Supercritical Fluid Extraction of Cyclic Oligomers from Depolymerizing PBT

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ABSTRACT: Cyclic oligomers of polyester show great potential for a reaction-injection-molding process, because of their initial low viscosity and rapid ring-opening polymerization at low temperatures (180°C) without exothermic reaction or condensates. In this work, we report the synthesis of cyclic oligo(butylene terephthalate) (COBT) from linear poly(butylene terephthalate) by a formation–extraction process employing supercritical fluids (SCF) CO_2 and pentane at $T = 230°C$ and $P = 250$ bar. Following this, depressurization of SCF leads to easy recovery of the COBTs. When compared with SCF CO_2, SCF pentane is found to be an attractive solvent because of its higher solubilizing capacity (0.8 mg COBT dimer/g pentane) for the COBTs. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4487–4492, 2006

Key words: polyesters; cyclic oligomers; ring-opening polymerization; recycling

INTRODUCTION

Poly(butylene terephthalate) (PBT) is one of the most important man-made polymers with applications as an engineering thermoplastic such as for molded electrical and automotive components and power tool casings. During its formation by melt polymerization, cyclic oligo(butylene terephthalate) (COBT) oligomers are also generated and are equilibrium components along with linear PBT.[1–3] When compared with PBT or its monomers, the COBTs show great potential for reaction-injection-molding (RIM), because of their initial low viscosity and rapid ring-opening polymerization at low temperatures (180°C) without exothermic reaction or condensates.[4] COBTs can be produced by the following routes. The first is the production from an acid chloride and a glycol in a dilute solution of dichloromethane.[5] An amine is added to promote the reaction. The use of these (expensive) reactants and the formation of HCl are considered undesirable. Cyclic oligomers can also be produced by cyclization from dilute solutions of linear oligomers or polymers.[6–19] Extraction of cyclic oligomers from solid PBT, for example by Soxhlet extraction with chloroform, 1,4-dioxane, toluene, or xylene has also been described.[20–22] Similarly supercritical fluid CO_2 has been employed, though primarily with the objective of chromatographic determination of cyclics content.[23,24] These extractions are limited to the extent of the equilibrium concentration of the cyclics (less than 3 wt %) in PBT, since cyclics are not continuously formed below T_m. Burch et al.[25] recently found that molten PET droplets suspended (5 wt %) in hexadecane at 287°C could be depolymerized to the extent of 30% into hexadecane soluble cyclic oligo(ethylene terephthalate) (COET). They proposed complete conversion of PET to COET by repeatedly replacing the rapidly equilibrating oligomer solution with fresh solvent. Similar attempts of cyclics preparation with dichloromethane or toluene at high pressures have been unsuccessful, and use of supercritical fluids (SCF) has been mooted.[25,26]

Efficient extraction processes are one of the most important parts in many industrial processes. In the past few decades, SCF extraction (SFE) has become an increasingly attractive alternative to conventional separation methods.[27] This trend is probably best attributed to the properties of SCF CO_2 such as nontoxicity, chemical stability, low cost, and perhaps the most important characteristic that the solubility power is strongly influenced by density that can be regulated by changes in pressure and temperature. For example, the extracted material can be recovered from the extract phase by depressurization. Besides CO_2, pentane is also used for SFE, for example, extraction of oil from used automotive tire samples.[28]

We here describe simultaneous cyclics production and extraction from molten PBT in a semi-batch fashion, using continuous flow of SCF solvents such as CO_2 and pentane (Scheme 1). When compared with the previous reports on SFE at temperatures (T) lower than the melting point (T_m),[20–22] the advantage of

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performing this extraction at T close to or greater than T_m is that the COBTs can be continuously produced *in situ* while these are being extracted. Thus, a high conversion of PBT to COBTs can provide the additional potential of recycling waste PBT. When compared with the process of Burch et al., involving extraction with hexadecane that requires solvent removal from the precipitate using hexane, the use of low boiling CO_2 and pentane by us provides easy separation of the COBT product.

During the extraction process, the amount of cyclic dimer extracted out of the PBT melt was conveniently quantified by ^{1}H-NMR, giving a good indication of the overall COBT's extraction efficiency of the system.

EXPERIMENTAL

Materials

Chloroform (99.9%), pentane (98.5%), acetone (99.8%), *o*-chlorobenzene (99%), 1,1,2,2-tetrachloroethane (97%), 1,4-butanediol (99%), dioxane (99.8%), diphenyl ether (98%), biphenyl (99%), methyl ethyl ketone (99.5%), and deuterated chloroform $CDCl_3$ (99.8%, 0.03 vol % TMS) were supplied by Sigma–Aldrich, and used without further purification. Carbon dioxide (99.995% purity) was supplied by Hoek Loos and used as received. PBT-195 and the cyclic oligo(butylene terephthalate) (COBT) mixture were supplied by GE Plastics (Bergen op Zoom, Netherlands). This COBT mixture was determined to contain 51% dimer, 49% higher cyclics by ^{1}H-NMR.

Extraction process

A 65 mL stainless steel autoclave (New Ways of Analytics, Germany) equipped with a magnetically coupled stirrer, electrical heating, and a pressure and temperature probe was used as the extraction vessel (Fig. 1). The pressure was measured with a high-pressure flush diaphragm transmitter (Omega) with an accuracy of ±1 bar. Temperature was measured with a NiCr–Ni standard measuring probe "Type K" Class 1 with an accuracy of ±1 K. Air-driven pump (Maximator, Germany) in combination with the cooling system for CO_2 (New Ways of Analytics, Germany) was used to pressurize CO_2, and is capable of maintaining the autoclave pressure at a set value (±5 bar). A Gilson 305 piston pump was used to pressurize and deliver pentane or cosolvent at the desired flow rate.

$$\text{linear PBT}_{\text{melt}} \leftrightarrow \text{COBT}_{\text{melt}} \rightarrow \text{COBT}_{(\text{SCF/vapor})} \uparrow$$

Scheme 1 The production and extraction of COBTs from PBT. Experiments are carried out by flowing a stream of the SCF at the desired temperature (230°C) and pressure (250 bar) through the stirred PBT melt, and depressurizing of the outgoing stream to recover the extract.

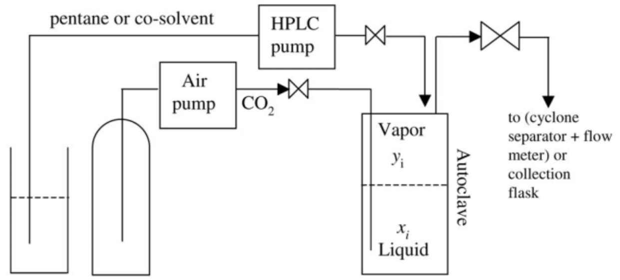

Figure 1 Schematic diagram of the extraction process.

Poly(butylene terephthalate) (PBT, or the COBT mixture) sample was placed in the autoclave at room temperature. The autoclave was closed and purged with the SCF for 5 min. The outlet valve was closed, the autoclave heated to the desired temperature, and pressurized with the fluid to 250 bar. The liquid and the vapor phases of the system were allowed to mix for 10 min while stirring (at 200 rpm, unless otherwise mentioned). The outlet valve was opened to release the vapor phase (~2 g/min) while the pump provided fresh fluid. In case of SCF CO_2, the air pump automatically maintained the autoclave pressure at 250 bar, as an outlet from the vapor phase of the autoclave was led to a high-pressure cyclone separator (Thar Designs Inc. 25 mL Cyclone) and then through a flow meter to measure the flow rate. In case of SCF pentane, liquid pentane was fed at the desired rate by the piston pump, and the outgoing fluid was led through a valve, thus condensing the liquid which was collected in a bottle. The extract precipitates in the bottle, and the solvent was slowly evaporated to leave the extract as residue. The extract was dissolved in $CDCl_3$, and analyzed by ^{1}H-NMR spectra on a Brüker 300 MHz spectrometer at 25°C. The molar amount of COBT dimer was quantified from known amount of an externally added standard 1,1,2,2-tetrachloroethane (TCE), and the ratio of the peak area at the following characteristics chemical shifts: COBT dimer ($\delta = 7.87$ ppm, *s*, 8H), TCE ($\delta = 5.91$ ppm, *s*, 2H).

Determination of the rate-limiting step during formation–extraction

To determine whether there is depletion of COBT content in PBT with extraction, the equilibrium concentration of the cyclic dimer in PBT in contact with SCF was first determined by ^{1}H-NMR. PBT (1 g) was placed in the autoclave and heated for 2 h at $T = 230$°C and 250 bar SCF pressure to equilibrate without flow of SCF. Following this, the autoclave was quickly depressurized to freeze the formation–extraction equilibrium, and a sample of the PBT in the autoclave was analyzed by ^{1}H-NMR for the mole ratio COBT dimer to the rest of the aromatics. In another similar experiment with 1 g PBT, but immediately after flowing SCF (at 8 g/min for CO_2 case, 2.5 g/min for pentane case) for the desired time (9 h for CO_2 case, 4 h for pentane case) at $T = 230$°C and 250 bar, the autoclave was rapidly depressurized. ^{1}H-NMR analysis was performed on the PBT phase sample to examine the COBT content during extraction.

Evaluation of polymerization potential of COBTs in pentane

COBT mixture (30 mg) was placed in the autoclave (see previous section), and pentane (50 mL) was added. The temperature was raised to the desired temperature. Extraction was carried out by flowing pentane (previous section) at a flow rate of 2.5 g/min for 15 min while maintaining 230°C and 250 bar pressure. The autoclave was depressurized and the residual dimer content was examined by ^{1}H-NMR.

RESULTS AND DISCUSSION

As discussed by Bartle et al.,[29,30] a SFE process may be controlled by mass transfer of the solute to matrix–solvent interface, or by the solubility of the solute in the solvent. In addition, the extraction rate increases with the concentration of the solute in the matrix. When the solute is being formed in the PBT phase simultaneously with its extraction (Scheme 1), the rate of its production can also control the overall extraction rate. For example, the reaction time to the equilibrium concentration of COBTs was reported to be 2 h for PET at 265°C under vacuum.[2] An analysis of these factors is of paramount importance in designing an efficient process. This is carried out here by analyzing the effect of varying the stirring rate, solvent to PBT ratio and the solvent flow rate during a semi-batch SFE process.

The extract may contain linear oligomers in addition to the cyclics, and we characterize the COBT dimer by ^{1}H-NMR. We concentrate on monitoring the amount of the COBT dimer, since the aromatic hydrogen of the COBT dimer appears at $\delta = 7.87$ ppm, sufficiently isolated from $\delta = 8.07$ ppm (and higher peaks) for both the higher CBT and the linear PBT. A known amount of the standard TCE ($\delta = 5.91$ ppm, s, 2 H) is added to the extract before carrying out ^{1}H-NMR analysis, to enable quantification of the extracted COBT dimer. The quantification of the COBT dimer in the PBT phase samples, and also in the extract, is expressed as the mole ratio D of the repeat units in COBT dimer to the aromatics repeat units. Hence, D is determined as the ratio of the $\delta = 7.87$ ppm and higher peak area to the $\delta = 8.07$ ppm peak area in the ^{1}H-NMR spectra.

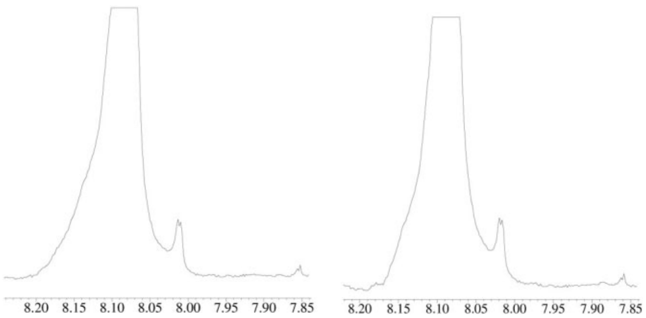

Figure 2 ^{1}H-NMR of PBT samples after (a) equilibration in the absence of CO_2 for 2 h and (b) SFE for 9 h with CO_2 flow.

SFE with CO_2

Formation of COBTs

If the extraction process during a simultaneous cyclics formation–extraction process is very efficient (Scheme 1), then the formation of COBTs can be the rate limiting step. If so, the concentration of the COBT in the polymer melt during continuous formation–extraction would decrease from the original equilibrium concentration. This possibility was examined through ^{1}H-NMR analysis of the following two PBT samples: (a) after allowing the PBT to equilibrate with nonflowing SCF CO_2 at $T = 230$°C and $P = 250$ bar, and (b) after SFE from the PBT with SCF CO_2 for 9 h at the same T and P (section 2.3). The corresponding values of D were found to be 0.002 in both cases (Fig. 2), and indicate that the equilibrium molar concentration of dimer is 0.2%, which does not deplete during the formation–extraction experiments reported here. Thus, the formation of COBTs is not the rate controlling step at the SFE conditions employed here.

Extraction from PBT above T_m

Table I shows the results of the simultaneous formation–extraction (see Extraction Process) with SCF CO_2 from PBT at $T > T_m$ of PBT.

When the SKF CO_2 flow rate is increased by a factor of 5.5 (Table I), the extraction efficiency (COBT dimer content in SCF CO_2) remains unchanged. If mass transfer of COBTs from the polymer melt to the SCF were rate limiting, then increasing its flow rate through the PBT melt would have resulted in a decreasing concentration of dimer in the outgoing fluid. Thus, it appears that at the given operating conditions, the cyclics production rate or the solubility of COBTs in CO_2 is the rate limiting factor. Since results of the previous section pointed to absence of a critical role of cyclics production, we conclude that the extraction rate was determined by solubility, that is the limited partitioning of the cyclics to the vapor phase in presence of the PBT melt phase. This points to a possible

TABLE I
Formation–Extraction from 10 g PBT with SCF CO_2 at 230°C, 250 bar for 150 min

Flow rate (g/min)	Extracted dimer (mg)	COBT dimer (mg/g CO_2)
1.3	1.3	0.007
7.2	7.1	0.007

role of cosolvents to enhance the efficiency of cyclics extraction to the vapor phase.

Use of cosolvents for formation–extraction with SCF CO_2

Often small quantities of a cosolvent are used in combination with SCFs. Known cosolvents in combination with supercritical CO_2 are for example acetone,[31] methanol,[32] hexane, and aniline.[33,34] A cosolvent can greatly enhance the efficiency of the extraction process,[35] for example, due to increase in the interaction, or the interaction between the cosolvents and the solute.[36–38] We carried out experiments with several modifiers (Table II) to increase the solvating power of CO_2. Several premixed mobile phases were tested during the formation–extraction of COBTs out of molten PBT, and the results are shown in Table II. Addition of cosolvent helped to increase the extraction efficiency when compared with SCF CO_2 alone. This could be related either to the increased mobility of the cyclics due to additional swelling of PBT by the modifier, or due to enhanced solubility of the cyclics in the modified SCF phase. However, the absolute values are small, thus requiring high solvent consumption.

The most efficient of the cosolvents considered in Table II is *o*-chlorobenzene. Considering its environmental hazard, we decided to try the next best cosolvent from the table, pentane, as a single SCF solvent for cyclics extraction.

SFE with pentane

Production of COBTs

The limitations imposed by cyclics production were evaluated in a manner similar to that employed for SCF CO_2 (discussed earlier). ^{1}H-NMR analysis of the following two PBT samples were examined (a) after equilibrating with pentane at $T = 230°C$ and $P = 250$ bar in the closed system, and (b) after SFE with pentane for 4 h at the same T and P (Fig. 3). The corresponding values of D were found to be 0.002 before and after extraction, indicating that the equilibrium molar concentration of dimer is 0.2%, which does not deplete during the formation–extraction experiments reported here. Thus, the cyclics production is not the rate-controlling step at the SFE conditions employed here.

TABLE II
Cosolvent (1 mol %) Influence on Formation–Extraction out of PBT (10 g) with SCF CO_2 at 230°C, 250 bar

Cosolvent	COBT dimer (mg/g CO_2)
None (CO_2 alone)	0.007
Dowtherm	0.013
o-Chlorobenzene	0.017
Methyl ethyl ketone	0.012
Dichloromethane	0.014
Acetone	0.014
Pentane	0.015

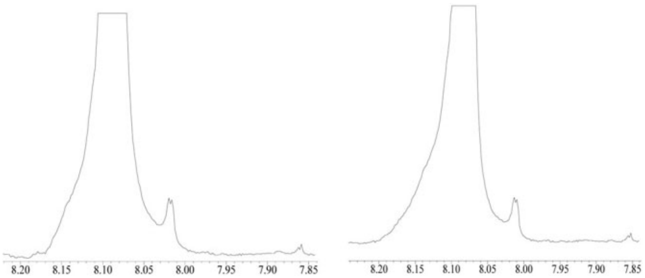

Figure 3 Fractional concentration ($D = 0.002$) of dimer ($\delta = 7.86$ ppm) after equilibration and after extraction for 4 h.

Polymerization potential of COBTs in pentane

The COBTs could possibly polymerize back to high molecular weight polymer when dissolved in pentane at the high temperature employed in our formation–extraction process. To determine whether this occurs, a COBT mixture (30 mg) in the autoclave was extracted with flowing pentane (2.5 g/min) at 230°C and 250 bar (discussed earlier). The entire COBTs content could be recovered with the outgoing pentane within 7.5 min. ^{1}H-NMR spectra of the extracted product was identical to that of the starting COBTs (Fig. 4), suggesting no change in fractional amounts of the constituents COBT dimers and higher cyclics/polymers. The so-indicated absence of polymerization is most likely a result of high dilution in pentane, even though bulk oligomers are known to polymerize at much lower temperature, such as 180°C.[3]

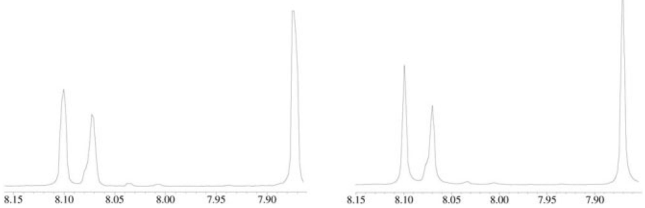

Figure 4 ^{1}H-NMR spectrum of COBTs before and after extraction pentane.

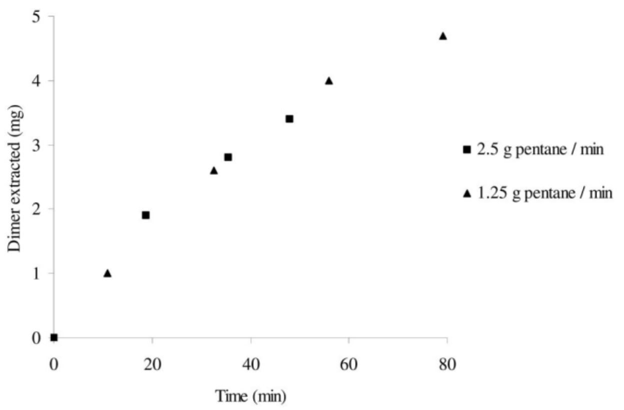

Figure 5 The influence of the pentane flow rate on the rate of extraction, $P = 250$ bar, $T = 230°C$, PBT = 1 g, stirring rate = 200 rpm.

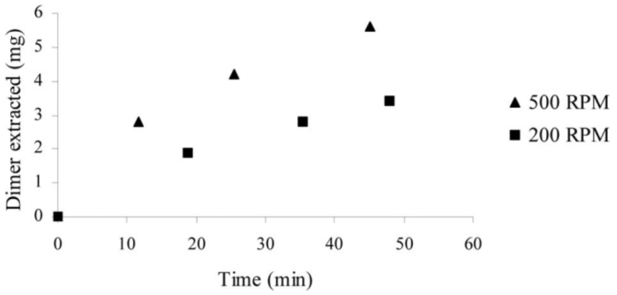

Figure 6 The influence of the stirring rate (shown on the plot) rate on dimer extraction from 1 g PBT in the autoclave at 230°C and 250 bar, with SCF pentane flowing at 2.5 g/min.

Solubility of COBTs in pentane

Similar to the experiments described in "Extraction from PBT above T_m" with SCF CO_2 extraction from PBT, COBT extraction experiments were carried out using pentane at two different flow rates through the autoclave containing PBT (1 g) at $T = 230°C$ and $P = 250$ bar. Figure 5 shows that the dimer extraction rate to be independent of the pentane flow rate, suggesting that solubility of COBTs in SCF pentane is not limiting the former's extraction rate. If solubility were limiting the overall formation–extraction process, the apparent extraction rate would have increased with increasing flow rate.

Though the equilibrium amount of dimer in the polymer melt is 0.2 wt % (see Production of COBTs), its extraction to the higher extent (~0.5 wt %) suggests that COBTs are produced from PBT in the autoclave while they are being extracted with the flowing SCF pentane.

To determine the maximum COBTs solubilizing capacity of SCF pentane, the autoclave was charged with a larger quantity of PBT (5 g), heated to 230°C, pressurized with pentane to 250 bar, and stirred for 8 h. When a small sample out of the SCF pentane phase (3 g) was withdrawn, the dimer concentration therein was found to be 0.8 mg dimer/g pentane. When compared with the COBT dimer solubility in CO_2 as the extraction solvent, the COBT dimer solubility in pentane is thus two orders of magnitude higher. The solubility could possibly further be enhanced by applying higher pressures, since solubility power is strongly influenced by density.

Mass transfer limitation to cyclics extraction with pentane

The results of the preceding section indicate the absence of limitations due to cyclics formation (see Production of COBTs) and solubility (see Solubility of COBTs in Pentane) on the overall formation–extraction process from molten PBT at the experiment conditions employed by us. We therefore studied the possible role of mass transfer limitation, by examining the influence of stirring rate. The effect of stirring rate on the COBT dimer extraction is shown in Figure 6. Clearly, the extraction rate increased with increasing stirring speed, indicating that mass transfer rate from molten PBT to SCF pentane phase is indeed the rate limiting step.

The increased rate of mass transfer at higher stirring speed can most likely be attributed to the enhancement in the melt–SCF interfacial area at the higher stirring speed. If that be the case, an additional route to enhancing the extraction efficiency could be through increased PBT melt amount. When the extraction was carried out with 10 g PBT versus 1 g PBT melt, the rate of extraction increased approximately by a factor of 4–5 (Fig. 7), thus again indicating the role of interfacial area in enhancing the mass transfer rate. While basing the cyclics extraction rate on the extracting fluid, we arrive at a value of 0.8 mg dimer/g

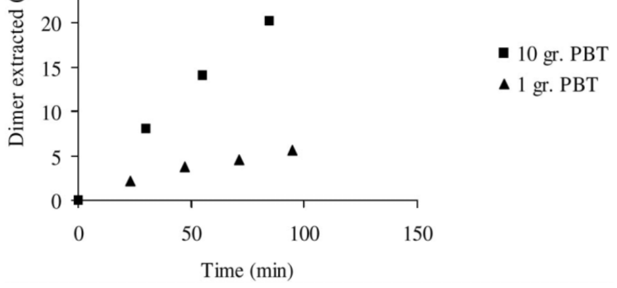

Figure 7 The influence of PBT amount (shown on the plot) on dimer extraction in the autoclave at 230°C and 250 bar, with SCF pentane flowing at 1.25 g/min, while stirring at 200 rpm.

pentane, which is close to the solubility limit (see Solubility of COBTs in Pentane).

When compared with the process of Burch et al., involving extraction with hexadecane that requires solvent removal from the precipitate using hexane, the low boiling CO_2 and pentane used by us provides easy separation of the COBT product because of their low boiling points. An advantage of the extraction process with the SCF pentane is that COBTs precipitates out of pentane upon cooling, allowing for easy separation and recycling. The disadvantages of the extraction process are the long extraction time, high pressures, and large amounts of solvent needed to be recycled.

CONCLUSIONS

CO_2 and pentane were examined as potential solvents for the formation extraction of COBTs out of PBT at $T = 230°C$ and $P = 250$ bar. Precipitation of the COBTs from SCF on depressurization allows easy recovery of the extracted product. ^{1}H-NMR proved to be a good method to quantify the extracted COBTs. Extraction with SCF CO_2 was severely limited by the poor solubility of the COBTs in CO_2 (0.007 mg dimer/g CO_2). Use of cosolvents allowed moderate increase in the solubility and hence extraction efficiency with SCF CO_2.

SCF pentane is found to be a more attractive solvent for formation–extraction route because of its higher solubilizing capacity for the COBTs. A solvent efficiency of 0.8 mg dimer/g pentane could be achieved during the extraction. This was achieved by identification of the mass transfer step as the critical rate limiting step, and then increasing the mass transfer rate through higher stirring rate and increased amount of PBT melt in the autoclave. However, high pressures, long extraction times, and large amounts of solvent are needed.

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