-6 nanofibers to 1651 cm^{-1} for NT composite film) and NH peak (from 3294 cm^{-1} for nylon-6 nanofibers to 3321 cm^{-1} for NT composite film). The blue shifts might be the result of the hydrogen bonding between nylon-6 and TPU. This could help in making a strong interface between the reinforcing fibers and TPU matrix and homogenous distribution of fibers in the whole bulk of the matrix polymer. Such hydrogen

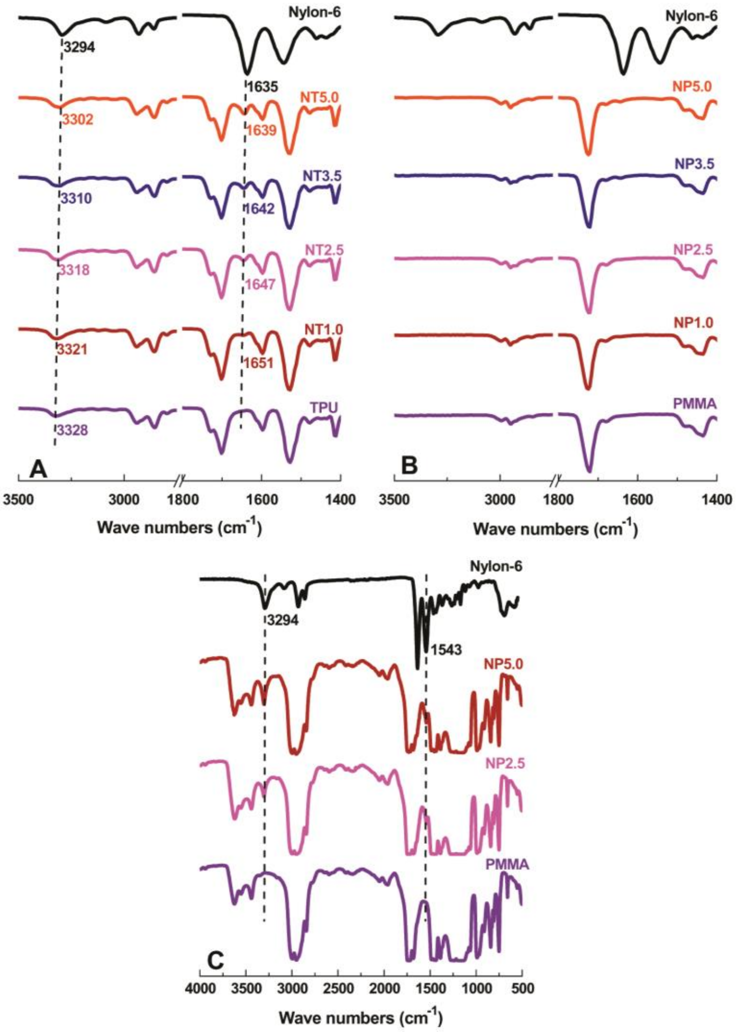


Fig. 2. (A and B) ATR-IR spectra of pure TPU film, pure PMMA film, nylon-6 nanofiber mat and short nylon-6 nanofiber reinforced TPU and PMMA composite films. (C) FT-IR spectra with transmission mode of pure PMMA film, nylon-6 nanofibers and composite films NP2.5 and NP5.0.

bonding was not possible between nylon-6 nanofibers and PMMA matrix.

There was no influence of the small amount of short fibers (<5 wt%) on the thermal stabilities of the matrix polymers (for details please see supporting information).

3.2. Mechanical properties

Nylon-6 single nanofibers show very high tensile strength (304 MPa) and modulus (30 GPa) depending upon the fiber diameter and therefore make them suitable candidate for reinforcement of thermoplastics like TPU and PMMA [20,21]. To reveal the effect of short nylon-6 nanofibers on the mechanical properties of the composite films tensile testing experiments were carried out (Fig. 3; Table 1). The neat PMMA film exhibited an average tensile strength of 36.2 MPa, elongation at break of 5.2% and *E* modulus of 697 MPa. The improvements of 18.7% in tensile strength and of 23.4% in *E* modulus were observed on adding 2.5 wt% amount of short nylon-6 nanofibers into PMMA matrix. However, further increase of the amount of the short nanofibers to 3.5 wt% led to a drop in tensile strength but still the *E* modulus was higher than that of neat PMMA. Although, a similar trend of the mechanical properties was also observed for the TPU/nylon-6 composite films but the improvement in the properties was much more significant than for PMMA. On increasing the amount of the short nylon-6 nanofibers till about 3.5 wt%, a slight increase in tensile strength (about 30% improvement) but a very significant increase in *E* modulus (about 185% improvement) was observed. Although further increase in the amount of short nylon-6 nanofibers to 5.0 wt% led to a drop of the tensile strength and *E* modulus, but still was higher than the pure TPU film (tensile strength increase was only 10% but *E* modulus increase was 150%). There was also an obvious increase in the toughness (measure of work done per unit mass to break the sample) of composite films.

A direct comparison of these results for short fiber reinforced composites with the long and continuous nylon-6 nanofiber nonwoven reinforced composites made by state-of-the-art methods like dip-coating followed by heat pressing or mold casting would not be very appropriate as the amount of reinforcing fibers used in such methods is always very high. Recently, we highlighted a novel composite fabrication method (layer-by-layer) for the same system (nylon-6 nanofiber reinforced thermoplastic polyurethane (TPU)) based on solution casting, electrospinning and film stacking using very small amounts (<5 wt%) of the reinforcing fibers [4]. Interestingly, a significant improvement in the *E*-modulus of TPU in the present work was seen on using short nylon-6 nanofibers in comparison to the use of long and continuous nylon-6 nanofibers as shown in our previous work [4]. Similar amounts of long and continuous nylon-6 nanofiber nonwovens (around 3.5 wt%) led to the improvement in E-modulus of about 82% as compared to 185% observed in the present work without significant decrease in the elongation at break (Table 1).

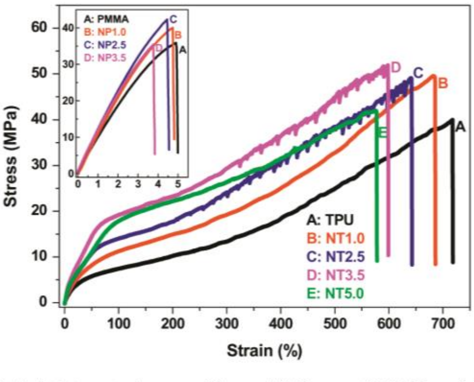


Fig. 3. Typical stress–strain curves of the pure TPU film, pure PMMA film and short nylon-6 nanofiber reinforced composites.

Mechanical properties of fiber reinforced composites are affected by several factors including fiber properties, the dispersion of fibers in matrix, and the interfacial adhesion between fibers and matrix. In order to discuss the dispersion of short nylon-6 nanofibers in the matrix and the interfacial adhesion between short nanofibers and the matrix, the tensile failure structure of the pure TPU film, pure PMMA film and the composite films (NP2.5, NP3.5, NT2.5, and NT5.0) were observed by SEM as shown in Fig. 4. It could be seen that the pure TPU and PMMA film presented a smooth and homogeneous fractured surface (Fig. 4A), while the composite films showed a rougher surface with short nylon-6 nanofibers embedded in the matrix. The interface between fibers and PMMA was not good with many voids between fibers and the matrix polymer (Fig. 4B). On increasing the amount of short nylon-6 nanofibers to 3.5 wt%, the aggregation of short nanofibers with many more voids/cracks were observed (Fig. 4C), which resulted in the drop of the mechanical properties. In contrast, the TPU/nylon-6 composite films showed a strong adhesion of nylon-6 nanofibers and TPU matrix without any cracks/holes showing better dispersion of fibers in TPU matrix than PMMA/nylon-6 system (Fig. 4E and F). This could be due to the hydrogen bonding as proved by ATR-IR between reinforcing nylon-6 nanofibers and TPU matrix. The strong adhesion and excellent wetting of nylon-6 nanofibers by TPU matrix was also proved by observation of spring nanofiber morphologies in the broken tensile testing specimens. Nylon-6 fibers were not soluble in DMF, the solvent used for making composite films but undergoes very fast wetting (in less than 1 s) as shown in our previous work [4]. Therefore, the choice of DMF for making dispersion of nylon-6 fibers with TPU used for making composite films together with their H-bonding characteristics ensured excellent and homogenous wetting of reinforcing nylon-6 nanofibers with TPU matrix. Many of the TPU coated nylon-6 nanofibers in composite films showed spring morphology (Fig. 4G and H) after tensile failure because of difference in elasticity and modulus of the two polymers. The formation of spring morphology by differential shrinkage of two components in a bicomponent fiber made by either side-by-side electrospinning or coaxial electrospinning with flexible thermoplastic elastomer (polyurethane) component and a rigid thermoplastic component (Nomex) is a well studied phenomenon in the literature [22,23]. All broken fibers after tensile testing did not show uniformly the spring morphology because of difference in the fiber length and orientation with respect to tensile testing direction.

3.3. Optical light transmittance

The transparency of TPU/nylon-6 and the PMMA/nylon-6 composite films was changed to different extents by incorporation of short nylon-6 nanofibers. The PMMA/nylon-6 composite films with 2.5 and 3.5 wt% short fibers had a transmittance of 76–85% and 66–80% in the light wave length range of 400–800 nm (Fig. 5). However, the TPU/nylon-6 composite films showed high transparency of more than 85% in the visible light range even with large amounts of short nylon-6 nanofibers (reached up to 5.0 wt%). The difference in refractive index between the fibers and the matrix polymer, the amount of the fibers in the composites, the diameter of fibers, the dispersion of fibers in the resin and interface between fibers and matrix are some of the important reasons affecting the transparency of the nanofiber reinforced composites [14,24,25]. The

Table 1
A summary of the mechanical properties of the pure TPU film, pure PMMA film and short nylon-6 fiber reinforced TPU and PMMA composite films.

Sample	Stress (MPa)	Strain (%)	*E* modulus (2%, MPa)	Integration of stress–strain curves (MJ/m^3)	Toughness (J/g)
TPU	40.2 ± 1.2	727.3 ± 29.2	27.0 ± 4.5	134.7 ± 9.8	111.3 ± 8.1
NT1.0	51.6 ± 3.0	707.6 ± 41.6	43.8 ± 5.0	179.1 ± 18.4	148.0 ± 15.2
NT2.5	51.5 ± 3.8	628.0 ± 35.0	66.3 ± 4.7	176.6 ± 19.2	146.0 ± 15.9
NT3.5	52.0 ± 2.8	606.0 ± 45.2	77.1 ± 8.0	182.2 ± 19.5	150.6 ± 16.1
NT5.0	43.9 ± 1.9	547.1 ± 67.6	67.5 ± 5.6	144.6 ± 22.5	119.5 ± 18.6
LF-3.4[a]	60.3 ± 5.9	812.3 ± 70.5	49.0 ± 2.8	233.9 ± 38.8	193.8 ± 32.2
PMMA	36.2 ± 0.4	5.2 ± 0.5	697 ± 21.5	1.1 ± 0.1	0.9 ± 0.1
NP1.0	40.9 ± 0.7	5.1 ± 1.7	803 ± 113	1.4 ± 0.5	1.2 ± 0.4
NP2.5	42.0 ± 2.8	4.4 ± 0.3	860 ± 61.5	1.0 ± 0.2	0.8 ± 0.2
NP3.5	36.0 ± 0.5	3.8 ± 0.3	766 ± 29.6	0.8 ± 0.1	0.7 ± 0.1

[a] Data taken from Ref. [4]. LF-3.4 is the nylon-6 (long and continuous nanofiber) reinforced TPU composite film made by layer-by-layer (LBL) process using 3.4 wt% of the nanofibers. The LBL process for making composite film involved solution casting of TPU followed by direct electrospinning of nylon fibers on the wet TPU and film stacking. The resulting composite had in total 3 layers of nylon-6 nanofibers sandwiched by 4 layers of TPU films.

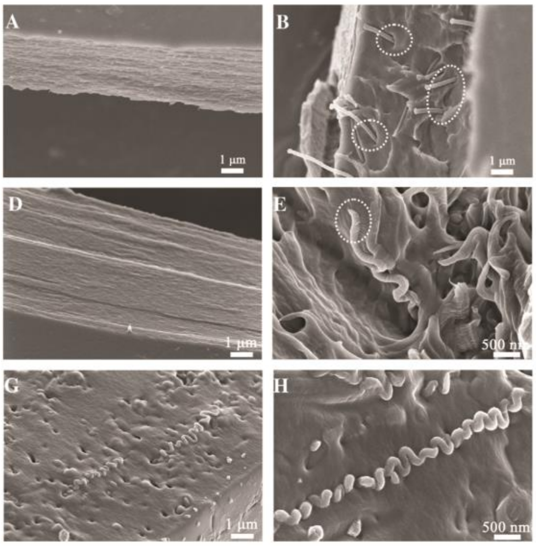


Fig. 4. SEM pictures of the tensile failure structure of pure PMMA film (A), NP2.5 (B), NP3.5 (C), TPU film (D), NT2.5 (E) and NT5.0 (F–H).

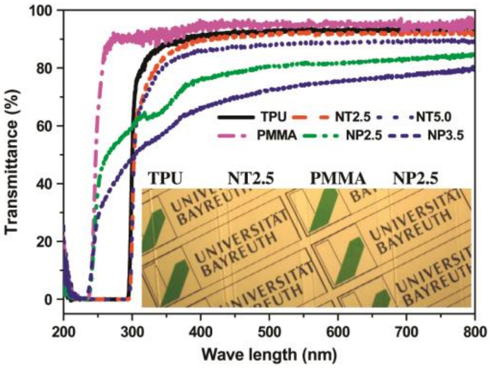
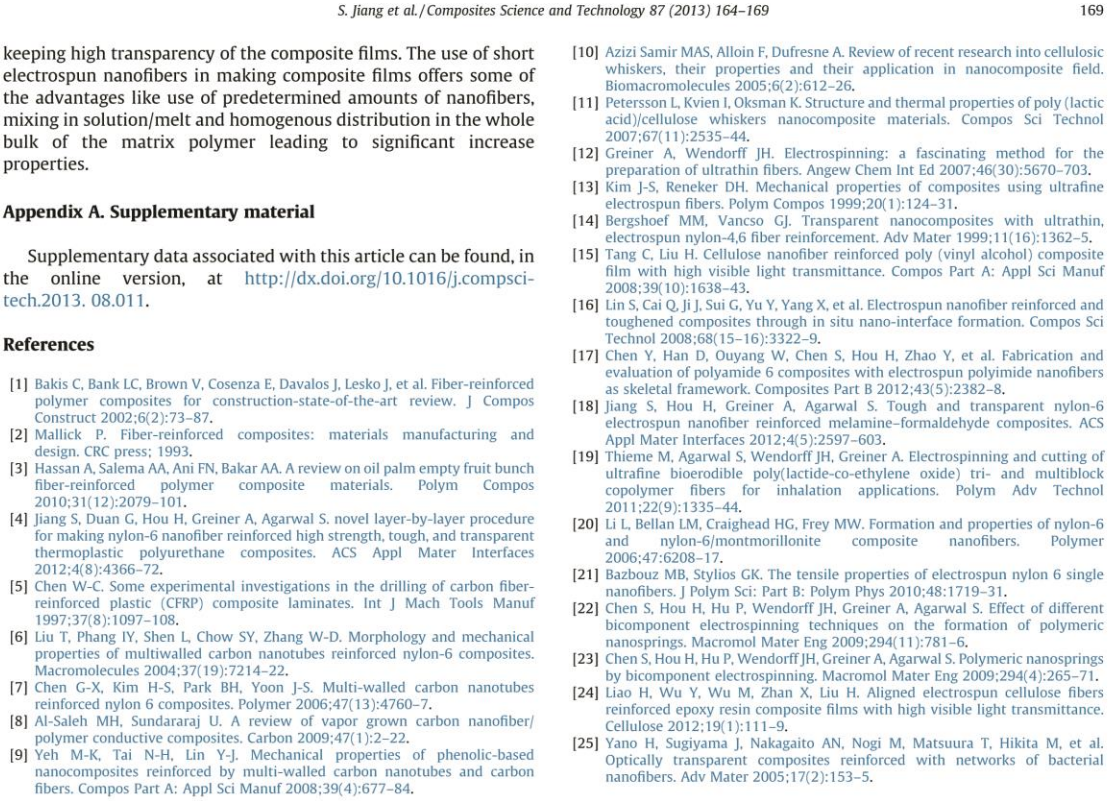


Fig. 5. UV–vis spectra of pure TPU film, pure PMMA film and short nylon-6 nanofiber reinforced composite films and digital photo of transparent neat films and composite films on glass slides.

reinforcing nylon-6 fibers used in the present work were very small in diameter (less than 200 nm) and the refractive index difference between fibers and matrix polymers was marginal (refractive index: 1.49 PMMA, 1.53 nylon-6 and 1.51 TPU). Very small amounts of short nylon-6 nanofibers (no more than 5 wt%) together with their homogenous dispersion and very good interface with the matrix TPU due to hydrogen bonding assured higher transparency of nylon-6/TPU composite films as compared to nylon-6/PMMA.

4. Conclusion

Very small amounts (less than 5 wt%) of short nylon-6 nanofibers were effective in reinforcing mechanical properties like tensile strength, modulus and toughness of TPU. A 185% enhancement in modulus of TPU was seen on using 3.5 wt% of reinforcing nylon-6 nanofibers. The reinforcing effect of nanofibers was dependent upon the matrix polymer. The increase in properties of TPU matrix polymer was significantly more than that for PMMA due to interactions (H-bonding) with the reinforcing nylon-6 fibers. The reinforcing effect of short nylon-6 fibers for TPU matrix was achieved



keeping high transparency of the composite films. The use of short electrospun nanofibers in making composite films offers some of the advantages like use of predetermined amounts of nanofibers, mixing in solution/melt and homogenous distribution in the whole bulk of the matrix polymer leading to significant increase properties.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compscitech.2013. 08.011.

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Supplementary Information

Characterization

The surface morphology and failure structure of the pure TPU film, pure PMMA film and the composite films were observed by a scanning electronic microscopy (SEM, JSM-7500 and Leo Gemini 1530). Prior to scanning, all the specimens were sputter-coated with approximately 120s of gold or 4 nm of platinum to avoid charge accumulations. The diameter and the diameter deviation were measured and calculated by Image J software. The mechanical properties were conducted by a Zwick/Roell BT1-FR 0.5TN-D14 machine equipped with a 200 N KAF-TC load sensor using a stretching rate of 50 mm/min for nylon-6/TPU series and 5 mm/min for nylon-6/PMMA series at room temperature. The specimens for tensile test were cut into dog-bone-shape with a length of 3.0 cm and a width of 0.2 cm. ATR-IR spectra and transmission IR spectra were carried on a Digilab Excalibur Series with an ATR unit MIRacle by Pike Technology. Thermal properties of the samples were determined by Mettler Toledo TGA/SDTA 851e at a heating rate of 10 ^{o}C/min in N_2 with a heating temperature from 100 to 800 ^{o}C. The transparency of the samples were determined by a UV/Vis/NIR spectrophotometer (Perkin-Elmer Lambda 9) in transmittance mode (200-800 nm). All the digital photos were taken by a Sony DSC-W570 digital camera. The optical microscope photos for the short nanofibers were taken from Leica DMRX optical microscope.

Thermal properties

Thermogravimetric analysis (TGA) is an effective way to evaluate the thermal stabilities of polymers and the composites. **Figure 5-S1** showed the TGA curves for PMMA, TPU, nylon-6 nanofibers and the corresponding composite films (NT and NP). Nylon-6, TPU and PMMA showed $T_{10\%}$ (temperature at which 10 % weight loss took place) of 405, 300 and 343 ^{o}C respectively. The thermal stability was not affected by addition of small amounts of short nylon-6 nanofibers.

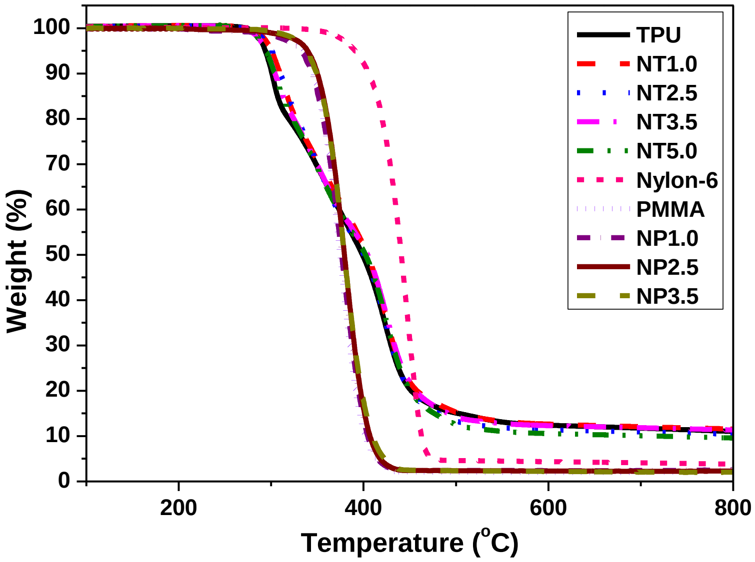
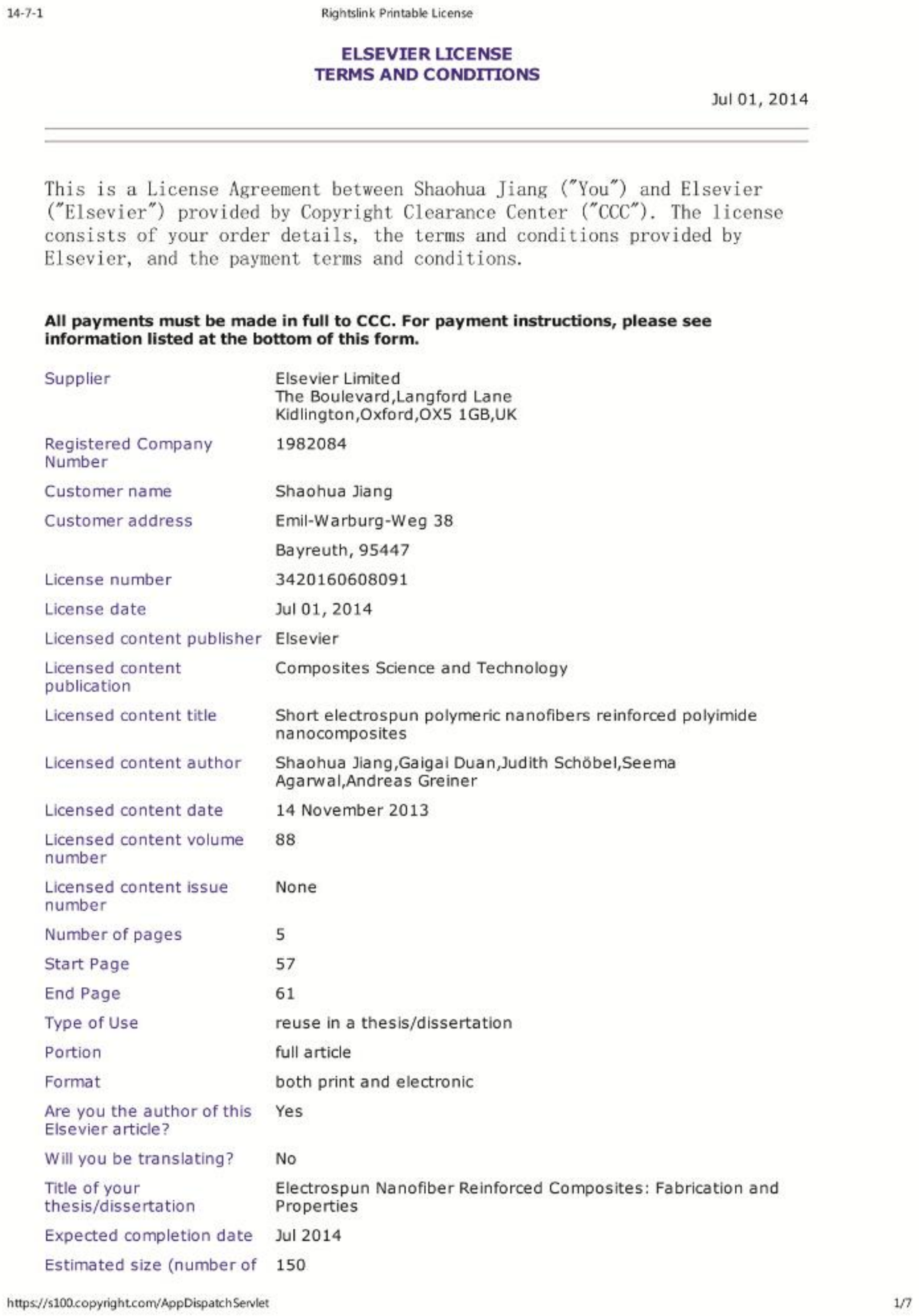


Figure 5-S1 TGA curves of pure TPU film, pure PMMA film, nylon-6 nanofiber mat and short nylon-6 nanofiber reinforced composite films.

3.4. Short electrospun polymeric nanofibers reinforced polyimide nanocomposites

Shaohua Jiang, Gaigai Duan, Judith Schöbel, Seema Agarwal* and Andreas Greiner*, "Short electrospun polymeric nanofibers reinforced polyimide Nanocomposites", *Composite Science and Technology*, **2013**, *88(14)*, 57-61



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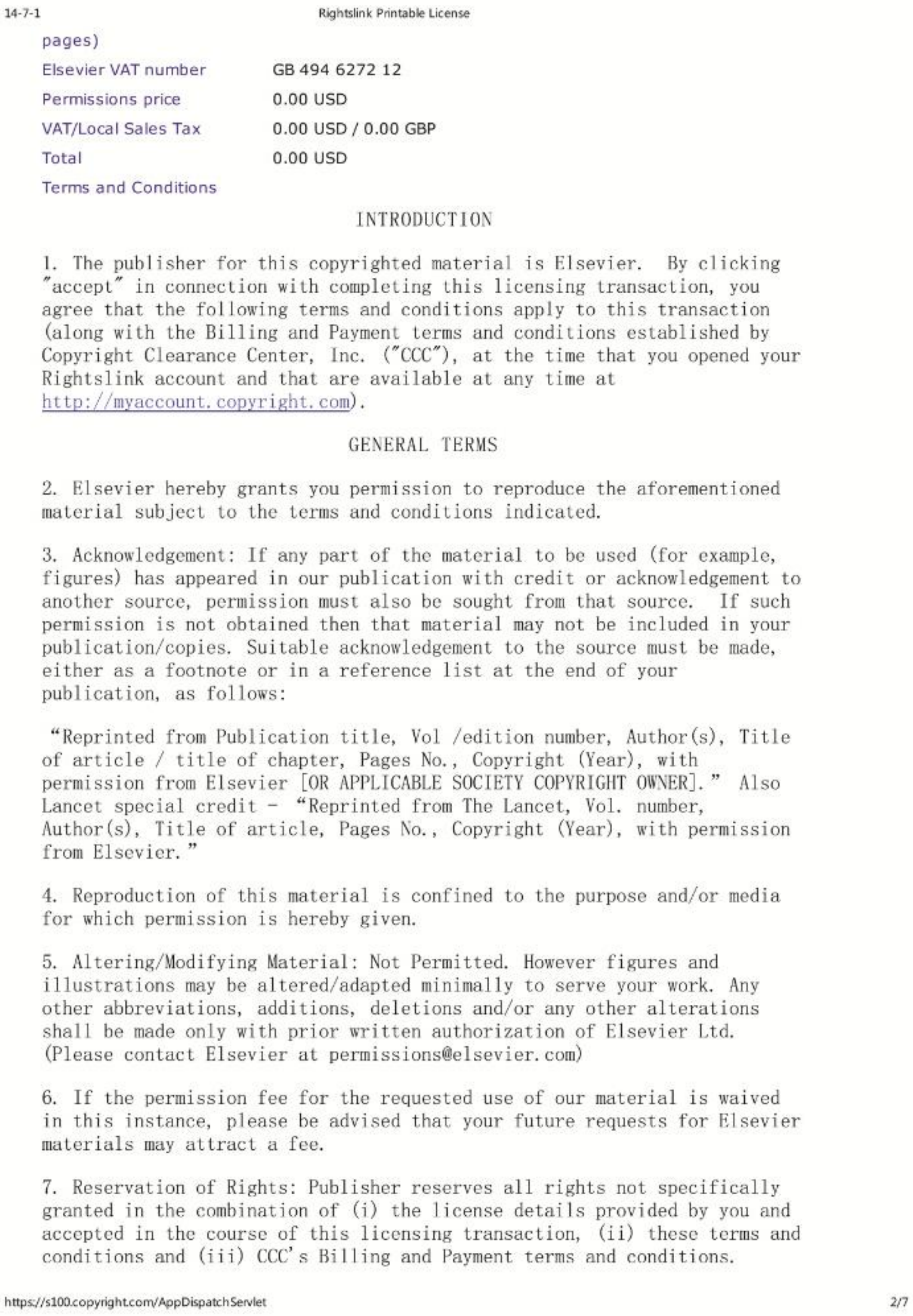

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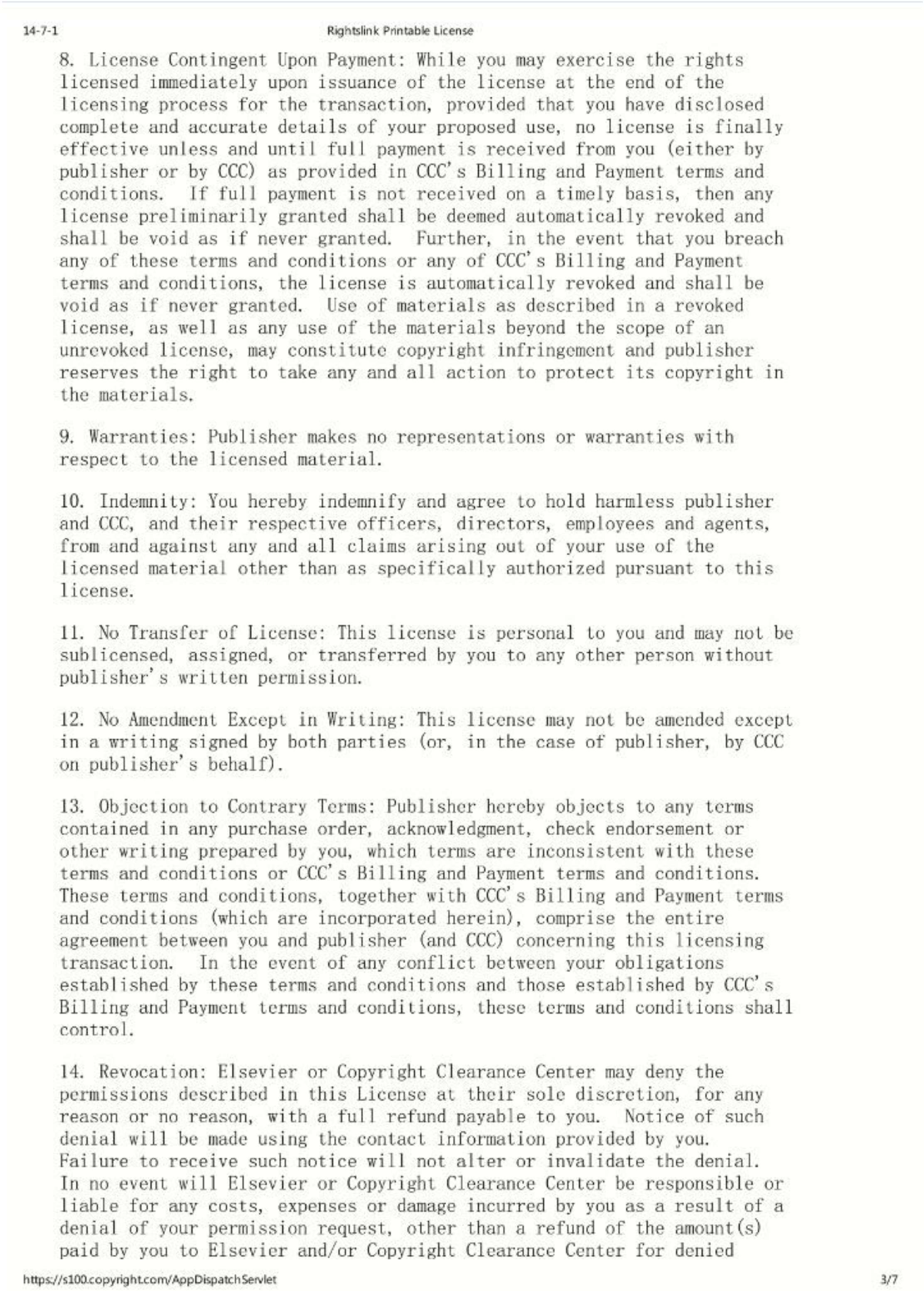

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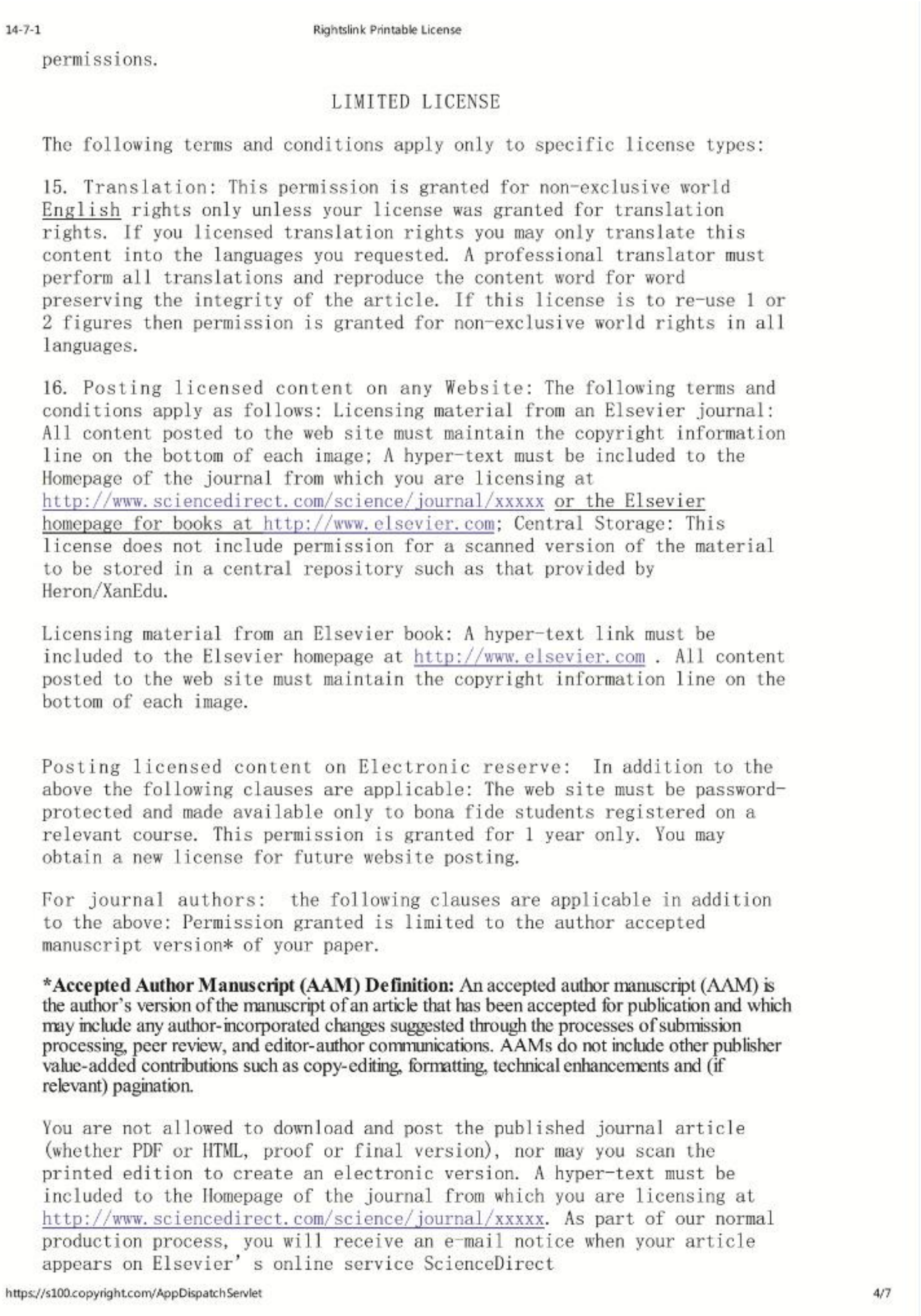

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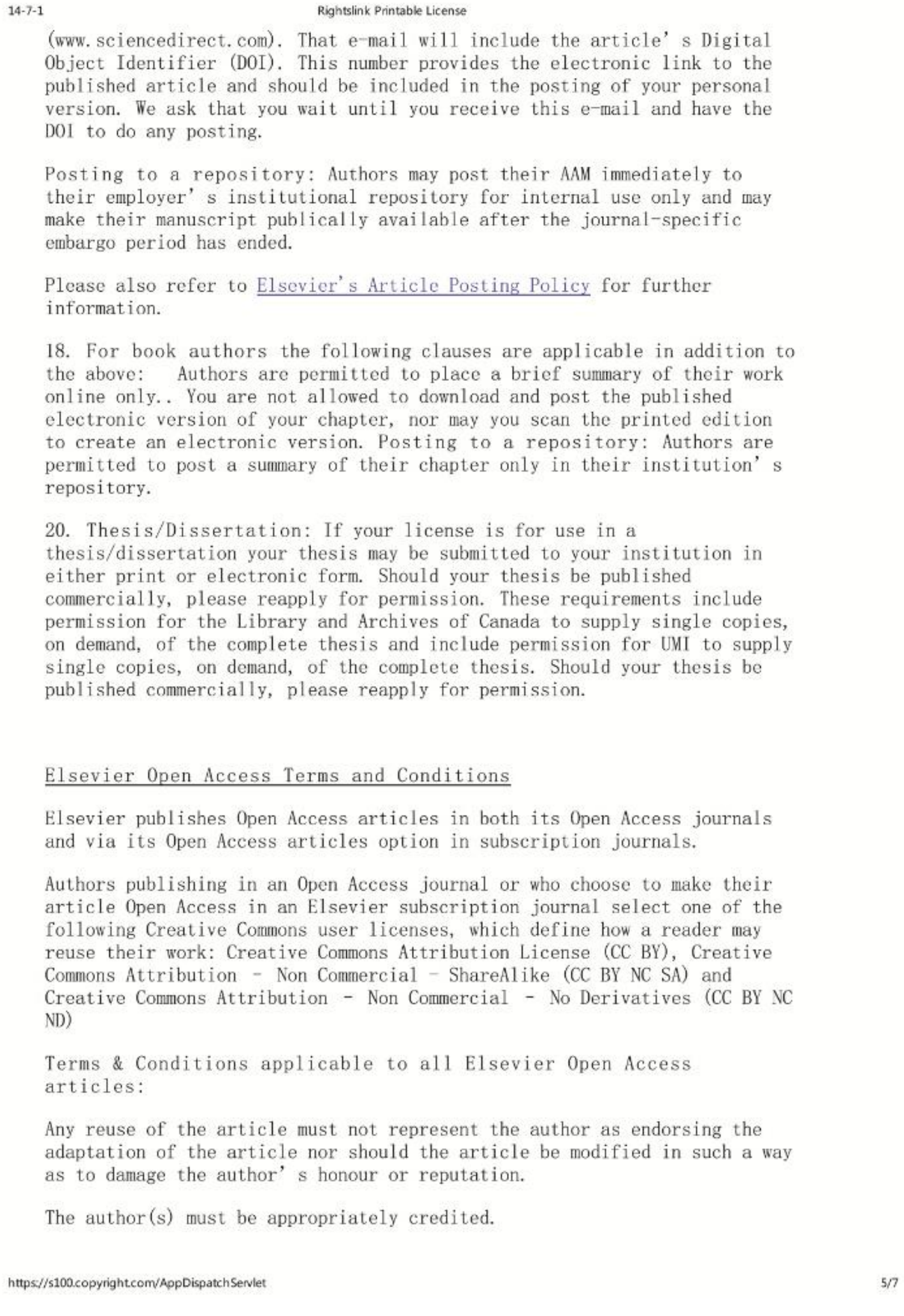

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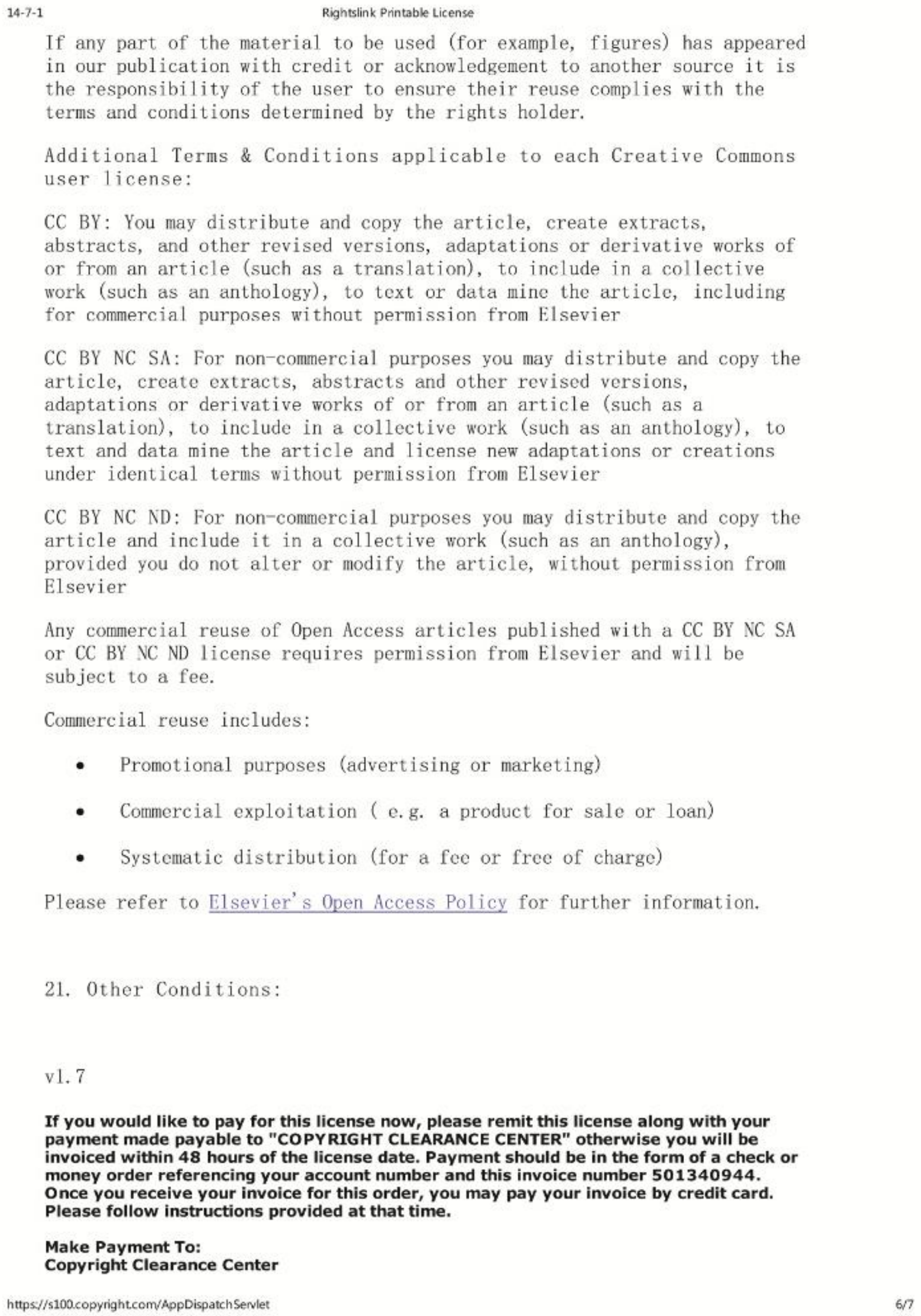

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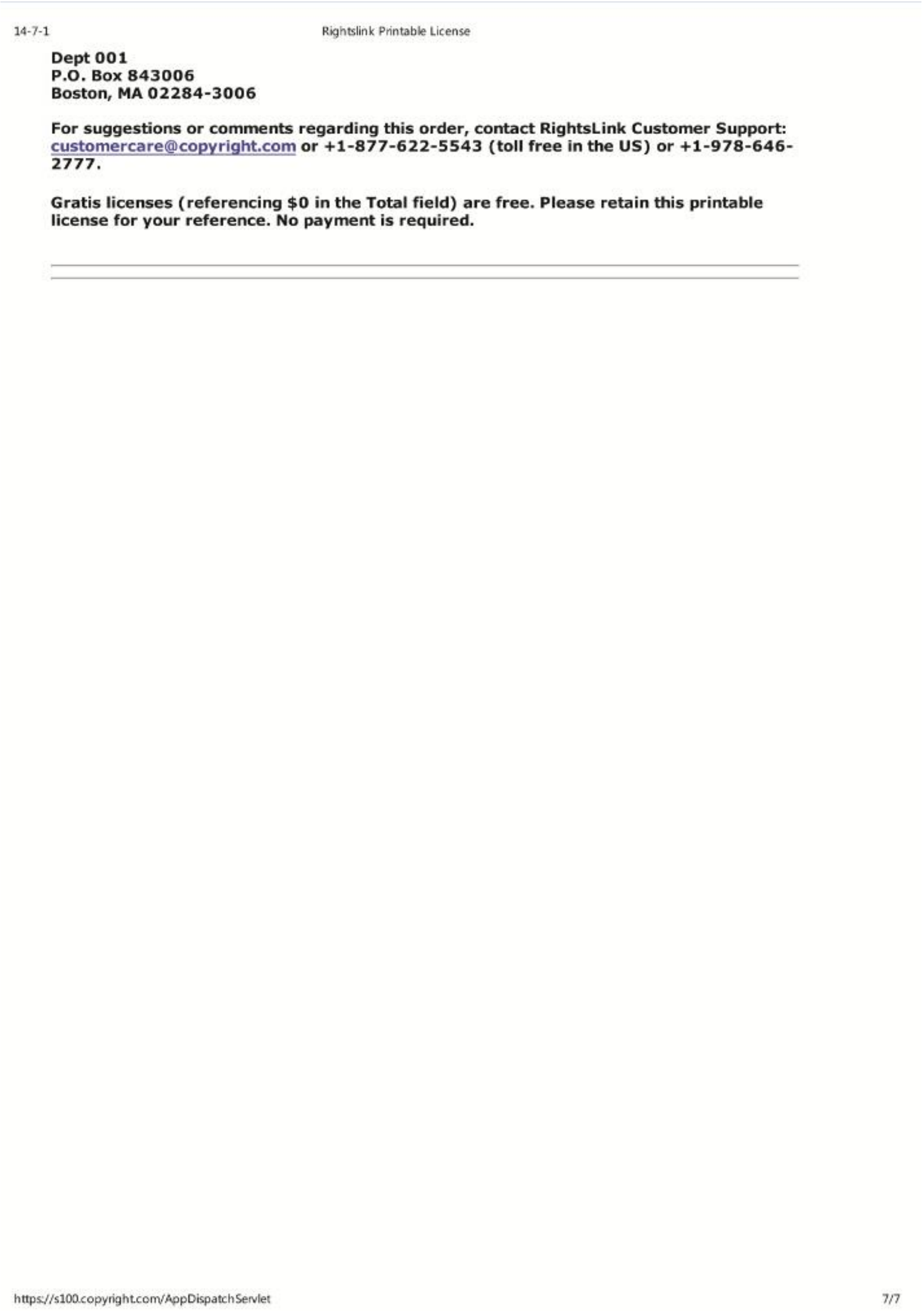

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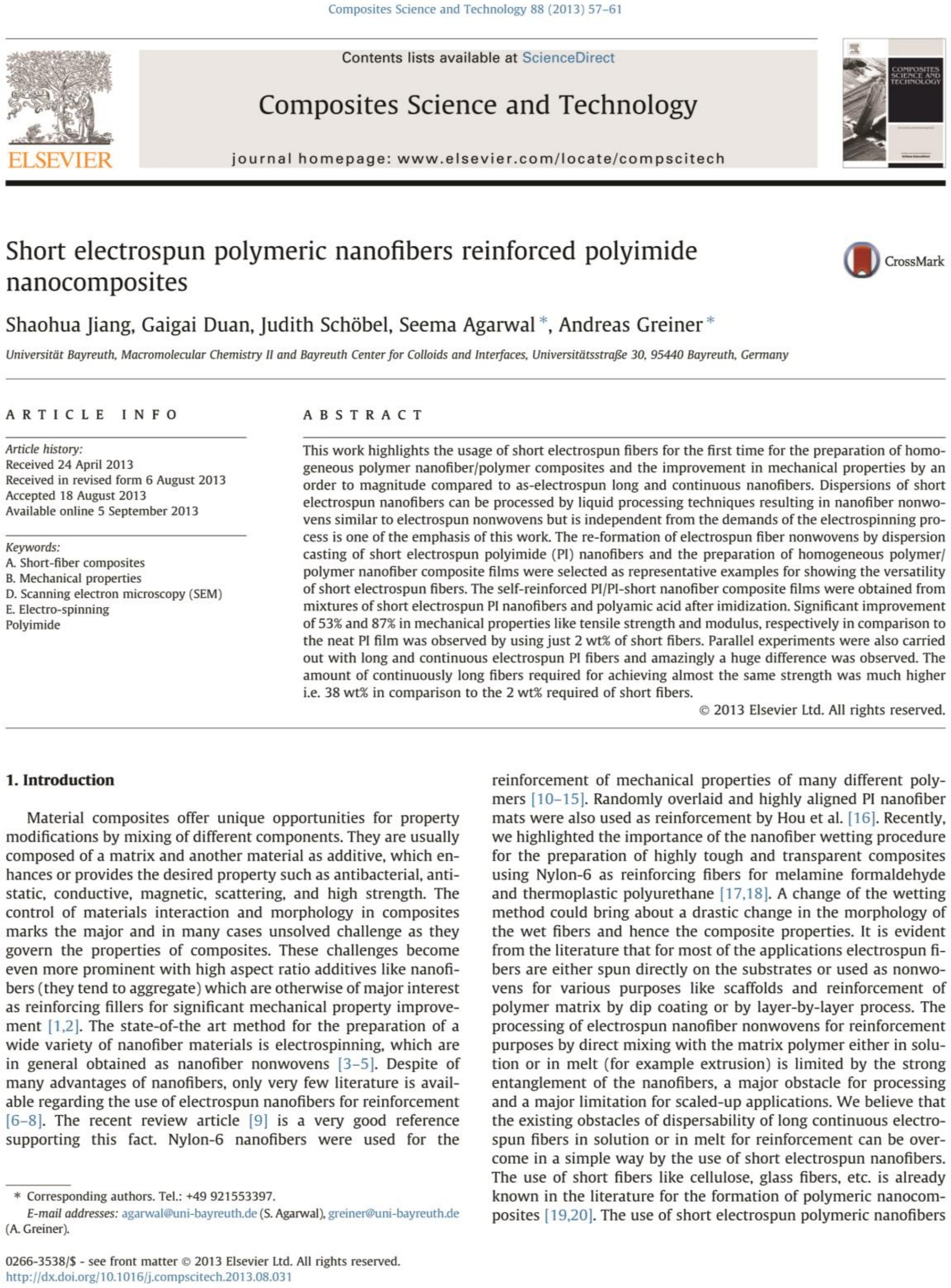

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Short electrospun polymeric nanofibers reinforced polyimide nanocomposites

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A. Short-fiber composites
B. Mechanical properties
D. Scanning electron microscopy (SEM)
E. Electro-spinning
Polyimide

ABSTRACT

This work highlights the usage of short electrospun fibers for the first time for the preparation of homogeneous polymer nanofiber/polymer composites and the improvement in mechanical properties by an order to magnitude compared to as-electrospun long and continuous nanofibers. Dispersions of short electrospun nanofibers can be processed by liquid processing techniques resulting in nanofiber nonwovens similar to electrospun nonwovens but is independent from the demands of the electrospinning process is one of the emphasis of this work. The re-formation of electrospun fiber nonwovens by dispersion casting of short electrospun polyimide (PI) nanofibers and the preparation of homogeneous polymer/polymer nanofiber composite films were selected as representative examples for showing the versatility of short electrospun fibers. The self-reinforced PI/PI-short nanofiber composite films were obtained from mixtures of short electrospun PI nanofibers and polyamic acid after imidization. Significant improvement of 53% and 87% in mechanical properties like tensile strength and modulus, respectively in comparison to the neat PI film was observed by using just 2 wt% of short fibers. Parallel experiments were also carried out with long and continuous electrospun PI fibers and amazingly a huge difference was observed. The amount of continuously long fibers required for achieving almost the same strength was much higher i.e. 38 wt% in comparison to the 2 wt% required of short fibers.

1. Introduction

Material composites offer unique opportunities for property modifications by mixing of different components. They are usually composed of a matrix and another material as additive, which enhances or provides the desired property such as antibacterial, antistatic, conductive, magnetic, scattering, and high strength. The control of materials interaction and morphology in composites marks the major and in many cases unsolved challenge as they govern the properties of composites. These challenges become even more prominent with high aspect ratio additives like nanofibers (they tend to aggregate) which are otherwise of major interest as reinforcing fillers for significant mechanical property improvement [1,2]. The state-of-the art method for the preparation of a wide variety of nanofiber materials is electrospinning, which are in general obtained as nanofiber nonwovens [3–5]. Despite of many advantages of nanofibers, only very few literature is available regarding the use of electrospun nanofibers for reinforcement [6–8]. The recent review article [9] is a very good reference supporting this fact. Nylon-6 nanofibers were used for the reinforcement of mechanical properties of many different polymers [10–15]. Randomly overlaid and highly aligned PI nanofiber mats were also used as reinforcement by Hou et al. [16]. Recently, we highlighted the importance of the nanofiber wetting procedure for the preparation of highly tough and transparent composites using Nylon-6 as reinforcing fibers for melamine formaldehyde and thermoplastic polyurethane [17,18]. A change of the wetting method could bring about a drastic change in the morphology of the wet fibers and hence the composite properties. It is evident from the literature that for most of the applications electrospun fibers are either spun directly on the substrates or used as nonwovens for various purposes like scaffolds and reinforcement of polymer matrix by dip coating or by layer-by-layer process. The processing of electrospun nanofiber nonwovens for reinforcement purposes by direct mixing with the matrix polymer either in solution or in melt (for example extrusion) is limited by the strong entanglement of the nanofibers, a major obstacle for processing and a major limitation for scaled-up applications. We believe that the existing obstacles of dispersability of long continuous electrospun fibers in solution or in melt for reinforcement can be overcome in a simple way by the use of short electrospun nanofibers. The use of short fibers like cellulose, glass fibers, etc. is already known in the literature for the formation of polymeric nanocomposites [19,20]. The use of short electrospun polymeric nanofibers

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for reinforcement purposes is not known to the best of our knowledge. Completely novel applications in a variety of fields including filtration, textiles, medical, composites, and agriculture can be envisioned as the modification of polymeric materials used for making short nanofibers for varied properties can be easily achieved by varying the chemical structure, functional groups, architecture, topology, etc.

Our concept for the use of short electrospun fibers is based on the assumption that short electrospun fibers with aspect ratio of about 100–200 could be dispersed better in liquid media as compared to as-electrospun fibers which are usually highly entangled. Furthermore, we assume with an aspect ratio of about 100–200 electrospun fibers would entangle enough in the dry state for the formation of self-supporting nonwovens. In order to verify these assumptions the re-formation of self-supported polyimide (PI) nanofiber nonwovens by dispersion casting of short electrospun polyimide (PI) nanofibers and the preparation of self-reinforced homogeneous polyimide/polyimide short nanofiber composite films were selected as representative examples in this work. The PI nanofiber nonwovens and single nanofibers possess superior mechanical properties as compared to the neat PI film due to the molecular orientation of macromolecular chains during drawing of fibers in the process of electrospinning making them suitable for self-reinforcement purposes [21,22]. The self-reinforced composites offer a variety of advantages (transparency, light-weight, strong interface between matrix and fiber, strength, impact performance, recyclability) and are well-known in the literature using long and continuous nanofiber reinforced PI composites [23] but not with homogenous nanofiber distribution in the polymer matrix to the best of our knowledge. The particular advantages of short polymeric electrospun nanofibers for composite preparation and their effect on mechanical properties are discussed in detail in the manuscript in comparison to the as-spun long nanofibers.

2. Methodology

2.1. Electrospinning and preparation of PI/PI nanofiber-composite films (PIPICOF)

The PI nanofibers for cutting were made in two steps using the process of electrospinning. In the first step, the precursor polyamic acid (PAA) was prepared by polycondensation of equimolar amounts of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) in DMF according to a previously published procedure giving 25 wt% solution [24]. The as-prepared PAA solution was diluted by DMF to a concentration of 20 wt% for electrospinning. The feeding rate of the solution was 3 mL/h. The applied electric filed was 100 kV/m by imposing a voltage of 35 kV to a 35 cm gap between the needle tip ($\Phi = 0.8$ mm) and the collector (a rotating drum). The drum had a diameter of 9 cm and a length of 21 cm, and rotated at 30 rpm for collecting the PAA nanofiber nonwoven. The obtained PAA nonwoven was dried at 60 °C for 1 h and at 100 °C for 2 h by vacuum and subsequently imidized in a high-temperature furnace under N_2 atmosphere using the following protocol: (1) heating up to 150 °C at a rate of 3 °C/min and annealing for 1 h; (2) heating up to 350 °C at a rate of 1.5 °C/min and annealing for 1 h; (3) cooling down to the room temperature. Short electrospun fibers were prepared by mechanical cutting as reported previously [25]. 500 g of water/isopropanol mixture (70:30 by weight) and 1 g of PI nanofiber mat were cooled with liquid nitrogen. The PI nanofiber mat was cut into short fibers in the cooled medium by a set-up made up of a motor-driven blade (blade: Wilkinson classic; motor: Kress 800 FME) with a rotating speed of about 1500 rpm for 10 min. The resulting short PI nanofibers were filtered off and different amount of these short nanofibers were redispersed in a 10 wt% solution of PAA in DMF. Subsequently, the mixture was casted to films, dried, and imidized using the same protocol as mentioned above for the electrospun PAA nanofibers. Following this procedure PI composite films (film thickness around 30–35 μm) with 0.5 wt%, 1.0 wt%, 2.0 wt%, and 3.0 wt% PI short nanofibers were obtained.

2.2. Characterizations

The details of instruments used for characterization of nanocomposites are given in the Supplementary information.

3. Results and discussion

With the method of fiber cutting reported here, homogenous dispersions of short PI fibers with fiber length of 50–500 μm and diameter of 0.2–0.5 μm were obtained (Fig. 1). PI fibers were filtered off and could be re-dispersed in water/isopropanol mixture without indication of aggregation.

Casting of dispersions of isopropanol/water (30/70 w/w) with 2.5 wt% (w/w) PI cut nanofibers on cellulose-based filter paper resulted in dense nonwoven-type layers of nanofibers on the surface of paper. The process of dispersion casting provided nanofiber coating very similar to the coating of filter papers by direct electrospinning. In the process, the liquid passed through the filter paper and the cut PI nanofibers were retained on the surface of the filter paper forming a nanofiber nonwoven (Fig. 2a). Higher magnifications revealed a dense entanglement of the cut nanofibers with each other as well as entanglement with the filter paper fibers. This caused improved adhesion on the filter paper substrate of the dispersion processed nanofibers as compared to nanofibers deposited by standard electrospinning as tested qualitatively by mechanical rubbing and tape test i.e. by putting a cellotape and pulling it followed by visual inspection of fibers adhered to the cellotape. This was most likely because of better contact between the substrate fibers and the short electrospun fibers (Fig. 2b). Naturally, the thickness of the nanofiber layers on the filter paper could be readily adjusted by the amount of dispersion providing a versatile tool for the adjustment of weight of nanofibers per unit surface area which is otherwise rather limited during direct electrospinning on a substrate.

In order to further investigate the versatility of short electrospun nanofibers for processing purposes we have prepared self-reinforced PI nanofiber composites. For the preparation of the self-reinforced PI/PI-nanofiber composites, different amounts of short PI nanofibers (0.5, 1, 2 and 3 wt%) were mixed with the PAA precursor solution (10 wt% in DMF). The PI nanofibers were dispersed in the solution of PAA precursor but do not dissolve or swell as PI is insoluble in DMF in contrast to the PAA precursor. The dispersions of PAA and short PI nanofibers in DMF were processed to PAA/PI-nanofiber-films by solution casting, which were dried and imidized following the same heating protocol as for the electrospun PI nanofiber nonwovens. The resulting PI/PI nanofiber-composite films will be referred as PIPICOF in the subsequent text. As expected the PIPICOF films became insoluble in DMF after imidization. For comparison, pure PI films without adding short PI nanofibers were also made following the same procedure. Analysis of the surfaces of PIPICOF showed smooth morphologies. None of the PIPICOF showed any indication of nanofibers on the film surface or as pulled out structures by SEM analysis. The PIPICOF showed excellent thermal stability similar to the pure PI film as measured by thermogravimetric analysis (TGA). All the samples had a 5% weight loss at a temperature of more than 550 °C. In spite of short PI nanofibers undergoing two times high temperature imidization processes, the thermal stability of the PIPICOF was as good as that of pure cast PI film (thermograms not shown here).

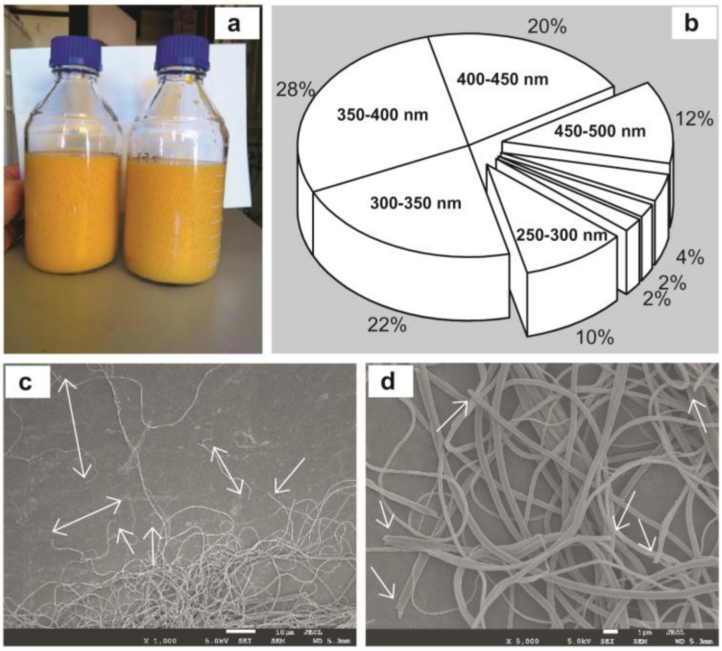

Fig. 1. Photograph of dispersions of electrospun fibers in isopropanol/water (30/70 w/w) after cutting (a), pie chart of the diameter distribution of PI nanofibers (b) and SEM micrograph of short PI nanofibers (c and d) with chain ends marked with white arrows. Scale bar of (c) = 10 μm and (d) = 1 μm.

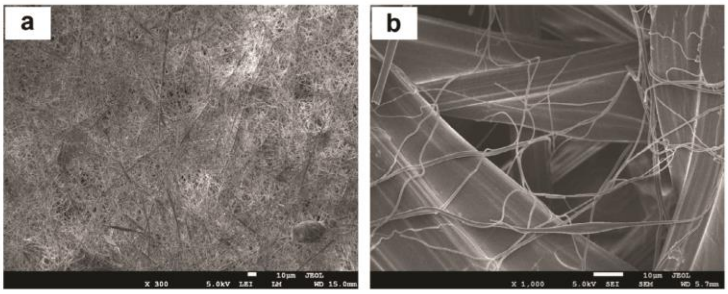

Fig. 2. SEM micrograph of dense layers of short electrospun PI nanofibers deposited from dispersion on filter paper (a) and at higher magnifications showing filter paper fibers with entangled nanofibers (b). Scale bar of (a) and (b) = 10 μm.

Of particular interest for self-reinforced nanofiber composites are the mechanical properties which were only analyzed until now with as-electrospun PI nanofiber nonwovens [22]. The question was whether the usage of short electrospun PI nanofibers would result in any significant difference of the mechanical properties as compared to PI/PI nanofiber composites with as-electrospun (not cut) PI nanofibers or the pure PI films. The typical stress–strain curves of neat PI film and PIPICOF were presented in Fig. 3a while the tendency bar chart of mechanical properties is shown in Fig. 3b. The results indicated that the mechanical properties of composites were significantly enhanced by the presence of short PI nanofibers in the PI matrix. The neat cast PI film exhibited an average strength of about 76 MPa, an E modulus of 882 MPa and a strain at break of 52%. Compared to it, the PIPICOF with very small amounts of PI fibers (maximum amount of short PI fibers was 3 wt%) exhibited enhanced mechanical properties for all samples showing reinforcing effect of short PI fibers. The tensile strength and E modulus of the PIPICOF showed an increase for low PI-nanofiber content (till about 2 wt%). A further increase in the amount of short PI fibers to 3 wt% led to a decrease in mechanical properties. The highest strength of 115 MPa and highest E modulus of 1651 MPa was obtained for the sample having 2.0 wt% of short PI nanofibers, which represented the improvements of 53% and 87% respectively in tensile strength and modulus, as compared to those of neat PI film. When 3.0 wt% short PI nanofibers were added, the PIPICOF showed strength of 72 MPa which was almost same as that of pure PI film but a decrease in strain at break. It is well-known that the fiber edges in short fibers can initiate a crack due to stress concentration and this become prominent after a definite amount of such fibers in composites [9]. This could lead to low strain at break.

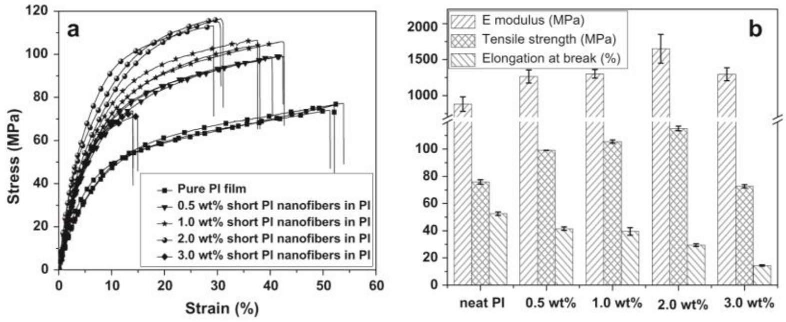

Fig. 3. Typical stress–strain curves of PIPICOF with different amounts of short PI nanofibers (a) and corresponding bar chart of mechanical properties (b).

To reveal the reasons for the deviation from a linear increase in mechanical properties with increasing fiber amounts, cross-section morphology of the composite films was investigated. In order to obtain the original morphology without damage by the external forces, all the samples were first frozen in liquid nitrogen, and then broken. The fractured surfaces of pure cast PI film and PIPICOF as observed by SEM are shown in Fig. 4. It can be seen that the pure PI film presented a smooth and homogeneous fractured surface, while the composite films showed the presence of embedded PI nanofibers. When the amount of the short PI nanofibers in PIPICOF was small, i.e. 0.5 wt%, 1.0 wt% and 2.0 wt%, the short PI nanofibers were isolated from each other which indicated a homogeneous dispersion of nanofibers in the matrix. Also, no cracks or holes were observed at the interface between fibers and matrix, and the nanofibers were intimately surrounded by the PI matrix. For PIPICOF with 3 wt% of PI short nanofibers aggregation was seen leading to the decrease in mechanical properties.

PI composite films with as-electrospun long and continuous PI fibers were reported to the best of our knowledge only in an article by Liu et al., however, without giving the amount of electrospun PI fibers embedded in PI composite film [23]. They reported a tensile strength of 174.1 MPa, an E modulus of 1.31 GPa and an elongation at break of 57.2% by use of aligned nanofibers. In order to have a sound comparison of composites with short electrospun fibers to composites with as-electrospun nanofiber mats we also prepared PI self-reinforced nanofiber composites but now with as-electrospun PI nanofiber mats. We used exactly the same PI nanofiber mats which were used also for the preparation of short nanofibers in order to avoid any doubts due to variations in molecular weight or molecular weight distribution. Dip-coating of PI nanomat in PAA-DMF solution followed by imidization was used for making PI self-reinforced nanofiber composites as described in details in the Supporting information. Obvious disadvantage of PI self-reinforced nanofiber composites with as-electrospun long PI nanofibers is the wetting of the reinforcing nanofibers mats with the matrix polymer which makes it impossible to prepare sound samples with less than 10 wt% nanofiber content and also impossible to prepare samples with predicted content of nanofibers. The

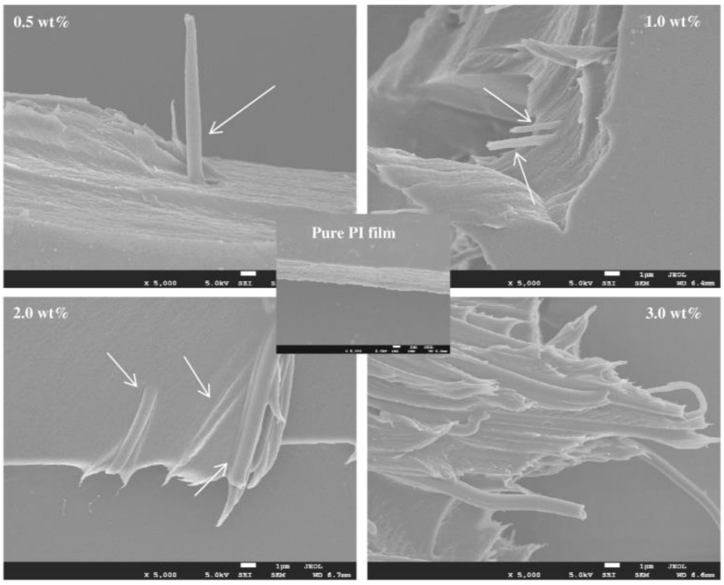

Fig. 4. Fractured surface morphologies of pure PI and PI/PI nanofiber-composite films with different amounts of short PI nanofibers. Scale bar = 1 μm.

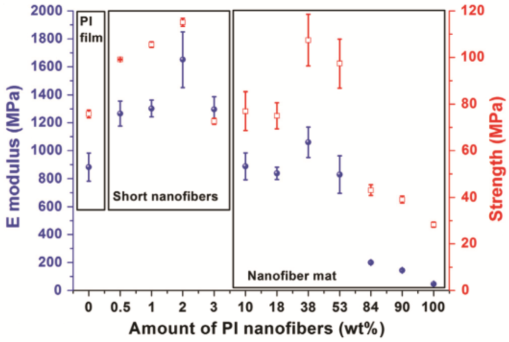

Fig. 5. Comparison of E modulus (●) and strength (□) of PIPICOF and PI self-reinforced nanofiber composites with as-electrospun PI nanofibers and a pure PI film.

comparison of the E modulus and the strength of a series of samples of PI self-reinforced nanofiber composites with different amounts of as-electrospun PI nanofibers with samples of PIPICOF clearly showed that the E modulus of a sample of PIPICOF with only 2 wt% of reinforcing nanofibers is significantly higher than any of the samples of the composites with as-electrospun nanofibers and pure PI film. Furthermore, the strength of the composite films with only 2 wt% of short nanofibers was as high as that of a composite with 38 wt% of as-electrospun long nanofibers (Fig. 5). It should be noted here, that it was not possible to prepare nanofiber composites with less than 10 wt% of as-electrospun long PI nanofibers due to lack in homogeneity.

4. Conclusion

In conclusion it has been shown, that the use of short electrospun fibers opens completely new opportunities for the processing of electropsun nanofibers. The wealth of structures, properties, and applications, which has been achieved till now by the use of as-electrospun nanofibers, which are basically very long fibers can be extended very significantly by cutting the fibers to short segments. These short fibers can be processed in liquid formulations and with this their processing becomes independent from the limitations given by the electrospinning process itself and will become available for every materials scientist for further processing in the creation of novel materials. The use of short electrospun fibers does not only offer advantages for processing but gives also chances for significant property improvements as shown here as an example for nanofiber reinforced composites. Clearly it has been shown that the mechanical properties of self-reinforced PI nanofiber composites with short electrospun PI fiber were better as compared to the as-electrospun PI nanofiber mats and this too at much lower fiber contents and with nonoriented fibers. Main reason for the superior properties with short fibers is obviously much better dispersability of the short PI nanofibers in the matrix polymer. The use of short electrospun fibers is surely not limited to fiber reinforced polymeric composites. Short electrospun fibers prepared from other polymers with functionalities different than polyimides could be used for the construction of electrical circuits or for targeted movement, etc. Furthermore, it can be expected that manifold new supramolecular structures can be prepared with short electrospun fibers which is presently under investigation.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compscitech.2013.08.031.

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Supporting Information

The preparation of PI self-reinforced nanofiber composites with long and continuous as-electrospun PI nanofiber mats was comprised of the following steps:

1) The detailed method for making PI nanofiber mat is described in the experimental part of the main manuscript.

2) The PI nanofiber mat was cut into small pieces (4 cm × 4 cm) and the small PI mats were immersed into the PAA/DMF solution (25, 20, 15, 10, 5 and 2 wt% respectively) for 5 min. Subsequently, the PI mats coated with PAA were dried and imidized using the same protocol as mentioned in the experimental part of the main manuscript for the electrospun PAA nanofibers.

3) Following the above steps, the PI composites with 10, 18, 38, 53, 84, and 90 wt% PI nanofiber mat from PAA/DMF solution (25, 20, 15, 10, 5 and 2 wt% respectively) were obtained.

4) Using above method, we could not make composites with predetermined amount of PI nanofiber mats due to the limitation of the process itself, but we could obtain the samples with a series amount of PI nanofibers in the composites. The exact content of the PI nanofiber mats in the composites could be calculated after the composites were completely fabricated

The mechanical properties (**Table 6-S1** and **Figure 6-S1**) of the resulting PI nanofiber composites were measured following the same protocol as shown in the manuscript for composites with short PI fibers.

Table 6-S1 Mechanical properties of PI self-reinforced nanofiber composites with as-electrospun PI nanofiber mats

Content of PI nanofibers (wt%)	E(MPa)	Strength(MPa)	Strain(%)
100 (PI nanofiber mat)	46.5 ± 4.44	28.24 ± 1.11	102.1 ± 5.8
90	144 ± 7.71	39.05 ± 1.51	88.0 ± 6.5
84	201 ± 10.1	43.06 ± 2.29	73.5 ± 2.9
53	829 ± 134	97.38 ± 10.56	64.7 ± 6.2
38	1060 ± 109	107.43 ± 11.09	57.6 ± 11.2
18	838 ± 43.3	74.98 ± 5.6	36.5 ± 6.9
10	888 ± 95.4	76.98 ± 8.33	29.3 ± 7.6
0 (PI film)	882 ± 100	75.84 ± 1.67	52.5 ± 1.3

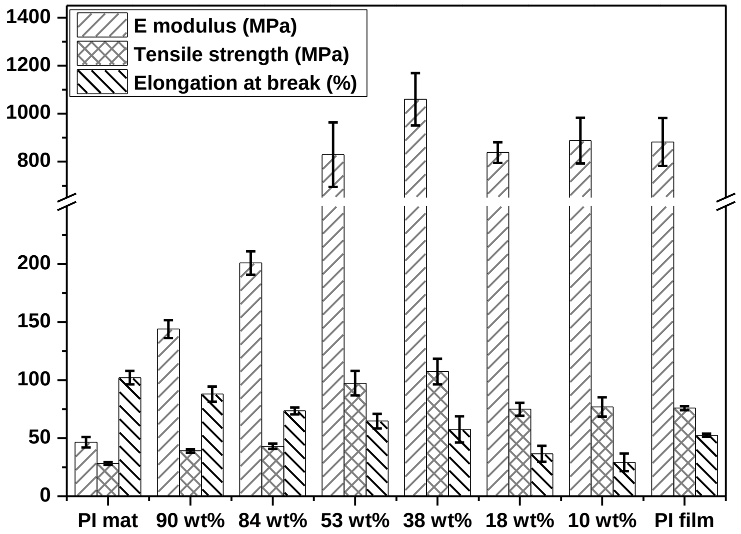

Figure 6-S1 Bar chart of mechanical properties of self-reinforced PI nanofiber composites with as-electrospun PI nanofiber mats.

SEM photographs of films surfaces of PI self-reinforced PI nanofiber composites with as-electrospun PI nanofibers with different amounts of PI nanofibers are shown in **Figure 6-S2**. As increasing the amount of PI mat in the composites (using higher concentration of PAA/DMF solution as the matrix solution), more fibers were glued by the PI matrix until only PI matrix film formed on the surface of the samples.

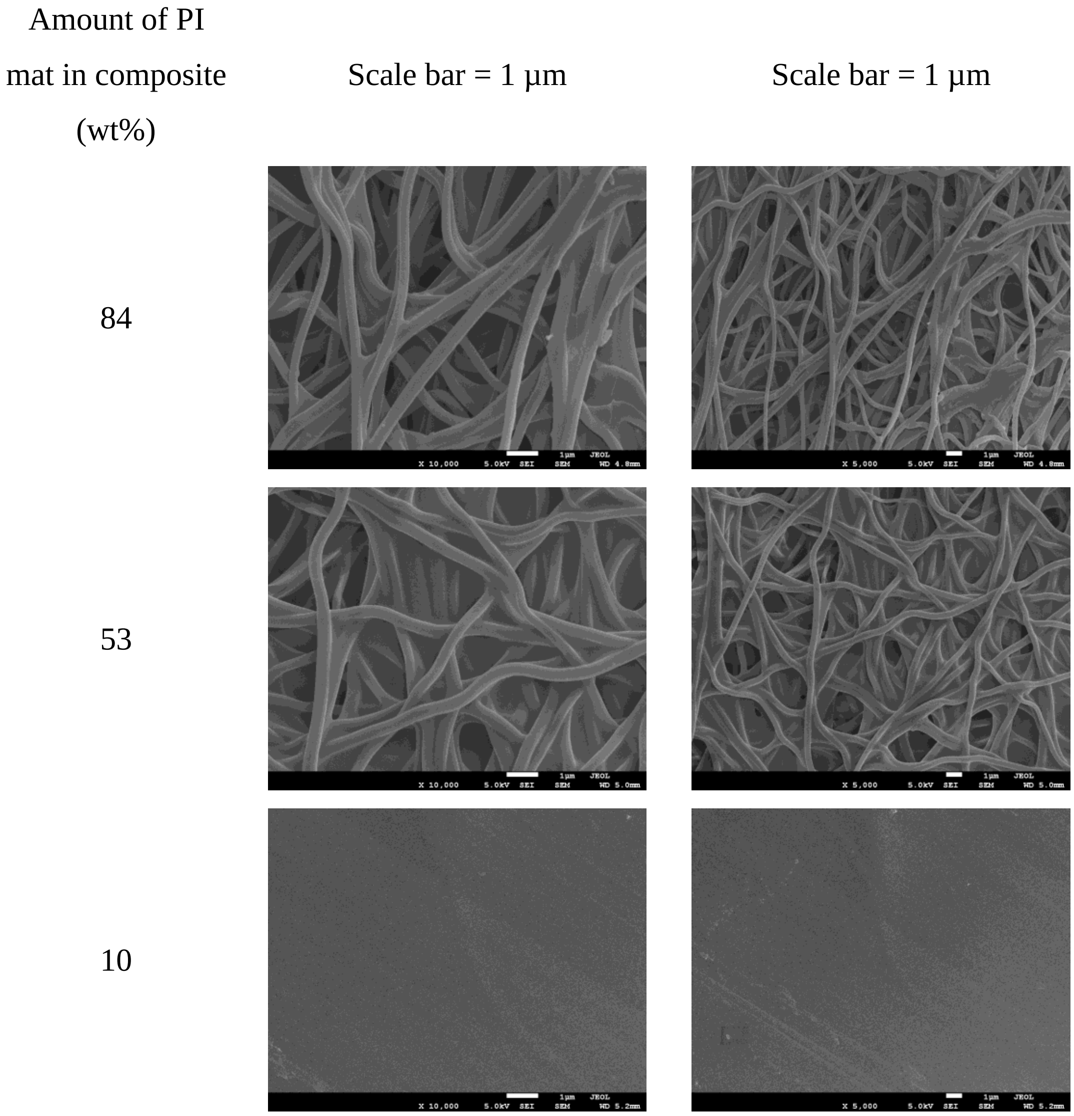

Figure 6-S2 SEM photographs of the surfaces of PI self-reinforced composites using as-spun PI nanofibers.

SEM micrographs of samples of PI self-reinforced PI nanofiber composites with as electrospun PI nanofibers after tensile tests are shown in **Figure 6-S3**. Samples with 84 wt% PI mat showed only small amount of fibers glued by the PI matrix. This is most likely the reason why the tensile properties of these samples were similar to the pure PI nanofiber mat. When increasing the amount of the PI matrix, more fibers were embedded into the matrix, so the tensile properties of the samples shifted to the pure

PI film. However, the photos also showed that the pores between the fibers could not be filled completely by the PI matrix, while using PI short fibers one could overcome the above drawbacks. That's another reason why short PI fibers are better than as-spun PI fibers mats.

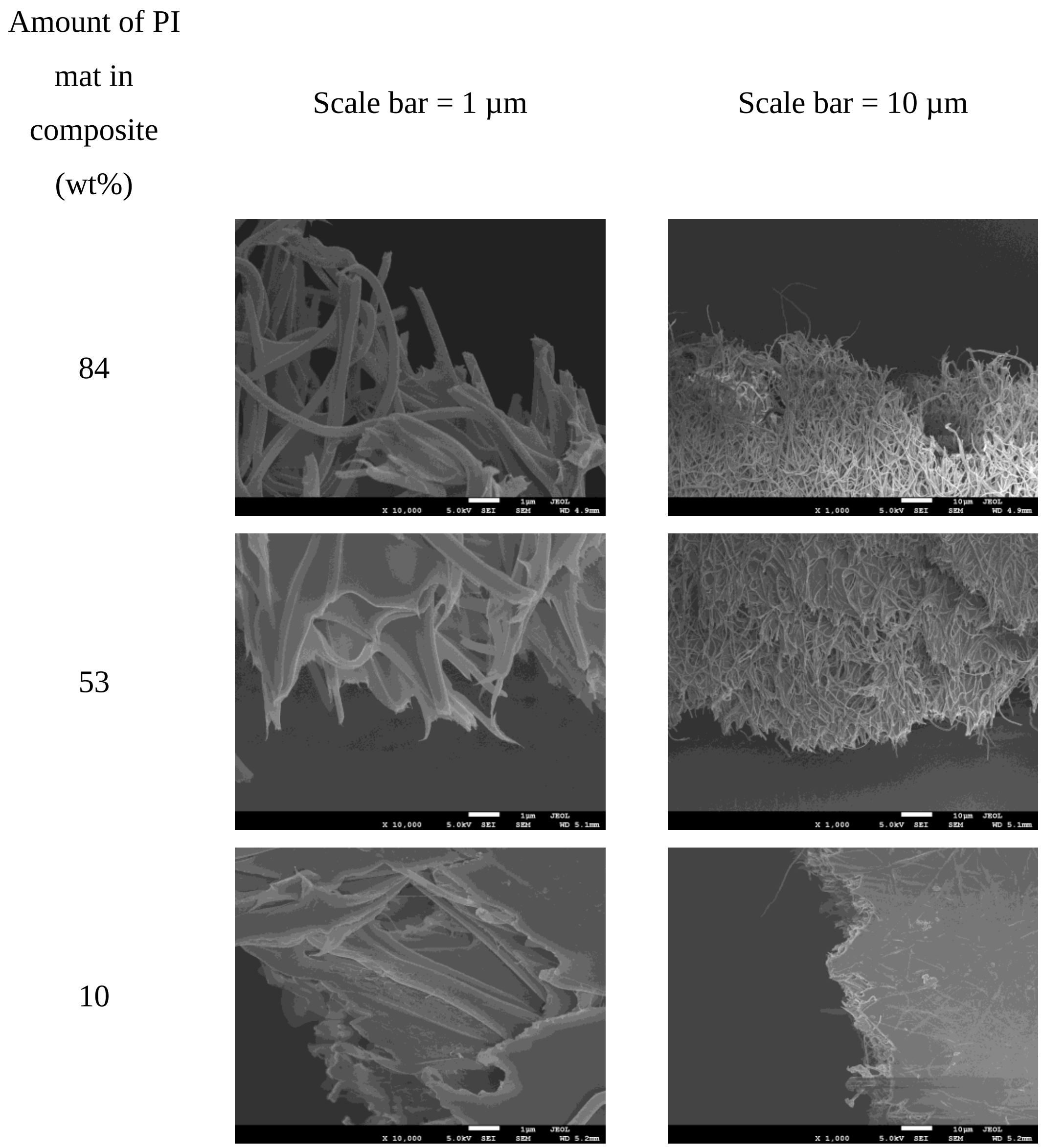

Figure 6-S3 SEM micrographs of samples of PI self-reinforced PI nanofiber composites with different amounts of as-electrospun PI nanofibers after tensile tests.

4. Outlook

In the last few years, electrospun nanofibers have been attracting more and more attention as reinforcement in composite fields due to their excellent mechanical properties. However, until now, the limited data from the only few countable reports can’t provide a comprehensive impression on the effect of electrospun nanofibers on polymer matrix. Therefore, in this thesis, high performance long and short electrospun nylon-6 and polyimide nanofibers were used to reinforce other polymers, like melamine-formaldehyde, thermoplastic polyurethane, poly (methyl methacrylate) and polyimide. The effect of the fiber contents and the fabricating methods on the wetting behavior and mechanical properties were studied. Nevertheless, for this relative new field of electrospun nanofiber reinforced polymer composites, more investigations are required in different directions.

(a) How to prepare strong nanofiber with excellent mechanical properties? Excellent mechanical properties of the nanofibers are the premise for nice nanofiber reinforced polymer composites. There are several ways to improve the mechanical properties of nanofibers. First, increasing the degree of crystallinity is a good way to increase the tensile strength and E modulus of nanofibers. Second, the improvement of molecular orientation along fiber axis could enhance the mechanical properties of electrospun nanofibers. Third, due to the size effect, fine nanofibers with diameter blow 250 nm might have higher mechanical properties. Fourth, another way to obtain high performance nanofibers could be achieved via making composite nanofibers by normal electrospinning with reinforcements like carbon nanotubes, cellulose crystals inside, or by coaxial or triaxial electrospinning with reinforcements inside or in the middle.

(b) The effect of diameter and aspect ratio of nanofibers on the properties of nanofiber reinforced polymer composites should be systematically studied. Work in this thesis have revealed that long and short electrospun nanofiber could effectively reinforce other polymers, but more studies about how diameter of nanofibers and aspect ratio of nanofibers affect the properties of composites are still absent.

(c) Nanofiber/matrix interaction. As for traditional fiber reinforced composites, fiber with modification aiming at the enhancement of fiber/matrix interface have been greatly investigated. However, in the case of electrospun nanofibers, there are still much less data available in the literatures. Chemical and physical modifications on electrospun nanofibers, such as plasma treatment, surface polymerization, physical absorption and chemical immobilization of suitable molecules, could be applied in the field of nanofiber reinforced composites to strengthen the interface of reinforcements and matrix. Another possible way is applying coaxial or triaxial electrospinning to get composite nanofibers, by which the external component offers a good chemical compatibility with the matrix, and the core component or the middle component acts as reinforcement to provide suitable mechanical properties.

(d) Electrospun carbon nanofibers as reinforcement. It is well known that carbon nanofiber has ultrahigh tensile strength and E modulus and is prefect candidate as reinforcement. However, it is rather difficult to get high quantities of carbon nanofibers by electrospinning. Therefore, how to prepare high mechanical performance carbon nanofibers by electrospinning and apply electrospun carbon nanofibers into composites is still a big challenge for researchers from polymer chemistry and polymer engineering.

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