

In Situ Preparation of Thermotropic Liquid Crystalline Polyester and Nylon 10T

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Abstract. Poly-decamethylene terephthalamide (PA10T) is one of high temperature special engineering plastics, which is widely used in aviation automobile, and electronic industries. However, its bad processability, poor crystallinity, and toughness may affect its further applications. In this work, the melting polycondensation synthesis of thermotropic liquid crystalline polyester (TLCP) prepolymer was explored. This synthesized TLCP was then added into PA10T via in-situ compounding, to obtain the poly-decamethylene terephthalamide / thermotropic liquid crystalline polyester composites (TLCP/PA10T). The TLCP was found easy to be oriented, which can reduce the entanglement of PA10T and improve the processing properties of PA10T. Moreover, the anisotropy under tensile conditions after the TLCP orientation can form microfibers and improve the mechanical properties of the composites. The relationship between crystallization properties, tensile strength and TLCP content of TLCP/PA10T composites was also studied. Such TLCP/PA10T composites can serve as a high temperature special engineering plastic in industrial manufacturing.

Keywords: Melt polymerization, Thermotropic liquid crystalline polyester (TLCP), Poly (decamethylene terephthalamide) (PA10T), Crystallization properties, Mechanical properties.

1. Introduction

Poly (decamethylene terephthalamide) (PA10T) is a semi-aromatic nylon made by condensation of decylenediamine and terephthalic acid. The long flexible diamine chain in the molecular chain makes the macromolecule have certain flexibility, so that it has a high crystallization rate and crystallinity, while its low water absorption rate, so that its products have good mechanical properties [1,2]. Compared with conventional aliphatic nylon materials, semi-aromatic nylons have more rigid molecular chains and restricted molecular chain movement which resulting in higher glass transition temperature (T_g) and better dimensional stability, mechanical properties [3], corrosion resistance, and thermal properties. Due to these excellent properties, PA10T is more suitable for certain small electronic components, such as LED reflection bracket and connector than conventional aliphatic nylon. Also, the modified products of PA10T can also be applied to some chemical reagents or heat-resistant environments, such as water treatment, Nano Molding Technology (NMT) and engine parts [4]. However, semi-aromatic nylon has the problems of crystallization, poor toughness and processability due to high melt viscosity [5]. To solve

these problems of semi-aromatic nylon, it can be modified to obtain a modified material of semi-aromatic nylon with good processing performance without losing its excellent mechanical properties and other advantages. The modification by adding inorganic fillers such as glass fibers (GF) [6] can enhance the mechanical properties, but at the same time, it will make the material less flowable and thus difficult to process.

Many studies have shown that thermotropic liquid crystal polymers (TLCP) can be used as a processing aid for thermoplastics to significantly reduce the melt viscosity of the blend system. Isayev [7] found that the 1.0 wt. % TLCP could significantly improve the processability of polycarbonate (PC). Chang [8] found that TLCP can effectively improve the processability of polyphenylene ether/polystyrene alloy. When the content of TLCP is more than 5.0 wt. %, compatibilizers must be added to improve the compatibility between TLCP and thermoplastic in order to obtain satisfactory blending. On the other hand, TLCP has good flowability, low melt viscosity, and excellent mechanical properties, and it is also close to the processing temperature of semi-aromatic nylons such as PA10T. Therefore, TLCP has been regarded as one of proper polymers for modification of

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PA10T. In the modification of PA10T by TLCP, TLCP is easily oriented, which can reduce the entanglement of PA10T and thus improve the processing properties of PA10T. On the other hand, TLCP orientation is anisotropic in tensile conditions and forms microfibrils, improving the mechanical properties of the composite.

In this work, TLCP prepolymer was successfully synthesized by melt polycondensation, after which, the poly-decamethylene terephthalamide / thermotropic liquid crystalline polyester composite (TLCP/PA10T) was obtained by adding TLCP into PA10T through in situ compounding. The mechanical properties, thermal properties and crystallization behavior of TLCP/PA10T composites with different mass fractions of TLCP have been studied. The reasons for the differences in properties of TLCP/PA10T composites with different mass fractions of TLCP have been discussed.

2. Materials and Method

2.1 Materials and Devices

p-hydroxybenzoic acid (HBA), terephthalic acid (TA) and isophthalic acid (IA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Chengdu, China), 4,4'-dihydroxybenzene (BP) was purchased from Sigma-Aldrich (Shanghai, China), sulphuric acid was purchased from XiLONG Scientific Co., Ltd. (Chengdu, China), acetic anhydride was purchased from Chron Chemicals Co., Ltd. (Chengdu, China), methylimidazole was purchased from Adamas Reagent, Ltd. (Shanghai, China), pentafluorophenol was purchased from Quanzhou Qianda Technology Co., Ltd. (Chengdu, China), PA10T prepolymer was used as purchased from Sichuan Lang Di New Material Co., Ltd (Deyang, China).

The polymerization reaction device was a self-designed high temperature and high-pressure reactor. The reactor was equipped with a stirring device, which could adjust the stirring speed. The reactor was electrically heated, with a temperature controller to control the real-time temperature of the reaction through a thermometer. The reaction kettle was connected with a vacuum pump and a nitrogen cylinder to take away the by-product acetic acid and provide inert gas protection.

2.2 Preparation of 4- Acetyloxybenzoic Acid (ABA)

All 30 g of p-hydroxybenzoic acid (HBA), 60 g of acetic anhydride and 0.09 g of sulfuric acid were added into a three-neck flask. After vacuumizing, nitrogen was introduced and heated to 80 °C for 2 h. After the reaction, the reaction system was poured into ice water, the system was stirred until all the precipitates were precipitated, the precipitates were filtered, washed with deionized water for 3 to 4 times until the pH value of the system was between 4 - 5 to obtain 4-acetoxybenzoic acid (ABA). The reaction equation was indicated in Figure 1(a).

2.3 Preparation of 4,4'- Diacetoxybiphenylene (BPA)

Typically, the BPA was firstly synthesized by adding 30 g of hydroquinone (BP), 60 g of acetic anhydride and 0.09 g of sulfuric acid into a three-necked flask. After vacuumizing, nitrogen was introduced and heated to 80 °C for 2 h. After the reaction, the reaction system was poured into ice water, the system was stirred until all the precipitates were precipitated, the precipitates were filtered, washed with deionized water for 3 to 4 times until the pH value of the system was neutral to obtain 4,4'-diacetoxybiphenyl (BPA). The reaction equations were indicated in Figure 1(b).

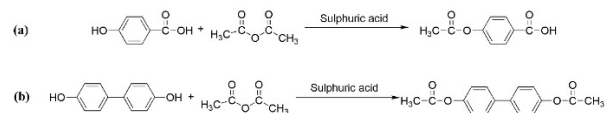


Figure 1. Schematic diagrams of preparation of (a) 4-Acetyloxybenzoic Acid (ABA) and (b) 4,4'-diacetoxybiphenylene (BPA).

2.4 Synthesis of TLCP

ABA and ABP monomer raw materials were weighted and mixed according to a certain proportion. Then the prepared catalyst methylimidazole aqueous solution was added into the reactor as 0.5 wt.%. The vacuum pump was used to remove the air in the reactor, nitrogen was injected for more than 5 times, then the reactor was heated to 170 °C for 1 h at the heating rate of 0.8 °C min⁻¹, until 240 °C. After heating, the exhaust port was opened to remove the small molecule by-product acetic acid, the reaction system was cooled down to 100 °C for 1h. The reactor was opened and added an appropriate amount of catalyst methylimidazole aqueous solution again, the air in the reactor was removed by using the vacuum pump, nitrogen was injected for more than 5 times, then the reactor was raised to 240 °C, the stirring device was turned on at the speed of 300 rpm min⁻¹. The temperature was raised to 300 °C at the rate of 0.6 °C min⁻¹, and finally the temperature was raised to 320 °C at the rate of 0.5 °C min⁻¹, stop the reaction [9].

2.5 Synthesis of TLCP/PA10T Composites

PA10T prepolymer and TLCP were weighed and mixed in different proportions and were put into polymerization reactor. The vacuum pump was used to remove the air in the reactor, nitrogen was injected for more than 5 times, the temperature of the reactor was set to 305 °C, the stirring device was turned on at the speed of 300 rpm min⁻¹, the vacuum pump was turned on to vacuum, stay for 1 h, the temperature was raised to 315 °C, stay for 1 h, the temperature was raised to 325 °C, stay for 1 h, raised the temperature to 335 °C, and the reaction was closed after 30 min [10]. The composite splines were prepared according to the requirements and specifications of ASTM D882-09 Standard. There were five groups of PA10T, 2.0 wt.% TLCP/PA10T, 5.0 wt.% TLCP/PA10T, 10.0 wt.% TLCP/PA10T and 20.0 wt.% TLCP/PA10T,

with five dumbbell splines (20.0 mm × 2.0 mm × 0.2 mm) in each group.

2.6 Characterizations

The samples were characterized by total reflection infrared spectroscopy using Nicolet iS50 Fourier transform infrared spectroscopy of Thermo Fisher Company. Differential scanning thermal analysis was performed using NETZSCH DSC 214 differential thermal analyzer. Thermogravimetric analysis was performed using NETZSCH TG 209F3 thermogravimetric analyzer. The crystallization of TLCP was analyzed by Ultima IV X-ray diffractometer of RIGAKU company. The texture structure of polymer samples was observed under Leica DM4P polarizing microscope. 5967 universal material testing machines of Instron company was used to test mechanical properties, test rate 5 mm min⁻¹.

3. Results and Discussions

3.1 FTIR Characterizations of TLCP Prepolymer and TLCP/PA10T Composites

The FTIR spectra of TLCP prepolymer is shown in Figure 2(a), the stretching vibration peak of C-H is displayed at 2925 cm⁻¹. C=C benzene ring skeleton vibration peaks are displayed at 1601 cm⁻¹, 1492 cm⁻¹ and 1425 cm⁻¹ which indicate the presence of benzene ring in the synthesized product. Characteristic peaks of para disubstituted benzene are displayed at 902 cm⁻¹, 880 cm⁻¹, and 690 cm⁻¹. The ester carbonyl stretching vibration peak of phenol is observed at 1737 cm⁻¹. The characteristic absorption peak of acetate of phenol at 1264 cm⁻¹ is the absorption peak of biphenyl. FTIR spectra prove that the synthesized TLCP is consistent with the citations [11].

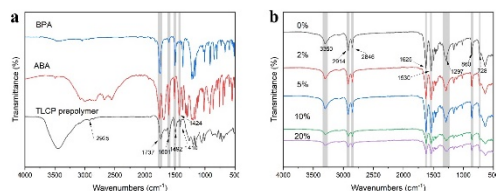


Figure 2. FTIR of (a) TLCP prepolymer, and (b) TLCP/PA10T composites.

The FTIR spectra of TLCP and TLCP/PA10T composites is shown in Figure 2(b), the stretching vibration peak of N-H is displayed at 3350 cm⁻¹. Stretching vibration peaks of CH₂ are displayed at 2914 cm⁻¹ and 2846 cm⁻¹. The stretching vibration peak of C=O bond is displayed at 1625 cm⁻¹. The peak displayed at 1530 cm⁻¹ is the combined peak of N-H bond in-plane bending and C-N bond stretching vibration. The peak displayed at 1297 cm⁻¹ is the combined peak of C-H bond in-plane bending and C-N bond stretching vibration. Peaks displayed at 860 cm⁻¹ and 728 cm⁻¹ are bending vibration absorption peaks in the C-H bond plane of benzene ring. The FTIR spectra indicates that the products are PA10T, which is corresponded with the citations [12].

3.2 Thermal Properties of TLCP Prepolymer and TLCP/PA10T Composites

The synthesized TLCP prepolymer was analyzed and tested by differential thermal analyzer. The sample was measured cyclically at the heating rate of 20 °C min⁻¹ under the protection of nitrogen within 5.0 mg, and the heating range was 25 °C to 330 °C. The sample was thermogravimetric analyzed by thermogravimetric analyzer. The test was carried out under nitrogen protection, and the temperature rise range was 25 - 600 °C. The thermal history of the sample was eliminated before the test, and the DSC curve is shown in Figure 3(a). As the product is TLCP prepolymer, compared with the commercial TLCP products, due to its small molecular weight and poor thermal stability, the melting point of TLCP prepolymer is about 265 °C according to the DSC curve, and the thermal decomposition temperature of TLCP prepolymer is about 500 °C according to the TGA curve. The TGA curve of TLCP prepolymer is shown in Figure 3(b). Figure 3(c) shows the TGA curves of PA10T and TLCP/PA10T composites. The analysis shows that comparing with PA10T, the thermogravimetric temperature of TLCP/PA10T compounded with TLCP decreases slightly with the increase of TLCP content, and the degree of reduction is almost negligible. Therefore, it could be seen that the addition amount of TLCP TLCP/PA10T almost does not affect the thermal stability of the composites. Table 1 indicates the specific data where T₅ represents 5 % of thermal weight loss.

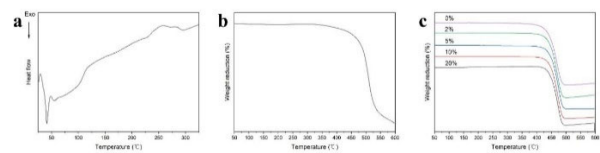


Figure 3. (a) DSC curve of TLCP prepolymer, (b) TGA curve of TLCP prepolymer, and (c) TGA curve of TLCP/PA10T composites.

Table 1. TLCP/PA10T composites T₅.

Mass fraction of TLCP in composite (%)	T ₅ (°C)
0	434.79
2	429.64
5	426.43
10	421.70
20	409.66

3.3 Crystallization properties of TLCP Prepolymer and TLCP/PA10T Composites

The synthesized TLCP prepolymer was characterized by Ultima IV X-ray diffractometer of RIGAKU company in Japan. Figure 4(a) is its X-ray diffraction pattern. The X-ray diffraction pattern shows that the TLCP prepolymer is in 2θ. There is an obvious diffraction peak at about 20 °, which is consistent with the citations [12]. Figure 4(c) shows the DSC second temperature rise curve of PA10T, TLCP and TLCP/PA10T composites. According to the analysis of the figure, TLCP does not melt obviously,

while TLCP/PA10T composite is similar to PA10T, and there is an obvious crystallization peak near the crystallization temperature of PA10T [13]. According to the analysis of the figure, the melting point of TLCP/PA10T composites decreases slowly with the increase of TLCP content. According to DSC (Figure 4(d)) the crystallization properties of TLCP/PA10T composites increase first and then decrease with the increase of TLCP content in the composites. When the proportion of TLCP is relatively small, on the one hand, TLCP can play the role of nucleation in the crystallization process, as a nucleating agent to crystallize PA10T. Although TLCP destroyed the regularity of PA10T, the relatively rigid molecular chain of TLCP and the role of nucleation limit the movement of PA10T molecular chain segment, TLCP plays a dominant role as a nucleating agent. Therefore, the content of TLCP increases gradually, and the crystallinity of TLCP/PA10T composites is higher. When the mass fraction of TLCP is increased to 5.0 wt. %, the crystallization performance of TLCP reaches the best. When the TLCP is greater than 5.0 wt. %, due to the increase of the proportion of TLCP, more and more TLCP formed microfibril structure. Therefore, the role of nucleating agent is gradually weakened, and the role of hindering the movement of PA10T segment is gradually dominant, showing a trend of decreasing crystallinity. From X-ray diffraction, 5.0 wt.% TLCP/PA10T has the largest crystallinity and the best crystallinity, which confirms the above analysis of crystallization behavior. In addition, it can be seen from Figure 4(b) that there is a diffraction peak with smaller peak intensity at high angle and low angle respectively in TLCP/PA10T compared with pure PA10T, and it can also be seen that the crystal forms of TLCP and PA10T are different.

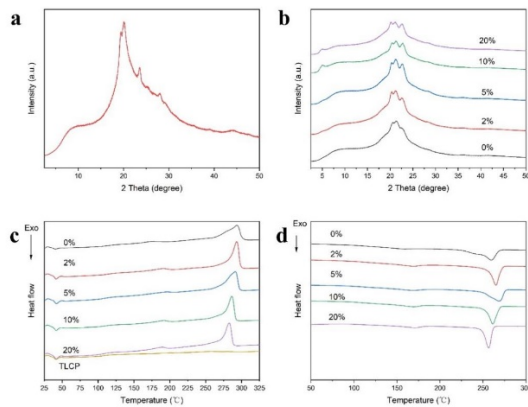


Figure 4. (a) X-ray diffraction pattern of TLCP prepolymer, (b) X-ray diffraction pattern of TLCP/PA10T composite, (c) DSC heating curves of PA10T and TLCP/PA10T composites, and (d) DSC cooling curves of PA10T and TLCP/PA10T composites.

TLCP prepolymer sample was placed on a glass slide, heated, melted, and pressed with another glass slide on the heated state, and observed after cooling. As shown in Figure 5(a), a typical nematic schlieren texture is observed. Polymerized TLCP sample is placed on a glass slide, heated, melted and pressed with another glass slide to an appropriate thickness and slid it in the same direction on the heated state, and then it is placed under a polarizing

microscope for observation and photography after cooling. As shown in Figure 5(b) and (c), TLCP forms a typical nematic band texture, showing stripes oriented along the direction of shear stress. It is speculated that this kind of band texture is formed by many microfibrils oriented along the direction of shear stress, regularly arranged and periodically bent into sawtooth shape. It can be inferred from the analysis of polarizing microscope photos that TLCP is composed of many ordered microcrystalline regions with random orientation before shear. When the TLCP is subjected to shear, the ordered microcrystalline regions with random orientation are aligned in the stress direction of shear. After the shear action stops, the highly oriented state gradually returns to the ordered microcrystalline region structure with regular.

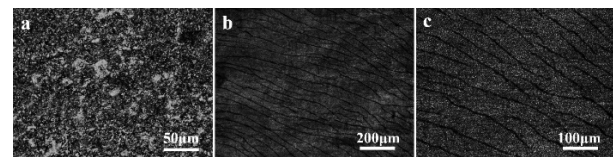


Figure 5. (a) Texture structure of TLCP prepolymer, and (b), (c) TLCP prepolymer texture (shear).

3.4 Mechanical properties of TLCP and TLCP/PA10T

As indicated in Figure 6, the tensile strength of TLCP/PA10T composite spline first increased but then decreased with the increase of TLCP content of the composite, and the tensile strength reached the maximum at 5.0 wt. %, which was 68 MPa. Based on the above analysis, the mechanical properties of the composite can be enhanced since there are few microfibrils formed by a small amount of TLCP added into the PA10T. With the gradual increase of TLCP content, the tensile strength of the microfibril gradually increase until the TLCP content exceeds 5.0 wt.%, which is due to the domination of the poor compatibility between PA10T and TLCP and the compatibility became worse. The test results of mechanical properties of composite splines also confirmed the previous analysis.

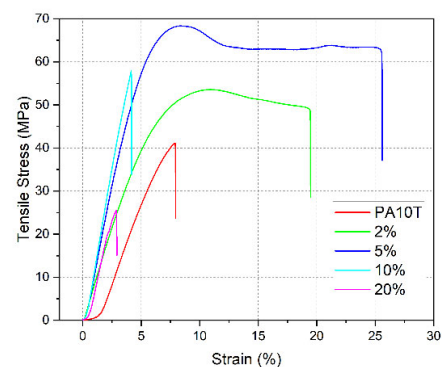


Figure 6. Stress-strain Diagram of PA10T and TLCP/PA10T composites.

4. Conclusion

Thermotropic liquid crystalline polyester (TLCP) prepolymer was demonstrated to be firstly synthesized and PA10T was successfully compounded in situ with TLCP prepolymer to explore the appropriate synthesis process of TLCP/PA10T melt polymerization. The effects of different mass fractions of TLCP on the thermal, crystalline, and mechanical properties of TLCP/PA10T composites were characterized in this work. The mechanical and crystalline properties of PA10T can be adjusted by varying the mass fraction of TLCP content. The TLCP/PA10T showed optimized mechanical and crystalline properties with TLCP content at its 5.0 wt.% and then deteriorated with the decrease of TLCP content. The tensile strength of 5.0 wt.% TLCP/PA10T composites reached 68 MPa which is also the optimal sample in this work. Results showed that TLCP/PA10T composites has better properties compared with conventional PA10T and can be widely used in aerospace, automotive industry, electronic industry and other fields.

Acknowledgments

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References

1. Chang, D. Y., & Chang, F. C. J. J. o. a. p. s. In situ reactive compatibilized noryl/LCP blends. 56(9), 1015-1028.
2. Chen, B.-K., Tsay, S.-Y., & Chen, J.-Y. Synthesis and properties of liquid crystalline polymers with low T_m and broad mesophase temperature ranges. *Polymer*, 46(20), 8624-8633.
3. Huang, B., & Walsh, J. J. Solid-phase polymerization mechanism of poly(ethylene terephthalate) affected by gas flow velocity and particle size. *Polymer*, 39(26), 6991-6999.
4. Isayev, A. I., & Modic, M. J. P. C. Self-Reinforced melt processible polymer composites: Extrusion, compression, and injection molding. 8(3), 158-175.
5. Liu, P., Wu, T., Ye, G., & Xu, J. Novel polyarylates containing aryl ether units: synthesis, characterization and properties. *Polymer International*, 62(5), 751-758.
6. Novitsky, T. F., Lange, C. A., Mathias, L. J., Osborn, S., Ayotte, R., & Manning, S. J. P. Eutectic melting behavior of polyamide 10, T-co-6,T and 12,T-co-6,T copolyterephthalamides. 51(11), 2417-2425.
7. Pan, X., Chi, Z., Cheng, D., Jin, M., & Bu, H. Solid-State Polymerization of a Liquid Crystalline Copolyester Derived from 2,6-Naphthalene Dicarboxylic Acid, Terephthalic Acid, 4-Acetoxybenzoic Acid and Hydroquinone Diacetate. *Journal of Macromolecular Science, Part B*, 44(2), 249-259.
8. Pisharath, S., & Wong, S. C. Development of the morphology and crystalline state due to hybridization of reinforced toughened nylon containing a liquid-crystalline polymer. *Journal of Polymer Science Part B-Polymer Physics*, 41(6), 549-559.
9. Ruggiero, V., & Acierno, D. Effects of the addition of small amounts of a thermotropic liquid crystalline polymer on the processing characteristics of polyphenylene oxide-polyamide alloys. *Advances in Polymer Technology*, 26(2), 109-120.
10. Wang, J., Li, L., He, Y., Song, H., Chen, X., & Guo, J. The effect of thermo-oxidative ageing on crystallization, dynamic and static mechanical properties of long glass fibre-reinforced polyamide 10T composites. 5(6), 172029.
11. Wang, W. Z., Liu, B. Y., Li, R. X., Zhang, Y. H. J. G. C. K. Y. G. P. M. S., & Engineering. Synthesis and physical and mechanical properties of poly(decanediamine p-phenylenediacetic amides). 25(4), 144-146.
12. Ward, Y., & Young, R. J. Deformation studies of thermotropic aromatic copolyesters using NIR Raman spectroscopy. *Polymer*, 42(18), 7857-7863.
13. Zou, G., Wang, P., Feng, W., Ren, Z., & Ji, J. Poly(decamethylene terephthalamide) copolymerized with long-chain alkyl dodecanedioic acid: Toward bio-based polymer and improved performances. 135(31), 46531.