RESEARCH ARTICLE

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Investigation of the Reaction Kinetics of Poly(butylene terephthalate) and Epoxide Chain Extender

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Polyesters, such as poly (butylene terephthalate) (PBT), owe a rather low melt strength, which is considered as not beneficial for foaming. To overcome this issue, a typical attempt is the incorporation of chemical modifications—so-called chain extenders (CE)—in the reactive extrusion process. In this study, the reaction kinetic variables are investigated depending on the material and process parameters. For this purpose, different series of experiments are performed with varying PBT with different molecular weights and the commonly used CE, Joncryl ADR4468, on a micro compounder. The screw force is recorded and analyzed using an Avrami and an Arrhenius plot. First, the amount of CE is systematically varied. To study the course of the reaction in more detail, the reaction is stopped in a series of measurements (10, 30, 60, and 90 s after complete filling). Gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FT-IR), and Raman spectra are recorded. In the second series, the effect of processing temperatures between 250 and 270 °C is investigated, and finally, in the third series, the average molecular weight of PBT is varied. It could be shown that the activation energy seems to be dependent on the initial molecular weight; lower molecular weights result in lower activation energy.

1. Introduction

Due to their excellent properties, polyesters such as poly (ethylene terephthalate) (PET) and PBT are classified as engineering plastics.[1–3] In particular, their enhanced thermal stability and mechanical resistance qualify them for use as construction materials in areas such as the automotive and electrical industries.[1,4,5] For lightweight structures, polyesters are used as foams to save weight while maintaining reliable mechanical properties. However, the foaming of these materials is challenging.

The great advantage of bead foams is that low density, complex shapes, and good insulation properties can be combined. However, up to now, the established bead foams are mainly made of commodity polymers, such as polystyrene and polypropylene,[6] and are also recently developed for polymers such as polylactide.[7,8] A current trend is to widen the field of applications of bead foam, for instance, to use cases demanding increased resistance to heat exposure; therefore, several attempts have been made mostly using engineering polymers, such as polyamide 12 (PA 12),[9] PET,[10] and PBT.[11,12] Anyhow, it has to be emphasized that unmodified polyesters, such as PBT and PET, usually owe rather insufficient rheological properties for foaming (i.e., low melt strength).[1,11,13,14] This makes it difficult to expand the material into a low-density foam. Furthermore, the fusion of individual beads is another challenge. The current state-of-the-art approach is the use of chemical modifications to overcome those issues, as it was shown in previous works.[11,15] Hence, the melt modification with CE during reactive extrusion processes is a promising approach to increase the molecular weight (branching and/or crosslinking) and consequently to change the rheological properties (i.e., increased shear viscosity and melt strength).[3,16–18] Chain extenders are multifunctional additives that can react with the terminal functional groups of the polymers. For polyesters, many different systems of substances are already known and studied that can be used as chain modifiers, such as isocyanides,[14,19] phosphites,[20,21] pyromellitic acid dianhydride,[3,22–24] epoxides,[2,18,25–29] and others,[30,31] with varying degrees of efficiency. As summarized in a recently published review article, one of the most commonly used chain extenders both in industry and academia is Joncryl ADR4468 from BASF.[32] The chain extension with Joncryl ADR4468 is relatively complex but mainly occurs through the reaction between the epoxide function of the chain extender and the carboxyl or hydroxyl group of the PBT (**Figure 1**).[16,17,33] Different

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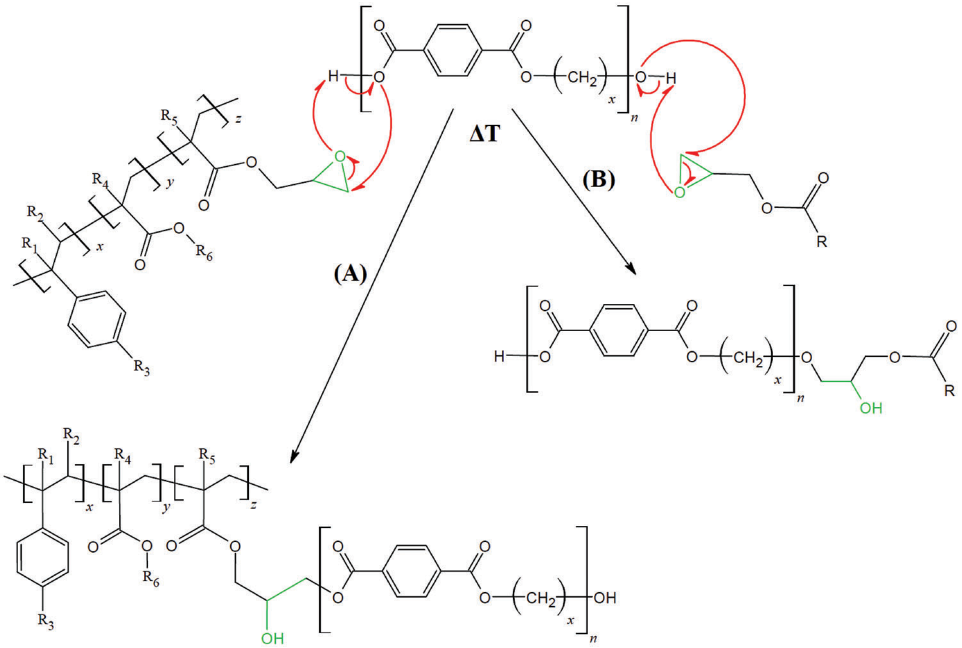

Figure 1. Mechanism of the linkage reaction of Joncryl ADR with the carboxylic acid group (A) and the hydroxy group (B) of a polyalkylene terephthalate.

side reactions (e.g., the unintended gelation of the CE) can happen simultaneously.[34] It is known that the reaction between the epoxide and the carboxyl group is preferred over the reaction compared to the hydroxyl group.[1,35] In this way, it can be assumed that the modified PBT would show a relatively low carboxyl group concentration and thus a higher hydrolysis resistance.[1]

Because of the CE reaction, the molecular weight rises and leads to an increased melt viscosity. Consequently, the torques during the processing change as illustrated in several studies.[16,17,35–38] For this purpose, often the polymer system is processed batch-wise in a laboratory kneader or micro compounder where the torque (or the screw force) is recorded over the processing time and the changes due to the mechanisms taking place can be followed. Three typical regimes could be identified in all batch processes. First, immediately after the polymer is fed, the torque rises and falls depending on how fast the polymer can be molten. Second, the torque remains relatively stable.[1,36] The level of the torque depends on the molecular weight and steric hindrance of the polymer chain.[14,39] The extrusion can proceed with homogeneous material properties. After a certain time, the torque decreases due to thermal–mechanical degradation.[36] The degradation depends on the processing conditions (temperature, rotor speed, screw shape), and above all, on the chemical structure of the polymer itself. For polyesters, hydrolysis (predominantly below 180 °C) and ß-H transfer (predominantly above 180 °C) are the main mechanisms.[40,41] Both lead to a reduction in molecular weight and thus to lower mechanical and rheological properties.[3,18] To overcome this reduction, a chain extender can be added. The modification does not prevent the degradation but can compensate for its effect on the molecular weight of the polymer. It is known that the torque can be increased after the addition of a certain amount of chain extender.[1,17,21,35,36] This increase can be directly related to the increase in viscosity due to the higher molecular weight of the modified polymer.[21,39,42] The slope of the increase depends on the amount and reactivity of the chain extender, the polymer itself, as well as the processing conditions.[1,17,20,35,43]

Ojijo et al.[35] used an Avrami-like equation (Equation (1)) to characterize the reaction rate constant of chain extension of Joncryl ADR4468, polylactic acid (PLA), and poly [(butylene succinate)-co-adipate] (PBSA), respectively.

$$\ln\left[-\ln\left(\Theta\right)\right] = n\ln\left(t\right) + n\ln\left(k\right) \tag{1}$$

where Θ is the consumption of the chain extender, t is the reaction time, and k is the reaction speed constant.

The starting point of the reaction in the kneading process was defined as the minimum torque ($Torque_{\mathrm{min}}$) and the maximum torque ($Torque_{\mathrm{max}}$) as the point at which the reaction reaches its equilibrium stage. Thus, the change in torque over time could be directly related to the consumption of the chain extender. Θ is the amount of fraction not yet converted (Equation (2)).[35]

$$\Theta = \frac{Torque_{max} - Torque_{time}}{Torque_{max} - Torque_{min}} \tag{2}$$

The reaction rate constant can be calculated from the double logarithmic plot of ln [− ln (Θ)] over ln(t). They found out that the reaction of Joncryl with PLA is generally faster than that with PBSA, due to the lower molecular weight of PLA used in that study. Furthermore, by using an Arrhenius plot, it was possible to calculate the activation energy E_{A} of both reactions (Equation (3)).[35]

$$k = Ae^{-\frac{E_A}{RT}} \tag{3}$$

Table 1. Molecular mass of the different PBT grades.

Polymer grade	M_w	M_n
PBT B1100	48 500	29 000
PBT B1300	62 300	31 200
PBT B1700	97 600	40 000

where A is the Arrhenius constant, R is the ideal gas constant, and T is the processing temperature in Kelvin.

Costa et al.[14] studied the chain extension of poly (butylene adipate-co-terephthalate) (PBAT) inline in a laboratory internal mixer. A relationship between the increase in shear viscosity and torque during compounding could be established. Similarly to Ojijo et al.,[35] it could be shown that the increase in torque is related to the increase in molecular weight and thus to the reaction taking place. Another finding was that the processing temperature has a huge influence on the resulting average molecular weight.[14] The higher the temperature, the higher the increase in molar mass. This temperature-molecular mass relationship was also shown for PBT by Guo and Chan.[1] This study deals with the reactive extrusion of PBT and diglycidyl tetrahydrophthalate on a corotating twin-screw extruder. A linear relationship between the required reaction time and the processing temperature was found. The higher the temperature, the faster the reaction proceeds as the viscosity of the polymer melt decreases. Also, a correlation between rotor speed and reaction rate was also found where higher shear rates increased the diffusion rate of the chain extender and thus the reaction itself.[1]

The determination of reaction kinetic quantities from the changes in torque is possible but depends on many other process parameters. Thus, when considering the reaction rate constant or activation energy, one must be aware that this quantity always refers to the overall process and not to the pure reaction.

The current study aims to describe the melt reaction of PBT with Joncryl ADR4468 and collect kinetic data depending on i) the amount of the CE, ii) the processing temperature, and iii) the initial viscosity (i.e., molecular weight). Raman spectra were used to evaluate the changes in chain architecture; therefore, typical bands (2942–2927 cm^{-1}) belonging to the aliphatic C–H-group that are created during the CE reaction were correlated with gel permeation chromatography (GPC) data. The obtained results of this study show a strong correlation with the foaming behavior of PBT from our recent works.

2. Experimental Section

2.1. Materials and Sample Preparation

PBT Pocan B1100, B1300, and B1700 with different molecular weights (**Table 1**) were purchased from Lanxess AG (Cologne, Germany). To modify the melt properties, Joncryl ADR 4468, referred to as CE, was supplied from BASF SE (Ludwigshafen, Germany). Before processing, both PBT and CE were cryo-milled and dried at 40 °C under a vacuum for 12 h.

2.2. Micro Compounder

PBT B1300 was melt mixed with up to 1 wt.-% CE on a lab-scale twin-screw micro compounder DSM15 (Xplore Instruments, Sittard, Netherlands). Experiments were carried out with 12 g of each composition at a constant screw speed of 50 rpm while the melt temperature was varied between 250 and 270 °C. Samples were taken after complete filling at reaction times between 10 and 300 s. PBT B1300 and CE were weighted separately and mixed by hand. The mixture was fed into the hopper of the compounder with rotating screws. In total, three series were made (**Table 2**).

In the first series of measurements, the melt temperature was kept constant at 250 °C and the amount of chain extender was varied between 0.25 and 1.0 wt.-%. To study the course of the reaction in more detail, the reaction time was varied; therefore, the compounding process was stopped after 10, 30, 60, and 90 s, respectively, and samples were taken. The second series of measurements was addressed to investigate possible chain degradation. Here, the reaction time was kept constant at 300 s and the reaction temperature was varied at 250, 260, and 270 °C, respectively. The third series of measurements was similar to the second series (i.e., variation of the melt temperature) but two other PBT grades that possess different molecular weights (Table 1) were used. The force at the screws was measured continuously and recorded over the reaction time. The direct recording of the torque, as it is commonly shown in many publications, is not possible due to the existing software. However, the significance of the measurement does not lose in quality, since the same force values were used in other software to calculate the torque which follows the same trends.

Prior to further characterization, all extrudates were cryo-milled (ZM300 Ultra Centrifugal Mill, Retsch, Haan, Germany) and vacuum dried for 12 h at 40 °C in an oven (VO, Memmert, Schwabach, Germany).

2.3. Spectroscopic Analysis: Fourier-Transform Infrared Spectroscopy and Raman

FT-IR spectra of the chain-extended PBT samples were recorded at room temperature in the mid-IR range (600–4000 cm^{-1}) using an FT-IR spectrometer (Thermo Fisher Scientific, Waltham, USA) equipped with a Platinum ATR accessory. Each spectrum was taken over 36 scans with a resolution of 2 cm^{-1}. The background was acquired before the measurement and subtracted from each signal. In order to compare the individual spectra, the signals were normalized to the band of the carbonyl group (1750 cm^{-1}). The results were analyzed using OPUS software (Bruker Optics).

To describe the changes in functional groups and chain architecture depending on the processing conditions, Raman analysis was carried out with a Raman spectrometer RXN-2 (Endress + Hauser AG, Switzerland, Reinach; formerly Kaiser Optics) on the cryo-milled polymer powder after the compounding. For the measurement, a non-contact optic (NCO) with a focus of 0.4 mm was used. Each sample was scanned five times with an exposure time of 300 s to ensure a sufficient spectral intensity of 75–95 %. The scanning area was from 400–4000 cm^{-1}. Spectra generation

Table 2. Overview of the micro compounder trials.

Series	Polymer grade	CE [wt%]	Temperature [°C]	Speed [rpm]	Time [s]
I	B1300	0.25/0.5/0.75/1.0	250	100	300
I.I	B1300	1.0	250	50	10/30/60/90
II	B1300	1.0	250/260/270	50	300
III	B1100/B1700	1.0	250/260/270	50	300

and manipulation were carried out with the software Peaxact 5.7 from S-Pact GmbH (Aachen, Germany).

2.4. Gel Permeation Chromatography

Molar masses and molar mass distributions were measured with GPC 1200 Infinity (Agilent Technologies, Santa Clara, USA). The setup consisted of a pre-column PFG 7 µm, a main column PFG 7 µm 300 Å (PSS, Mainz, Germany), and a refractive index (RI) detector (Gynotek SE-61). Samples of 20 µL were injected by an autosampler at a flow rate of 0.5 mL min^{-1} at 23 °C. Calibration was carried out with poly (methyl methacrylate) (PPS calibration kit, PSS, Mainz, Germany) as standard for the range of 720–189 000 Da. Hexafluoroisopropanol (HFIP, HPLC grade) with potassium trifluoroacetate (8 mg mL^{-1}) was used to dissolve the samples. Toluene (HPLC grade) was used as an internal standard at a concentration of 2 mg mL^{-1}. Samples were filtered through a 0.22-µm PTFE filter prior to injection. To process and analyze the data, the software PSS WinGPC Unity was used.

2.5. Rheological Investigation

To determine the melt viscosity of the different PBT samples, frequency and time sweep measurements using the plate-plate method was performed on an RDA3 rheometer (TA Instruments, New Castle, USA) at a temperature of 250 °C under nitrogen atmosphere on round melt pressed samples with a diameter of 25 mm. The gap size was set as 1 mm. Experiments were carried out with a strain of 10 %. The strain was determined in a previous strain sweep to ensure that all measurements were in the linear viscoelastic range. The frequency sweeps were done in a frequency range of 500 to 0.01 rad s^{-1}. Time sweep measurements were carried out at a frequency of 1 rad s^{-1} for 60 min.

3. Results and Discussion

3.1. Series I: Varied Amount of Chain Extender

In the first series, the amount of chain extender was systematically varied between 0.25 and 1.0 wt.-%. The curves of the screw force over the reaction time of the modified PBT samples are plotted in **Figure 2** and are compared with the curve of the neat PBT B1300 (black curve). The curves were recorded for 300 s to follow the effects of the CE reaction on the processing at 270 °C. The curve of the screw force of the neat material could be divided into two regimes. The first, between 0 and 60 s, corresponds to the feed and melting process of the polymer powder. After that, a slight but continuous decrease in the screw force over time can be observed. It can be assumed that this is attributed to the alignment of the chains but also to the shear-induced degradation at these elevated temperatures.[44] As suggested by Al-Itry et al.,[16] it can be expected that hydrolysis and random main chain scission might be the possible mechanisms during the melt processing already at temperatures below 180 °C. At temperatures above 180 °C, the ß-C–H hydrogen transfer mechanism dominates the random main chain scission.[16]

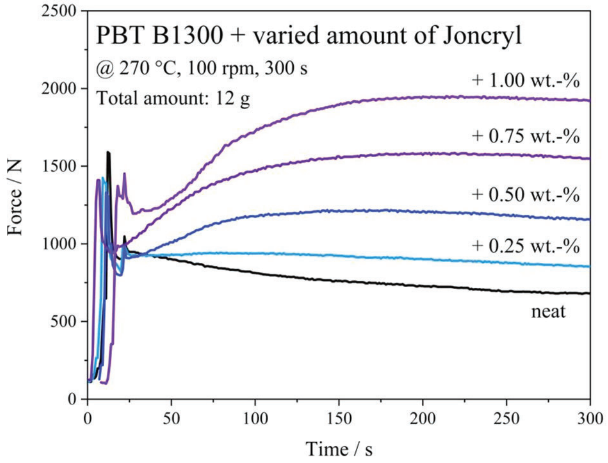

Figure 2. Screw force of the polymer melts over time of neat and modified PBT B1300.

By adding the reactive chain extender, the regime differs after the first 60 s, this phase can be attributed to the CE reaction taking place. The increased screw force is due to the increased viscosity of the polymer caused by the higher average molecular weight.[35,39,42] It should be noted that the chain extension does not prevent degradation,[18] but the reaction rate of the modification reaction exceeds that of the degradation.

This can be seen by the fact that after reaching a maximum in screw force, it slightly decreases most presumably due to chain alignment and possible cleavage of the main chain. However, this does not mean that the reaction between CE and the polymer is complete. Moreover, due to steric hindrances, the reactivity of branched polymers is significantly lower than that of linear polymers.[1,17] It is also clear that as the concentration of the chain extender increases, the screw force increases more. This can be explained by the fact that there are more reactive centers in the system, increasing the probability of a reaction. A linear relationship was found between the amount of chain extender added and the increase in screw force. In addition to the amount

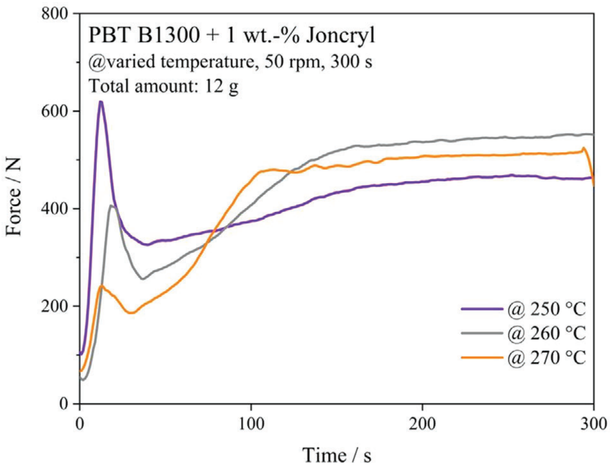

Figure 3. Screw force of the polymer melts over time of PBT B1300 + 1 wt% CE at varied temperatures.

of CE,[20,36,45] the type of polymer and CE,[35,36,45] the shear rate (rotor speed)[1,46] and the processing temperature[35] also have a major influence on the mechanism. It is well known that a reaction can only occur when the reactive centers are present. Increasing the shear rate can increase the diffusion rate of CE in the polymer.[1] Increasing the processing temperature has a similar effect.[1,14] It reduces the viscosity of the polymer and thus increases the diffusion rate. In addition, more energy is available to the system at higher temperatures which favor the CE reaction.

3.2. Series II: Varied Processing Temperature

In the following, the effect of temperature on the reaction between PBT B1300 with 1 wt.-% CE is investigated in more detail to determine the activation energy and reaction rate constant in the given system. Due to system limitations (i.e., maximum torque), the speed was reduced to 50 rpm.

In **Figure 3**, the curves of the screw force over time of PBT B1300 with 1 wt% CE at 250, 260, and 270 °C, respectively, are shown.

It can be seen in Figure 3 that the higher the reaction temperature, the lower the maximum force during feeding because the polymer melts in a shorter time and its viscosity is inversely related to temperature.[2] Thus, a higher reaction temperature results in both a higher energy input to start the reaction and a higher chain mobility. Furthermore, it could be seen that the screw force of the reaction at 250 °C increases slowly over 200 s. While at both 260 and 270 °C, the force increases significantly more over a much shorter period. The modified Avrami equation mentioned above was used to describe reaction kinetics. The slope of the linear function between 20% and 80% conversion from the ln [− ln (Θ)] over ln(t) plot (**Figure 4**) was used to calculate the reaction rate constant for the three different temperatures.

The reaction rate constant is the natural negative exponent of the division of the intercept and slope of the straight-line equation (Equation (4))

$$k = e^{-\frac{b}{m}} \tag{4}$$

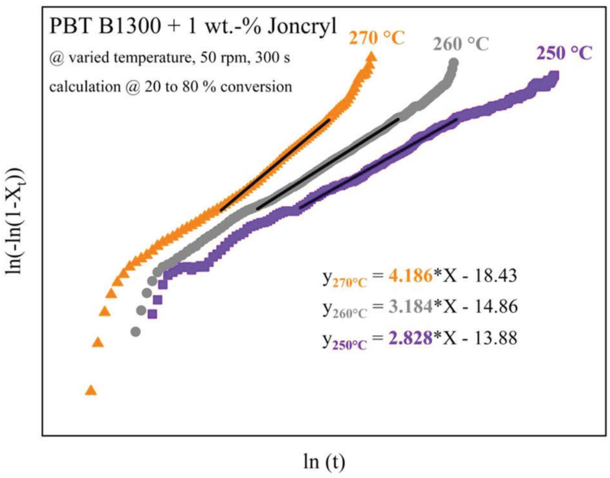

Figure 4. Modified Avrami plot of the conversion of PBT and CE at varied processing temperatures.

Table 3. Reaction rate constant of PBT and Joncryl ADR4468 at varied temperatures.

Temperature [°C]	Reaction rate constant [k min^{-1}]
250	$7.7 \times 10^{-3} \pm 1.2 \times 10^{-3}$
260	$9.9 \times 10^{-3} \pm 8.1 \times 10^{-4}$
270	$1.2 \times 10^{-2} \pm 9 \times 10^{-4}$

where k is the reaction rate constant, b is the intercept, and m is the slope of the straight-line equation.[35] The values of the reaction rate constant are given in **Table 3**. From the calculated k values, it can be seen that the higher the processing temperature, the faster the reaction. This phenomenon is already known in the literature.[35,37] Increasing the processing temperature from 250 to 260 °C results in an increase in the reaction rate constant from 7.7×10^{-3} to 9.9×10^{-3} min^{-1}, corresponding to an acceleration of 1.3 times. A further increase of 10 K to 270 °C also leads to acceleration by a factor of 1.3. According to the Arrhenius equation, the reaction rate should double if the temperature is increased by 10 K. The discrepancy between the calculated acceleration and the theoretical one could be explained by the fact that in polymer melts, the steric hindrance and viscosity are relatively high so the reaction is mainly driven by the diffusion rate of the epoxy function.[1,39,41,45]

The activation energy of the studied system was calculated using the Arrhenius equation (Equation (3)). Plotting $ln(k)$ versus $1/T$ gave a straight line from which the activation energy of the reaction could be derived. An activation energy of 52.9 kJ mol^{-1} was calculated for the PBT-CE reaction.

To better understand and follow the reaction, the experiment conducted at 250 °C was stopped after 10, 30, 60, and 90 s, respectively, and the filament obtained was ground and dried overnight at 40 °C under a vacuum. Subsequently, the molar mass (SEC) and chemical composition (FTIR) of the dried samples were investigated (**Figure 5**). From the SEC, it is evident that the mean molar mass is already shifted to higher values after 10 s reaction time (**Table 4**). Above 60 s reaction time, a shoulder is observed in the SEC. The increase in the screw force corresponds to the

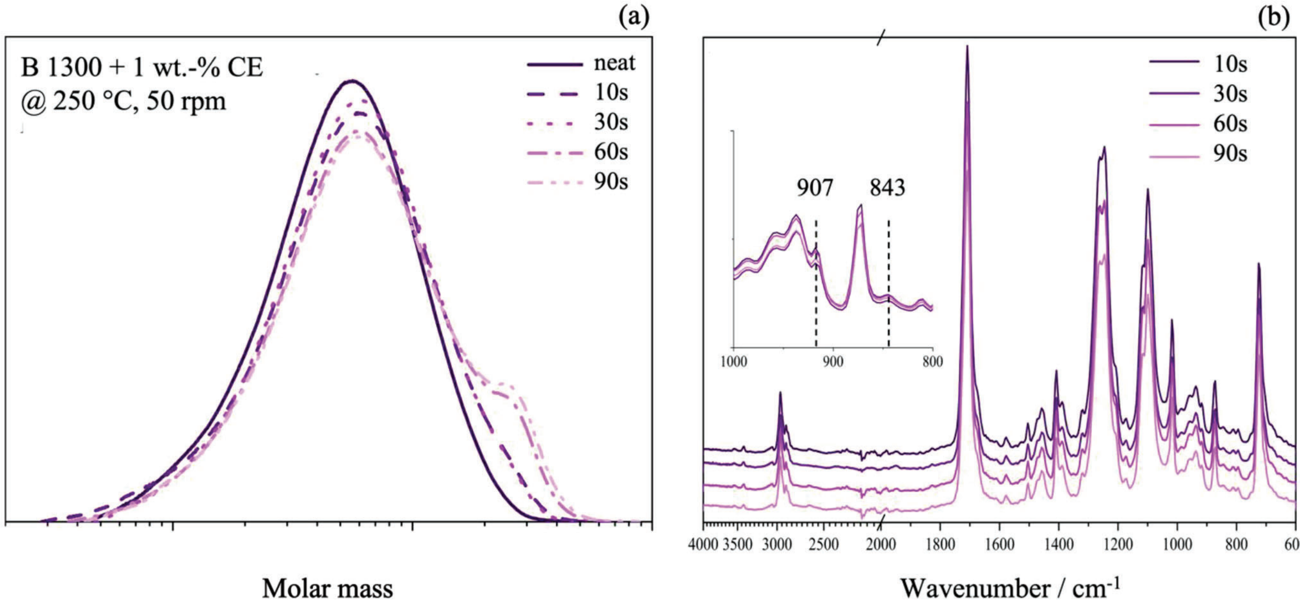

Figure 5. a) Molar mass distribution determined by SEC (eluent: HFIP, standard: PS); b) ATR-FTIR spectra of the modified PBT after varied reaction time.

Table 4. Molar Mass of PBT-CE reaction after varied reaction times.

Reaction time [s]	Molar mass (M_w)	Molar mass (M_n)	M_w/M_n
10	7.2×10^4	3.8×10^4	1.9
30	8.5×10^4	4.1×10^4	1.8
60	8.9×10^4	4.2×10^4	2
90	9.2×10^4	4.4×10^4	2

reaction taking place since a higher molar mass leads to a higher viscosity and thus to increased flow resistance.[1,29,36,39]

The FT-IR spectra (Figure 5b) provide qualitative evidence of a chemical reaction between the polymer and the CE. The reaction between the epoxide function and the hydrogen of the carboxyl group follows a ring-opening mechanism. During this reaction, an ester bond (1577 cm^{-1}) is formed between the polymer and the CE.[32,36] The FT-IR absorption of the asymmetric and symmetric ring deformation of the cyclic epoxide in CE is 843 and 907 cm^{-1}, respectively.[2,35] These two IR absorptions should decrease during the reaction, while the IR absorption of the ester bond should increase. A slight decrease in the intensity of IR absorption of both epoxides is observed during the first 90 s of the reaction.

To confirm the finding of FT-IR, RAMAN spectroscopy was also performed with these samples. From the model constructed based on the spectra of the pure materials, PBT B1300 and CE, respectively, it was found that the ester linkage (2942–2927 cm^{-1}) between the chain extender and the polymer increases over time (**Figure 6**). From the change in signal area over time, the average molecular weight could be calculated using the model of the company S-Pact (Aachen, Germany). The calculation is in approximate agreement with the data obtained from the GPC measurement. Thus, the increase in screw force over time can be clearly attributed to the change in molecular weight.

3.3. Series III: Influence of the Molecular Weight

In a further step, this procedure was applied to two other PBT grades with lower and higher molecular weight, that is, one with a lower shear viscosity, PBT B1100, and one with a higher one, PBT B1700. This allowed us to study the influence of viscosity on reaction kinetics in more detail. **Figure 7** shows the curves of screw force versus time for the three different polymers with 1 wt% CE at 260 °C. It can be seen that the higher the molecular weight and thus the initial viscosity, the steeper the curves during the reaction.

The shear viscosity before and after chain extension, the reaction rate constant, and the activation energy are listed in **Table 5**.

The activation energies of the three different polymers were calculated using the Arrhenius equation, as mentioned earlier. For PBT B1100, an activation energy of 19.2 kJ mol^{-1} was determined. The activation energy of PBT B1700 could not be determined correctly at temperatures above 260 °C. Furthermore, it was found that only PBT B1700 exhibits significant shear-induced degradation, similar as described in previous work,[11] during the period studied. The lower activation energy of PBT B1100 compared to PBT B1300 can be attributed to the viscosity of the neat materials. The shear viscosity of PBT B1300 measured under oscillation at 250 °C is 1.7 times higher than that of PBT B1100. Thus, the diffusion rate of the epoxy function in PBT B1100 is higher than in PBT B1300. On the other hand, the viscosity of PBT B1300 increases 24-fold from 117 to 2830 Pa s, while the viscosity of PBT B1100 increases ninefold from 70 to 625 Pa s. Thus, the change in viscosity of PBT B1300 is much greater than that of PBT B1100. This phenomenon can be attributed to

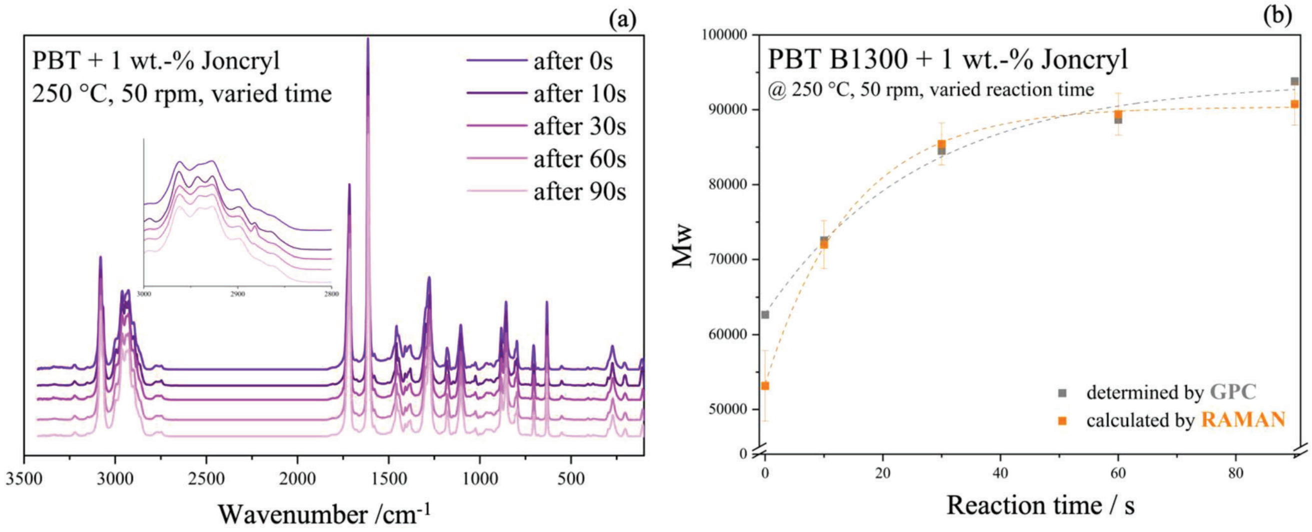

Figure 6. a) RAMAN spectra of the modified PBT after varied reaction time; b) Comparison of molar weight determined by SEC (eluent: HFIP, standard: PS) and calculation by RAMAN spectra.

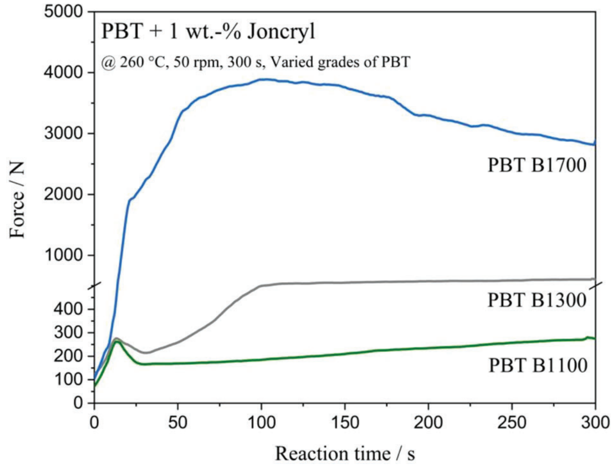

Figure 7. Screw force of the polymer melts over time of varied PBT grades + 1 wt% CE at 260 °C.

Table 5. Viscosity and kinetic data of the different PBT grades.

	η_{neat} [a] [Pa s]	$\eta_{modified\ @\ 260°C}$ [a] [Pa s]	k 10^{-3} [min^{-1}]	E_A [kJ mol^{-1}]
PBT B1100	77 ± 7	625 ± 119	$5.5 \pm 4.6 \times 10^{-1}$	19.2 ± 2.9
PBT B1300	117 ± 11	2830 ± 386	$9.9 \pm 8.1 \times 10^{-1}$	52.9 ± 4
PBT B1700	603 ± 78	12 320 ± 584	$19 \pm 8.7 \times 10^{-1}$	–

[a] Viscosity at 250 °C, 0.5 s^{-1}, 10 % strain.

the fact that the reaction rate constant of PBT B1300 is higher than that of PBT B1100. The higher the viscosity, the higher the shear stresses generated and thus the higher the forced diffusion rate of the epoxy function.[37,47]

It could be shown that the viscosity of the neat polymer has a great influence on the activation energy and the reaction rate constant. The higher the viscosity, the more energy is required to start the reaction. At the same time, the reaction rate constant increases with viscosity, which is due to the increased shear stresses, as can be seen in Figure 7. PBT B1700 has the highest reaction rate constant at 260 °C of all the polymer grades studied. However, due to the viscosity, the shear forces are so high that shear-induced degradation occurs predominantly within the time period studied. This can also be seen from the increase in viscosity. This increases from 603 to 12 320 Pa s, which corresponds to an increase by a factor of 20 for PBT B1700. Whereas PBT B1300, which has a medium viscosity, is a promising material for the CE reaction because it has both a relatively low activation energy and a sufficiently high reaction rate constant. This is proven by the fact that the viscosity of PBT B1300 increased 24-fold, which was the largest increase we saw in this study.

3.4. Change in Viscosity and Foam Structures

Viscosity also has a significant effect on foam morphology, as already shown in earlier works.[11,15,48] The bead foams were produced as described in our previous study via a tandem foam extrusion line coupled on an underwater granulator using CO_2 as a blowing agent.[11] The influence of molecular weight and varied viscosity based on different chain architectures on foam density, cell density, and morphology was investigated. It was found that low to medium molecular weight leads to weak rheological properties, especially low melt strength. Therefore, the cells in the foamed beads tend to coalesce, as shown in **Figure 8**A,B. Similar behavior of pure PBT B1300 was also noted and discussed before in ref. [11] (Figure 8B). PBT B1700 already has a higher viscosity than PBT B1100 and PBT B1300, as discussed previously. Therefore, the polymer exhibits higher expansion resistance and could thus prevent cell coalescence. On the other hand, a bead density of 335 ± 4 kg m^{-3} was found.[48]

The use of chain extenders would increase the viscosity due to the chemical reaction. For the modified PBT B1300, a homogeneous cell structure was found, with an average cell size of 155 ± 37 μm and a bead density of 179 ± 2 kg m^{-3}.[11] This could

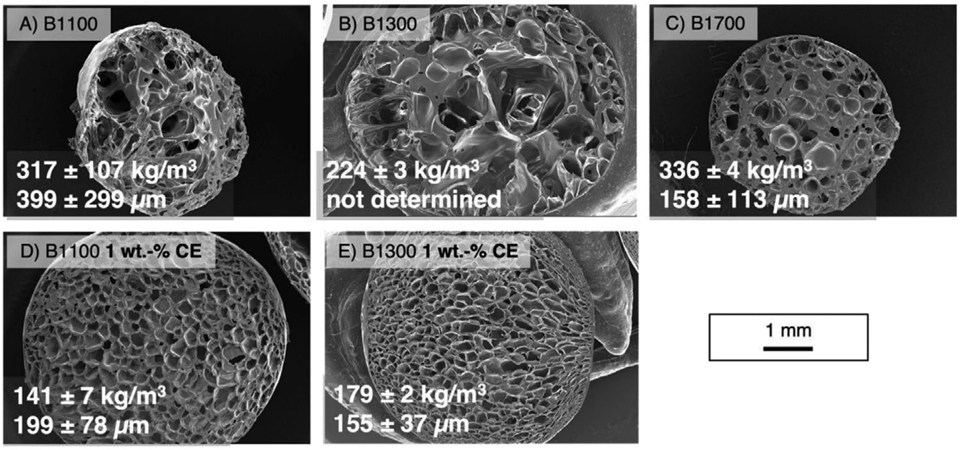

Figure 8. Foam morphologies of PBT foamed beads with and without CE. A) B1100 and C) B1700. B) B1300 and E) B1300 1 wt% CE. (A,C) Reproduced with permission.[48] Copyright 2022, American Chemical Society. (B,E) Reproduced with permission.[11] Copyright 2018, American Chemical Society.

be due to the fact that the viscosity of the polymer increased significantly, as we have already shown. Furthermore, it was shown that the elongation of the polymer increased since tangles can occur due to the long-chain branching and result in strain hardening behavior which is absent in linear PBT.[11] For the PBT B1100, we also observed an improvement in foamability. The chemical modification increased the viscosity by nine times, resulting in a bead density of 141 ± 7 kg m^{-3} and an average cell size of 199 ± 79 µm. The difference in density and cell size is due to PBT B1300 having a higher reactivity with CE than PBT B1100. This leads to a significantly higher increase in viscosity, and as already explained in refs. [11, 48], the rheological properties are crucial for foam formation.

4. Conclusion

The flow behavior of PBT can be improved by reactive extrusion with Joncryl ADR4468. A linear relationship was found between the screw force and the amount of CE added due to the ongoing reaction. An activation energy of 52.9 kJ mol^{-1} was determined for the PBT B1300-CE reaction between 250 and 270 °C at a rotor speed of 50 rpm. It was also shown that the reaction rate increased from 7.7×10^{-3}/min to 1.2×10^{-2}/min when the processing temperature was increased from 250 to 270 °C. For the first time, Raman spectroscopy was used to follow the reaction between the polymer and the CE over time. The predicted molar masses could be correlated with GPC. The influence of molecular weight, that is, initial viscosity, was analyzed by comparing three different PBT grades. It was shown that the lower the initial viscosity, the lower the activation energy E_A. On the other hand, the reaction rate constant k also correlates with the viscosity. The higher the initial viscosity, the higher the reaction rate constant. This can be attributed to the increased diffusion due to the increase in shear. For PBT B1100 and PBT B1300, a reaction rate constant of 5.5×10^{-3}/min and 9.9×10^{-3}/min, respectively, was determined at 260 °C. An increase in the viscosity of PBT B1100 and PBT B1300 by 9 and 24 times, respectively, was observed under oscillated shear at 250 °C. This increase in viscosity also affected the foamability of these two polymers. As shown, a homogeneous cell structure could be achieved after the reactive modification.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

chain extenders, micro compounders, poly (butylene terephthalate), reaction kinetics, reactive extrusion

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