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DNA as a Natural Flame Retardant for Cellulose Acetate Polymer Mixtures

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The combustion properties of natural DNA mixed with the nature-derived thermoplastic cellulose acetate (CA) were determined. The flame retarding properties of DNA in mixtures with CA were significant and concentration dependent, the higher the DNA content the better the flame retardation. Ammonia was detected during the heating of CA-DNA mixtures. In contrast, carbon monoxide (CO) formation was distinctly reduced during combustion of the CA mixtures with DNA when compared with pure CA. Thus, DNA can be considered as a natural and re-growing polymeric flame-retardant for versatile applications of CA-based thermoplastic polymers in order to form eco-friendly polymer mixtures.

1. Introduction

Polymer materials derived from natural and re-growing sources are growing in importance.[1] Cellulose, for example, is an abundant polysaccharide accessible from plants and cellulose-based polymers. Cellulose can also be obtained from waste and bio-products of the textile, agro and food industries.[2] The thermoplastic cellulose derivative cellulose acetate (CA), which is obtained from acetylation of cellulose followed by partial deacetylation, offers a plethora of possible industrial applications and can replace many oil-based thermoplastic polymers.[3] The usage of delicate additives can improve the properties of such thermoplastic polymers, and intumescence flame retardants appear especially promising.[4] Ammonium polyphosphate (APP) and melamine polyphosphate (MPP) are the most prominent industrially applied intumescence flame retardants with distinct advantages such as lower loading amounts over inorganic flame retardants.[5–7] APP and MPP generate active intumescence flame retardants in combination with pentaerythrol, where ammonia and melamine embody the blowing agent (nitrogenous gas), polyphosphate forms the carbonization catalyzing acidic component and pentarerythrol the charring component.[6] The foamy char built by these intumescence flame retardants increased the distance between flame and polymer and reduced flame development as well as smoke production.[8,9]

Divers efforts to improve the combustion properties of CA by flame retardants were undertaken and are currently under investigation.[10,11] For instance, ammonium phosphates have shown promising effects in combination with CA.[12] Recently, CA mixtures with the established bis-phosphonamidate EDA-DOPO derived from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) or with MDOP (the salt of DOPA, which is the oxidation product of DOPO, and of melamine) exhibited significant peak heat release rate reduction values.[13–15] However, natural and biodegradable additives of relatively low cost are preferred, which can be obtained by simple isolation from re-growing natural sources or waste material in order to generate eco-friendly polymer mixtures with nature-derived thermoplastic polymers such as CA.[16]

DNA (deoxyribonucleic acid) is generally known as the crucial biopolymer that harbors the genetic information of every organism.[17] But DNA also possesses properties which qualify this natural product for various applications in material science, e.g., as a sun screen.[18] Due to its chemical composition DNA can also be considered as a biological intumescence flame retardant which contains acidic polyphosphate scaffolds, charring deoxyribose carbohydrates, and *N*-

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heterocyclic building blocks as blowing components, which form ammonia and nitrogen during combustion.[19] DNA as additive for widely applied polymers such as EVA, PP, ABS, PET, and PA6 surpassed or reached the combustion properties of currently applied and available flame retardants such as commercially available formulations, intumescent flame retardants and nanocomposites.[20] In addition, DNA additives displayed flame-retarding effects in mixtures with low-density PE.[21] Flame-retarding DNA additives were investigated for cotton, and DNA was also combined with chitosan to enhance its char formation by phosphate release during combustion.[22–24] These promising achievements suggest that DNA might also be a suitable flame retardant additive for thermoplastic cellulose acetate derived which is made from natural sources. In this report, we describe the thermal and flame retarding effects of DNA when admixed to the important nature-derived and biodegradable polymer CA as well as the identification of volatile components which occurred during heating and combustion of these polymer mixtures.

2. Results and Discussion

2.1. Combustion analyses

Pure CA and mixtures of CA with DNA at two different and feasible concentrations (5% and 10% DNA, w/w, in CA) were combusted in a cone calorimeter and analyzed for their flame retarding properties. The time-dependent heat release curves (time-dependent heat release rate/HRR) of pure CA and of the mixtures of CA with DNA (5% or 10%, w/w) are shown below (Figure 1). The flame-retarding effects of DNA are concentration-dependent and the higher the DNA concentration the stronger the effect. The 10% DNA mixtures displayed stronger effects than the 5% DNA mixtures. The formation of highly efficient DNA degradation products such as phosphoric acids and *N*-heterocycles can be assumed as a reason for this effect.[19,23]

Photographic images of the CA mixture with 10% DNA showed a distinct char formation during pyrolysis which can be based on a possible intumescence mode of flame retarding activity of DNA (Figure 2). The CA-DNA mixture led to peculiar snail-type combustion material indicating the formation of a stable barrier material mass suppressing gas exchange and heat release during flame exposure. DNA can act as a Lewis acid (based on the formation of polyphosphoric acid upon heating) and showed dehydrating effects for cotton treated with DNA upon combustion, which promoted char formation of the material.[20]

The combustion data of CA and its mixtures with DNA are given in Table 1. The 10% DNA mixture showed distinctly stronger peak heat release rate (PHRR) reduction when compared with the 5% mixture. The 10% DNA mixture exhibited the strongest PHRR reduction by 25.5% which was twice as high as the PHRR reduction of the 5% DNA mixture. The PHRR reduction of the 10% DNA mixture was higher than the reduction reported of a 10% EDA-DOPO mixture with CA (PHRR reduction of 17.7%).[13] DNA consisting of polyphosphates, deoxyriboses and *N*-heterocyclic purine and pyrimidine bases is obviously superior to the synthetic aromatic phosphamide EDA-DOPO in this regard. It was shown that DNA formed

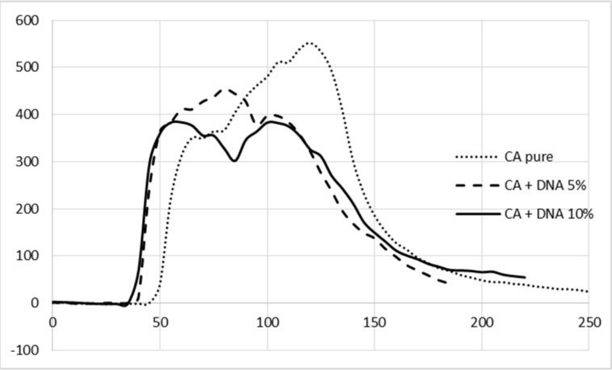

Figure 1. Representative time-dependent heat release curves of pure CA and of CA mixtures with DNA (%, w/w as indicated); x-axis: t (s); y-axis: HRR (kW/m^2).

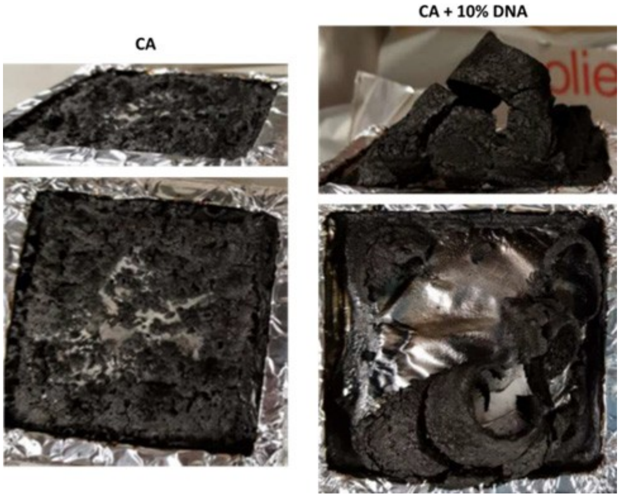

Figure 2. Representative photographs of the char of burnt CA and the burnt CA mixture with 10% DNA.

Table 1. Combustion data of pure CA and of its DNA mixtures at the indicated concentrations (%, w/w).

Compd.	CA	5% DNA	10% DNA
PHRR (kW/m^2)[a]	513 ± 39	451 ± 5.0	382 ± 2.0
PHRR red. (%)[b]	–	12.1	25.5
THR (MJ/m^2)[c]	53.1 ± 2.8	39.5 ± 0.05	41.7 ± 1.0
SEA (m^2/kg)[d]	84.8 ± 5.5	23.4 ± 0.4	17.2 ± 9.0
Residual mass (g)	3.30 ± 0.79	4.23 ± 1.03	5.39 ± 0.53
t_{ig} (s)[e]	58 ± 5.0	46 ± 4.0	44.5 ± 3.5
CO (kg/kg)[f]	0.037 ± 0.023	0.013 ± 0.002	0.022 ± 0.006
CO_2 (kg/kg)[g]	1.45 ± 0.02	1.39 ± 0.01	1.32 ± 0.04

[a] PHRR: peak of heat release rate. [b] PHRR red.: PHRR reduction when compared with pure CA. [c] THR: total heat release. [d] SEA: specific extinction area. [e] t_{ig}: time to ignition. [f] CO: median CO formation. [g] CO_2: median CO_2 formation.

isocyanic acid, water, CO_2 and ammonia during combustion, which contribute to the flame retarding properties of DNA in addition to the less volatile DNA degradation products formed by the phosphates, *N*-heterocycles and deoxyriboses.[19]

Shorter times to ignition (t_{ig}) were observed for the DNA mixtures than for pure CA. It is possible that intact DNA as a Lewis base (i.e., an electron donor) at low temperatures can promote ignition leading to the shorter t_{ig} values of the CA-DNA mixtures.

Total heat release (THR) was distinctly reduced in the CA-DNA mixtures when compared with pure CA. The maximum of THR reduction (i.e., ca. 20% reduction) was already achieved in the 5% DNA mixtures and the 10% DNA mixtures showed THR values in the same range. Cotton fabrics impregnated with 5% or 10% DNA showed stronger THR reduction (reduction of ca. 60%) than the 5% and 10% DNA-CA mixtures used in this study while low-density PE mixtures with 5–10% DNA showed smaller THR reduction (less than 10%) than found in this work for DNA-CA mixtures.[21,23] A strong reduction of the specific extinction area (SEA), which is a means of measuring smoke development, was observed for the 5% DNA and the 10% DNA mixtures of CA. In addition, higher residual masses were observed for the 5–10% DNA mixtures than for pure CA samples indicating the enhanced formation of charred material due to the admixed DNA. Values of CO_x formation and O_2 consumption during combustion of CA and the DNA mixtures were also determined (Table 1). All DNA mixtures showed distinctly lower carbon monoxide (CO) release when compared with pure CA and when compared with reported values of 10% EDA-DOPO in CA (0.096 kg/kg), which showed even higher CO values than CA probably because of the aromatic DOPO component of EDA-DOPO.[13] The reduction of the carbon dioxide (CO_2) formation depended on the DNA concentration, the more DNA the less CO_2 was formed. In addition to the cone calorimeter tests, UL-94 flammability tests were carried out. Both 10% DNA-CA and pure CA samples (125 × 13 mm) passed horizontal (HB classification) UL-94 tests. The 10% DNA mixtures burned less than pure CA and showed residual lengths of 71.75 ± 5.23 mm after the UL-94 tests while the residual lengths of the pure CA residues were distinctly shorter (43.99 ± 5.97 mm). All samples failed in the vertical (V0, V1 and V2 classification) UL-94 tests.

The charred residues of the DNA-CA samples were analyzed by scanning electron microscopy/SEM (Figure 3). Already at low magnification, bubble-like structures became visible (Figure 3a). These bubbles of varying sizes, which were absent in the pure CA samples, were tightly embedded into the CA char and indicate a hallmark of intumescence flame retardants whose mode of action is based on gas/blowing agents formation and charring during the burning process (Figures 3b and S1).

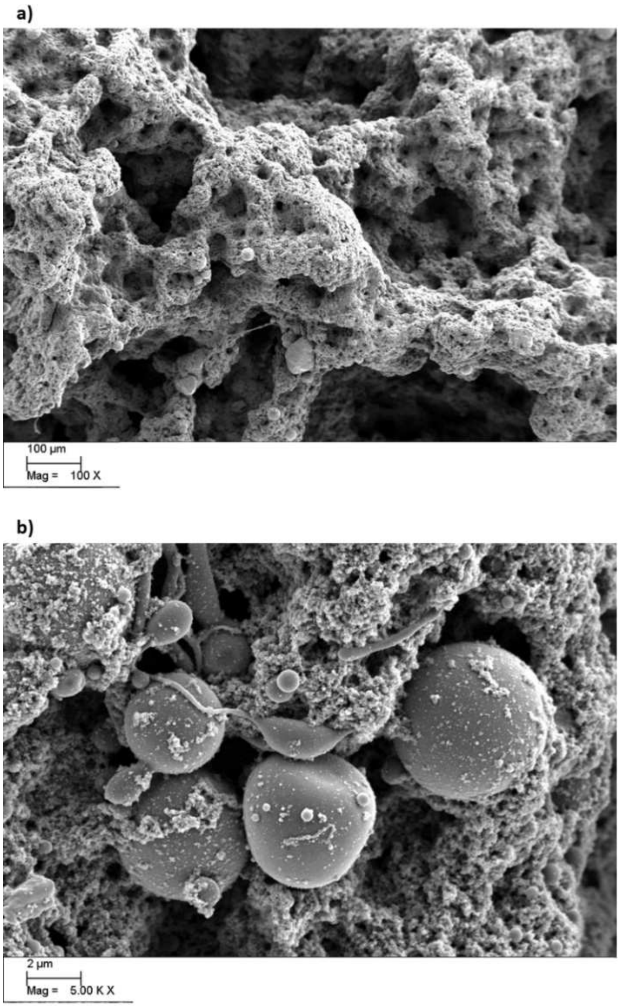

Figure 3. Scanning electron microscopy images of 10% DNA-CA mixture after UL-94 HB test.

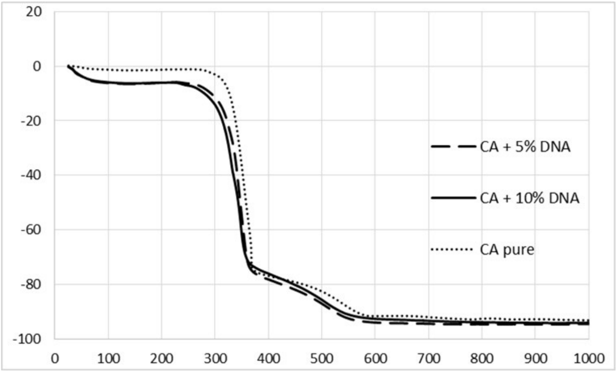

Figure 4. Temperature-dependent thermogravimetric (TG) analysis measurement of the CA-mixture with DNA in comparison with pure CA; x-axis: T in °C; y-axis: mass reduction in %.

2.2. Thermogravimetric analyses and differential scanning calorimetry

Thermogravimetric analysis (TGA) measurements were carried out in order to investigate the thermal stability of the tested CA DNA mixtures (Figure 4, Table 2). Only slight differences between the mixtures of CA with DNA and pure CA were observed. There are greater residual masses left for the 5% and 10% DNA mixtures (18.5% residual mass for the 5% mixture

Table 2. TGA values of CA samples (mass loss ΔM in % depending on temperature T in °C).

Compd.	T (°C)	ΔM (%)
CA	25–75	1.7
	270–385	73.9
	390–590	15.9
5 % DNA	25–80	6.1
	255–390	70.0
	390–590	18.5
10 % DNA	25–80	5.2
	255–390	68.2
	390–590	18.0

and 20.0 % residual mass for the 10 % mixture) at temperatures above 360 °C than for pure CA (15.9 %). The mass losses at temperatures of up to 100 °C, which are indicative of H_2O loss, were 6.1 % for both DNA mixtures but only 1.7 % for pure CA. It is possible that the increased H_2O content / release of the DNA mixtures contributed to the flame retarding properties of DNA.

Differential scanning calorimetry (DSC) measurements were carried out in order to investigate the heat flow of the tested CA DNA mixtures with rising temperatures (Figure 5). Mixtures of CA with 5 % or 10 % DNA showed a distinctly reduced heat flow when compared with the heat flow of pure CA. In addition, the initial heat release peak at the beginning of the burn off at around 290 °C is significantly lower for the DNA mixtures.

2.3. Thermogravimetry coupled mass spectrometry analyses

A sample of CA mixed with 10 % DNA was investigated by TGA-coupled mass spectrometry concerning the appearance of volatile decomposition products and the results were compared with a pure sample of CA (Figure S2, Figure S3). Ammonia (NH_3, $m/z = 17$) was detected during the heating of the CA-DNA mixture and can be assigned to the DNA component of the mixture since pure CA does not contain nitrogen components. This finding is in line with previous reports about the degradation products of DNA, which include ammonia.[19] In addition, H_2O ($m/z = 18$), CO_2 ($m/z = 44$) and traces of CO ($m/z = 28$) were detected upon heating of CA and of CA mixed with DNA. All these volatile combustion components can contribute to an efficient fire suppression. However, flammable acetic acid ($m/z = 60$) was also detected in considerable amounts. Acetic acid was described before as a main decomposition product of CA and vinyl acetate polymers upon pyrolysis.[25,26] Formaldehyde ($m/z = 29$, i. e., the base peak of published formaldehyde mass spectra) was identified as another significant volatile combustion product, which is in line with previous findings from cellulose pyrolysis.[27] Table 3 shows the identified volatile molecules built upon heating of CA with 10 % DNA.

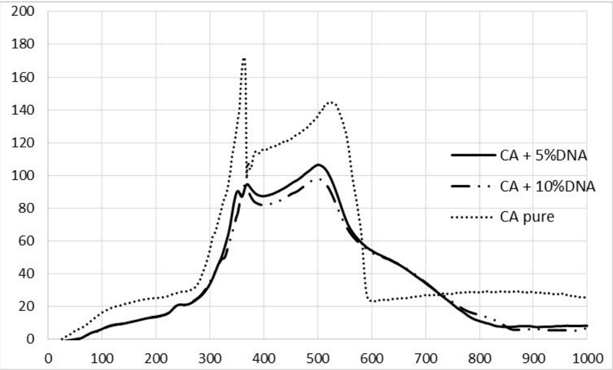

Figure 5. Differential scanning calorimetry (DSC) measurement of the CA-mixtures with DNA in comparison with pure CA; x-axis: T in °C; y-axis: heat flow in mW.

Table 3. Volatile molecules and their *m/z* values identified by TGA-MS of CA mixed with 10 % DNA (w/w).

Compd.	m/z
NH_3	17
H_2O	18
CO	28
HCHO	29
CO_2	44
CH_3COOH	60

3. Conclusion

DNA, in mixtures with CA, showed significant flame retardant properties. These properties comprise a reduced peak heat release rate and a lowered CO formation. The effect of the DNA additive is intriguing and the DNA degradation products might give an explanation for this phenomenon. Thermal degradation analyses of DNA mixed with CA led to the formation of volatiles such as formaldehyde, acetic acid, H_2O, CO_2 and NH_3 as degradation products at high temperatures. The influence of other commonly applied additives such as plasticizers and stabilizers on the flame retarding effects of DNA in CA polymers should also be investigated as to potentially stabilizing effects and the formation of by-products. A better understanding of the flame retarding mechanism of DNA can certainly lead to optimized CA polymer mixtures for manifold applications, which will be of importance for the preparation of re-growing and naturally degrading polymer mixtures in future.

Supporting Information Summary

The online version of this article contains supplementary material (experimental procedures, SEM images, TGA-coupled mass spectra, dTG spectra), which is available to authorized users.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] G.-Q. Chen, M. K. Patel, *Chem. Rev.* **2012**, *112*, 2082–2099.
[2] Z. Hussain, W. Sajjad, T. Khan, F. Wahid, *Cellulose* **2019**, *26*, 2895–2911.
[3] K. Edgar, *Encyclopaedia of polymer science and technology, Vol 9: Organic cellulose esters*, Wiley, New York, **2004**, p. 129.
[4] E. D. Weil, *J. Fire Sci.* **2011**, *29*, 259–296.
[5] B. Dittrich, K.-A. Wartig, R. Mülhaupt, B. Schartel, *Polymer* **2014**, *6*, 2875–2895.
[6] P. Lv, Z. Wang, K. Hu, W. Fan, *Polym. Degrad. Stab.* **2005**, *90*, 523–534.
[7] G. Camino, N. Grassie, I. C. McNeill, *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 95–106.
[8] A. B. Morgan, C. A. Wilkie, *The non-halogenated flame retardant handbook*, John Wiley & Sons, Hoboken, **2014**.
[9] S. K. Sharma, *Fire Technol.* **2003**, *39*, 247–260.
[10] S. Gaan, L. Mauclaire, P. Rupper, V. Salimova, T.-T. Tran, M. Heuberger, *J. Anal. Appl. Pyrol.* **2011**, *90*, 33–41.
[11] L. Jiang, K. Li, H. Yang, X. Liu, W. Xu, B. Deng, *Cellulose* **2019**, *26*, 5211–5226.
[12] M. D. C. Lucena, A. E. V. de Alencar, S. E. Mazzeto, S. D. Soares, *Polym. Degrad. Stab.* **2003**, *80*, 149–155.
[13] J. Koedel, C. Callsen, M. Weise, F. Puchtler, A. Weidinger, V. Altstaedt, R. Schobert, B. Biersack, *Polym. Test.* **2020**, *90*, 106702.
[14] N. M. Neisius, M. Lutz, D. Rentsch, P. Hemberger, S. Gaan, *Ind. Eng. Chem. Res.* **2014**, *53*, 2889–2896.
[15] D. Shen, Y.-J. Xu, J.-W. Long, X.-H. Shi, L. Chen, Y.-Z. Wang, *J. Anal. Appl. Pyrol.* **2017**, *128*, 54–63.
[16] M. Malinconico, P. Cerruti, G. Santagata, B. Immirzi, *Macromol. Symp.* **2014**, *337*, 124–133.
[17] A. Travers, G. Muskhelishvili, *FEBS J.* **2015**, *282*, 2279–2295.
[18] A. E. Gasperini, S. Sanchez, A. L. Doiron, M. Lyles, G. K. German, *Sci. Rep.* **2017**, *7*, 6631.
[19] J. Alongi, A. Di Blasio, J. Milnes, G. Malucelli, S. Bourbigot, B. Kandola, G. Camino, *Polym. Degrad. Stab.* **2015**, *113*, 110–118.
[20] J. Alongi, F. Cuttica, F. Carosio, *ACS Sustainable Chem. Eng.* **2016**, *4*, 3544–3551.
[21] S. A. Isarov, P. W. Lee, J. H. Towslee, K. M. Hoffman, R. D. Davis, J. M. Maia, J. K. Pokorski, *Polymer* **2016**, *97*, 504–514.
[22] J. Alongi, R. A. Carletto, A. Di Blasio, F. Carosio, F. Bosco, G. Malucelli, *J. Mater. Chem. A* **2013**, *1*, 4779–4785.
[23] J. Alongi, J. Milnes, G. Malucelli, S. Bourbigot, B. Kandola, *J. Anal. Appl. Pyrolysis* **2014**, *108*, 212–221.
[24] F. Carosio, A. Di Blasio, J. Alongi, G. Malucelli, *Polymer* **2013**, *54*, 5148–5153.
[25] W. P. Brown, C. F. H. Tipper, *J. Appl. Polym. Sci.* **1978**, *22*, 1459–1468.
[26] C. Hoffendahl, G. Fontaine, S. Duquesne, F. Taschner, M. Mezger, S. Bourbigot, *RSC Adv.* **2014**, *4*, 20185–20199.
[27] X. Zhang, J. Li, W. Yang, W. Blasiak, *Energy Fuels* **2011**, *25*, 3739–3746.

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