Modification of rheological properties of a thermotropic liquid crystalline polymer by melt-state reactive processing

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ABSTRACT

Thermotropic main-chain liquid crystalline polymers typically have very low melt viscosity with strong temperature dependence compared to other common thermoplastics. While this is beneficial in some processing applications, such as injection molding, it presents challenges for others, such as coextrusion. In this study, the rheological properties of a thermotropic main-chain liquid crystalline polymer (Vectra A950) were enhanced by melt-state reactive processing with triphenyl phosphite (TPP), which can react with up to three polymer chain-ends through their chain-end functionalities. The influence of processing time and TPP content on the shear viscosity and other important material properties were investigated. Optimal conditions, which increased the shear viscosity by nearly a factor of 20 over the neat polymer, were found to be 4 wt% TPP and 30 min of reaction time at 290 °C. Further results from differential scanning calorimetry, wide-angle X-ray diffraction and polarized optical microscopy confirmed that coupling with TPP did not affect the microstructure, melting/crystallization behavior or liquid crystallinity. The stability of TPP-modified samples was also studied at 80 °C in air and following melt reprocessing at 290–300 °C under N2 or air. Samples were stable (as measured by shear viscosity) for more than one month at 80 °C in air or when reprocessed in N2 at 290 °C for up to 10 min. However, when reprocessed at 300 °C in air, the viscosity enhancement was partially reversed due to scission of P–O bonds that were formed during the initial reaction between the polymer chain-ends and TPP.

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1. Introduction

Liquid crystalline polymers (LCPs) are very attractive high performance materials due to their excellent mechanical, optical, and transport properties [1,2]. As a result, LCPs have been successfully developed as ultra high strength fibers. One of the most famous examples is Kevlar (p-phenylene terephthalamide), whose tensile modulus is in the range of 9–17 Mpsi, while traditional commercial polymer fibers like nylon and PET are only about 0.9 and 1.8 Mpsi, respectively [1]. If crosslinks are introduced, the liquid crystalline networks can display remarkable elastic properties due to the transition from a polydomain to a monodomain structure [3]. Recent studies have found that these LCP networks can be used as shape memory materials through hydrogen bonding or light activation [3,4]. Recent research has also shown that sidechain LCPs can be easier to process, due to their solubility in common solvents, while exhibiting interesting optical properties by their self-assembly leading to potential applications in display devices [5].

Besides their mechanical and optical properties, LCPs have very attractive gas and liquid transport characteristics. Paul and coworkers [6–8] have found that LCPs possess up to 1000 times lower gas permeability than many other conventional polymers, which has been attributed to low gas solubility and diffusivity in these materials afforded by the low free volume of LCPs. Due to their combined barrier properties and extraordinary chemical resistance, LCPs could potentially be widely used in high performance membrane and packaging applications.

Main-chain LCPs commonly have low melt viscosities, which can be beneficial for some melt processes such as injection molding. However, this feature is still a significant challenge in the application of LCPs in many areas. For instance, it is desirable to prepare membranes, packaging film and other devices containing LCPs through multilayer coextrusion [9]. Multilayer coextrusion of two or more polymer layers can be performed most effectively when the melt flow characteristics (i.e., viscosities, elasticities, etc.) of the layer components are closely matched, a similar situation to
that required for the formation of well-dispersed polymer blends [10,11]. However, the viscosities of LCPs are difficult to match to conventional film materials in temperature ranges where conventional polymers do not degrade.

One approach for enhancing the melt viscosities of LCPs is to form composites, especially with short fibers and other inorganic fillers [12–14]. King and coworkers [12] studied the rheological properties of carbon fillers (e.g., graphite, carbon black and carbon fiber) with Vectra A950RX composites and showed that both carbon black fillers and carbon fibers can significantly increase the viscosity. Other kinds of fibers, such as glass fibers, have also been employed to modify the mechanical properties of LCPs [13]. Although forming composites can improve the rheological and mechanical properties of LCPs, the presence of fillers can affect the unique properties of the LCP on macroscopic and microscopic length scales [13,15]. Addition of micro-scale fillers can also affect optical clarity. Since many applications of LCPs are highly dependent on their unique liquid crystal structures, a method which can modify the rheological properties without affecting the intrinsic micro- or macro-scale structures or optical clarity, would be very attractive.

Previously, triphenyl phosphite (TPP) has been added during melt processing of polyamides and polyesters to increase their molecular weight (MW) and viscosity [16,17]. The associated reaction mechanism has been studied by Aharoni et al. [18,19] and Jacques et al. [20,21]. As shown in Fig. 1, TPP can react with polymer end functionalities, such as hydroxyl and carboxyl groups, which result in the coupling of polymer chains and an associated increase of the molecular weight and melt viscosity. A series of studies on the reactions induced by TPP during melt mixing of PET/PBT (polyethylene terephthalate/polybutylene terephthalate) blends [22–24] showed a rapid increase in MW and viscosity during the reaction. Since LCPs contain similar end groups that can react with TPP, this appears to be a very promising approach for modifying the rheological properties of LCPs without destroying their liquid crystal structures.

In this paper, we investigate the reaction of Vectra A950, a commercial thermotropic main-chain liquid crystalline polymer, during melt processing in the presence of TPP. The influence of different parameters on melt viscosity, such as reaction time and concentration of TPP added, were studied. Furthermore, we used optical microscopy, thermal analysis and X-ray diffraction methods to confirm that the microstructure, melting/crystallization, and liquid crystallinity of Vectra A950 are not disturbed by reacting with TPP.

2. Experimental

2.1. Materials

Vectra A950 (Ticona, USA), a random copolyester of 73% hydroxybenzoic acid (HBA) and 27% 2,6-hydroxynaphthoic acid (HNA) with a reported melting point of 280 °C, was kindly donated by Ticona and used as received. Triphenyl phosphite (TPP, Aldrich, >97%) was used as received.

2.2. Processing methods

Roughly 5 g of Vectra A950, previously dried at 100 °C in a vacuum oven for more than 24 h, and TPP were added into the DSM
microcompounder, which could be reasonably sealed by closing the hopper plunger. The mixing temperature was 290 °C with a rotor speed of 100 rpm. The initial mixing process was performed in a nitrogen atmosphere by purging with extra dry nitrogen gas.

Different amounts of TPP were added during the process. TPP concentrations are always reported in weight of additive per weight of base polymer. In all experiments, the zero time corresponds to the first point of addition of the polymer-TPP mixtures into the microcompounder. The products (Vectra-TPP) were extruded, cut into pellets, and dried under vacuum at 100 °C for about 12 h. In this paper, neat Vectra will refer to Vectra that has not been processed in the microcompounder, while the

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Fig. 2. (a) Steady shear viscosity of neat Vectra compounded at 290 °C in the absence of TPP for 5 (□), 10 (○), 20 (△), and 30 (○) minutes; (b) steady shear viscosity of Vectra compounded at 290 °C with 4 wt% TPP for 5 (□), 10 (○), 20 (△) and 30 (○) minutes; (c) stress relaxation curves for Vectra compounded with 0 wt% or 4 wt% TPP for 30 min at 290 °C; (d) storage (G') and loss (G'') modulus as a function of frequency for Vectra compounded at 290 °C with 4 wt% TPP (G', G'' ▲) compared to neat Vectra (G', G'' □).

Fig. 3. ATR-FTIR spectra of neat Vectra, Vectra compounded with 2 wt% TPP, and Vectra compounded with 4 wt% TPP for 30 min at 290 °C. All spectra are normalized to the carbonyl peak around 1750 cm⁻¹.
designations of Vectra with 0 wt% TPP means the sample has been microcompounded in absence of TPP.

2.3. Rheological characterization

A TA Instruments AR-2000ex rheometer was used in all experiments. Steady and dynamic shear, and stress relaxation experiments were performed with a 25 mm 0.1 radian cone-and-plate geometry with gap of 143 μm. Dynamic shear experiments were conducted in the linear viscoelastic regime, as determined by a strain sweep, using 1% strain. Stress relaxation was measured following a 2% step strain. All the experiments were conducted in the presence of extra dry nitrogen in order to prevent oxidative/ hydrolytic degradation of the sample. Before loading, the rheometer was equilibrated at the test temperature. The pelletized product was loaded in the rheometer directly. Since the rheological properties of LCPs are highly dependent on the thermal history [25,26], direct loading of polymer pellets without pressing a 25 mm disk by compression molding can eliminate the effect of complex thermal history on rheological results. The camera in the rheometer oven was used to ensure that bubbles or overflows were not present in our samples. By implementing these protocols, the rheological testing data were very reproducible.

2.4. Infrared spectroscopy

Infrared spectra were measured in attenuated total reflection (ATR) mode using a Thermo Mattson Infinity Gold FTIR with Spectra-Tech Thermal ARK module. Samples were run for 512 scans with a 4 cm⁻¹ resolution to obtain sufficient signal-to-noise ratio. In all cases, background spectra, taken immediately before the sample spectra, were subtracted from the sample spectra. It was confirmed by phosphorus combustion analysis that the sample preparation method of annealing at 200 °C under vacuum overnight resulted in no residual, unreacted TPP remaining in these samples prior to measurement.

2.5. Thermal analysis

Thermal transition temperatures were determined by a differential scanning calorimeter (DSC) (Mettler-Toledo DSC1). All DSC runs were collected under a nitrogen gas atmosphere with a heating rate of 5 °C/min and cooling rate of 10 °C/min. The thermal stability of the samples was determined using thermal gravimetric analysis (TGA) (Mettler-Toledo TGA/DSC1). The experiments were performed under nitrogen and air with a heating rate of 20 °C/min.

2.6. Polarized optical microscopy

A polarized optical microscope (Olympus BX60) with a camera and a programmable temperature stage (Mettler FP90) was used to collect micrographs of thin film samples placed on a glass slide under crossed polarizers.

2.7. Wide angle X-ray diffraction (WAXD)

X-ray diffraction measurements were carried out using a Philips Xpert system with Cu Ka radiation (wavelength of 0.1542 nm) generated at 40 kV and 40 mA. All the samples were compressed into thin films 1 mm in thickness in the presence of N₂ at 300 °C and then annealed at 200 °C for 2 h under vacuum before measurement.

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Fig. 4. (a) Steady shear viscosity at 0.16 s⁻¹ shear rate for Vectra samples (a) compounded with 0 (○), 1 ( ), 2 (+), 3 (▲), 4 (○), and 5 (△) wt% TPP at 290 °C as a function of mixing time; (b) compounded with different concentrations of TPP for 30 min at 290 °C. The solid line is only a guide to the eye.

Fig. 5. Reaction mechanism of hydroxyl and carboxylic acid end groups with 5 wt% TPP. R represents the Vectra polymer chain.
3. Results and discussion

3.1. Effect of TPP on rheological properties of Vectra

When Vectra is microcompounded without TPP for different time periods, no apparent changes in viscosity were observed (Fig. 2a), indicating that although Vectra contains hydroxyl and carboxyl end groups [27], the conditions in microcompounding alone are not conducive for coupling reactions between chain ends. In addition, the consistency of the viscosity results illustrate that no degradation occurs during melt processing at 290 °C.

According to the mechanism shown in Fig. 1, up to three Vectra chain ends can react with TPP, and as a result, the viscosity and MW of Vectra is increased due to coupling of polymer chains. Since it is difficult to obtain MW values of Vectra samples directly by chromatography methods because of poor solubility in common solvents, stress relaxation, dynamic modulus and viscosity studies are an alternative method for characterizing the increase in MW. Fig. 2b illustrates that adding 4 wt% TPP into the compounding can increase the viscosity of the samples dramatically (i.e., close to a factor of 20 increase) across a wide range of shear rates, which can be attributed to MW growth. In contrast, previous studies on chain extension of PET with TPP have observed a factor of two increase in intrinsic viscosity [28]. Direct comparison of the behavior of neat Vectra and Vectra-TPP samples also revealed less shear thinning for Vectra-TPP samples, which can be ascribed to an increased role of entanglements [29]. Similar results were found in stress relaxation experiments (Fig. 2c), where a significant shift in shear modulus \( G(t) \) was observed consistent with a growth in MW. This is also consistent with dynamic shear data shown in Fig. 2d. Further, for samples where 4 wt% TPP was added, the \( G(t) \) approaches zero at long relaxation times suggesting that Vectra did not undergo crosslinking, which would be expected to produce a permanent, nonrelaxing stress.

In order to reveal details of the reaction chemistry that takes place during compounding, infrared spectra of neat and TPP compounded samples were measured as shown in Fig. 3. Neat Vectra samples exhibit a strong peak around 1050 cm\(^{-1}\) that is assigned to the C–O stretch in the polymer backbone [30]. An increase in signal of the peak at 1050 cm\(^{-1}\) was observed in Vectra-TPP samples and is assigned to the C–O–P stretch in phosphate esters formed by reaction of Vectra with TPP [31,32]. Phosphorous (P) combustion analysis indicates there is 990, 260 and 0 ppm elemental P covalently attached to the polymer in these samples compounded with 4 wt%, 2 wt% and 0 wt% TPP, respectively. These infrared spectroscopy and phosphorous analysis results confirmed that the MW increase induced by TPP is consistent with the formation of phosphate ester bonds.

Fig. 4a shows that the steady shear viscosity of all Vectra samples studied increases with mixing time with the exception of the 5 wt% TPP sample, which exhibits a maximum at 20 min. Generally, for 1–4 wt% TPP, the steady shear viscosity of the Vectra samples increased as more TPP was added, reaching a maximum in samples with 4 wt% TPP (see Fig. 4a and b). The different behavior of the 5 wt% TPP samples may be attributed to a shift from the favored chain extension mechanism (Fig. 1c, top path) to the terminating reaction mechanism (Fig. 1c, bottom path) resulting in a smaller MW increase (see Fig. 5) [23]. An additional factor is that phenol by-product production could be increased as more TPP is added, which may shift the reaction equilibrium towards the reagents by Le Chatelier’s principle resulting in less MW enhancement and a lower viscosity.
3.2. Effect of TPP on thermal properties and microstructure of Vectra

Samples displaying the largest increase in viscosity (4 wt% TPP at 30 min mixing time) and the deviation from the observed viscosity trend (5 wt% TPP at 30 min mixing time) were further studied to determine the effect of TPP on thermal properties of Vectra. TGA results shown in Fig. 6a demonstrate that for Vectra compounded with 0, 4, and 5 wt% TPP, the degradation temperature ($T_d$) at 5% weight loss does not change significantly from 495 °C, consistent with earlier studies on neat Vectra [33]. This result indicates that adding TPP does not affect the thermal stability of the polyester chains.

Furthermore, Fig. 6b and c shows DSC thermograms that indicate the crystallization temperature ($T_c$) and the melting point ($T_m$) of Vectra after reacting with TPP are nearly identical (both onset and endset) with neat Vectra, regardless of the TPP content. Additional WAXD experiments shown in Fig. 7 confirm that the crystalline morphology of these samples was also unaltered with two peaks at $2\theta \approx 20.2^\circ$ and $27.9^\circ$ (corresponding d-spacings are 0.439...
and 0.319 nm, respectively), which correspond to the 110 and 211/210 planes of a hexagonal lattice. This is in agreement with the findings of Flores [34], who determined that the structure of neat Vectra was orthorhombic, and with those of Karacan [35], who further defined it as a type III orthorhombic structure. Thus, reaction with TPP does not affect the crystallization behavior or crystal structure of Vectra.

Many of the special properties of LCPs originate from their liquid crystallinity. In order to confirm that TPP does not disturb the LC behavior of Vectra, polarized optical microscopy images were acquired under cross-polarizers. As shown in Fig. 8, these images revealed that after reacting with 4 and 5 wt% TPP, the Vectra samples still exhibit a liquid crystalline state with thread-like patterns indicative of a nematic phase, consistent with previous studies of neat Vectra [36].

3.3. Stability of Vectra-TPP samples

Earlier studies [37] investigated the stability of PET-TPP systems and found that although reaction with TPP can increase the MW of PET a significant decrease in viscosity after storage at ambient conditions for 2 days, was observed. This was ascribed to the degradation of the extended PET chains via scission of the P–O linkage by the reaction by-products. However, the Vectra-TPP systems in the present study displayed no apparent changes in viscosity even for a storage time as long as 4 weeks at a temperature of 80 °C in air.

We further explored the Vectra-TPP stability after melt reprocessing. As shown in Fig. 9a, a dramatic drop in viscosity was observed after Vectra-TPP samples were compression molded at 300 °C in air for 10 min. This reduction in viscosity is believed to be caused by scission of the P–O bonds during the molding process. Further signs of oxidation were visible through a color change of the Vectra-TPP samples from light beige to dark brown. In comparison, no significant viscosity reduction or color change occurred for neat Vectra samples after being compressed under the same conditions (Fig. 9b), suggesting that the Vectra backbone is stable when heated in air.

In addition, the TGA curves shown in Fig. 10 are similar for both neat Vectra and Vectra-TPP samples in that the first major degradation occurred at around 500 °C with about 43% weight loss, which is consistent with earlier studies of neat Vectra [38]. These results confirm that adding TPP will not affect the thermal stability of the Vectra backbone in air and the decrease in viscosity is likely a result of MW decrease in Vectra-TPP samples by scission of the P–O bond formed during the initial chain extension reaction.

Fresh samples of Vectra compounded with 4 wt% TPP were reprocessed in the microcompounder under N₂ atmosphere for different times to determine if the samples were stable in the absence of oxygen. Fig. 11 shows that no significant changes were observed in the viscosity of these samples, even after reprocessing for 10 min at 290 °C, which demonstrates that the Vectra-TPP system is thermally and chemically stable in the presence of N₂; more specifically, the P–O bond does not undergo scission in the presence of inert gas. On the other hand, the viscosity decreases when heated under air because the P–O bond created during chain extension is highly susceptible to hydrolysis, as shown in Fig. 12 [39,40], and reaction with by-products leading to the scission of the polymer chains.

Earlier studies have reported [23,37] that PET-TPP systems are not stable, even at room temperature. To remove residual reaction by-products, these studies performed chain extension reactions followed by Soxhlet extraction in acetone, which prevented the degradation of the polymer during storage. In order to investigate the effect of reaction by-products on the Vectra-TPP system reported here, samples compounded with 4 wt% TPP were Soxhlet extracted in acetone before and after compression molding at 300 °C in air. Fig. 13 shows that the steady shear viscosity of Vectra compounded with 4 wt% TPP was not decreased, even after reprocessing.

**Fig. 11.** Steady shear viscosity of Vectra compounded with 4 wt% TPP after reprocessing in the microcompounder at 290 °C under N₂ atmosphere for 0 (●), 5 (□) and 10 (△) minutes.

**Fig. 12.** Hydrolysis reaction of the P–O bond in Vectra-TPP samples (R – phenyl groups or polyester chain) [39,40].

**Fig. 13.** Steady shear viscosity of Vectra compounded with 4 wt% TPP (△) without compression molding, (□) unextracted after compression molding at 300 °C in air, and (○) after acetone extraction followed by compression molding at 300 °C in air.
extracted in acetone for 4 days to remove the by-products before compression molding the samples under the same conditions as before (300 °C for 10 min in air). Fig. 13 shows the rheological behavior of the extracted Vectra-TPP samples, illustrating that after extraction and compression molding a smaller drop in viscosity occurred. Also, there was no color change when these samples were compression molded, suggesting that oxidation was reduced. These results confirm that polymer chain scission is not only an effect of hydrolysis, but also of oxidation due to reaction with by-products. Therefore, extraction with acetone gave a much higher stability to the chain-extended Vectra towards degradation during reprocessing.

This procedure of modifying Vectra’s rheology with TPP additives followed by acetone extraction is currently being evaluated for use in the multilayer coextrusion process. These results will be presented in a subsequent publication.

4. Conclusions

In this research, TPP was used to enhance the rheological properties of Vectra A950, which normally has a very low melt viscosity with a strong temperature dependence. Through the reaction between TPP and up to three chain-ends of Vectra, the MW and viscosity of Vectra could be increased due to chain coupling. The influence of reaction time and TPP concentration on the rheology, thermal behavior and microstructure were investigated. Compounding with 4 wt% TPP for 30 min at 290 °C in a microcompounder produced optimal results, increasing viscosity by up to 20 fold compared to the neat polymer. Moreover, results from DSC and TGA show that the Vectra-TPP samples have a melting point and degradation temperature under N2 around 280 °C and 495 °C, respectively, which are consistent with earlier studies on neat Vectra. In addition, WAXD confirms that the crystal structure is not changed by adding TPP, and polarized optical microscopy images reveal the thread-like patterns expected for nematic structures are retained in Vectra-TPP samples.

The chemical stability of TPP-modified samples was also studied. When Vectra-TPP samples were stored at 80 °C in air for 4 weeks or reprocessed at 290 °C with N2 purge for 10 min, no significant drop in shear viscosity was found, revealing that the samples were quite stable. However, when reprocessed at 300 °C in air, the viscosity enhancement was partially reversed due to hydrolysis and oxidation of the P-O bonds formed during the initial reaction between the chain-ends and TPP. This can be partially mitigated by subsequent acetone extraction to remove reaction by-products present in the Vectra-TPP samples. This approach could be used to enhance the rheological compatibility of Vectra when used in multilayer melt coextrusion processes. Studies to confirm this are currently underway.

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References