



Poly(trimethylene terephthalate) Block Co-polymer with Epoxy Resin: Preparation, Characterization and Properties

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Processing of thermoplastics can be facilitated by plasticizer, though after processing the plasticizer remains to modify the properties of the product. Investigation of the plasticizing action of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin for poly(trimethylene terephthalate) (PTT) using Fourier transform infrared spectroscopy, Raman spectroscopy and differential scanning calorimetry led to the introduction of a novel block co-polymer (DGEBA-*block*-PTT-*block*-DGEBA). The novel block co-polymer, formed by the reaction between the end groups of PTT and the oxirane ring of DGEBA, was dependent on the pH of the medium.

1. Introduction

Poly(trimethylene terephthalate) (PTT), first synthesized and patented in 1941 [1], remained obscure till recent times due to the high cost of production. Recent discovery of bioengineering route to synthesize 1, 3-propanediol [2] [3], has rekindled the scientific interest in this polymer. The unique zig-zag structure of PTT renders it a stretch recovery which is about 2-3 times greater than polyamides and other polyesters [4]. The use of epoxy resin as a modifier for PTT based blends has been tried by different researchers [5], [6] but the mechanism of modification was not addressed in these studies. The main aim here was to investigate how the addition of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin affect the melting properties, glass transition temperature of PTT and the mechanism for plasticizing action of DGEBA which remained unattended is explained here.

2. Experimental

2.1 Materials used

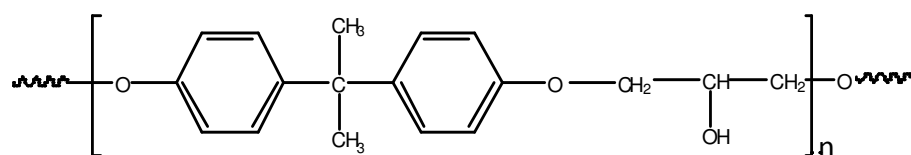
DGEBA epoxy resin (Lapox L-12) with an epoxy equivalent between 5.25-5.40 eq·kg⁻¹ and viscosity between 1.15-1.20 g·cm⁻³ was procured from Atul Industries, India. Poly(trimethylene terephthalate) (PTT or SORONA 3G) with a density between 1.3-1.5 g·cm⁻³, M_n of 22,500 g·mol⁻¹ and degree of polymerization of 2.5 was kindly supplied by DuPont Industries USA. Details of the materials used are given in Table 1 and their chemical structures are given in Figure 1. All materials were used without further purification.



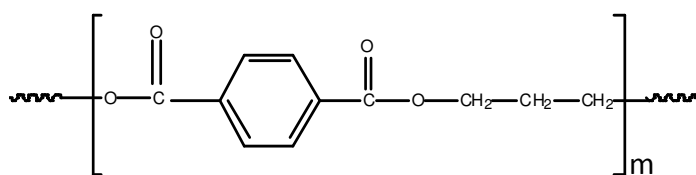
Table 1. Characteristics of PTT, DGEBA and DDS

	Poly(trimethylene terephthalate)	Diglycidyl ether of bisphenol-A	Diammino diphenyl sulfone
$M_w^{(a)}$ (g·mol ⁻¹)	58,400	-	-
$M_n^{(a)}$ (g·mol ⁻¹)	22,500	-	-
Viscosity ^(b) (g·cm ⁻³)	-	1.15-1.2	-
Epoxy content ^(b) (equ·kg ⁻¹)	-	5.25- 5.40	-
$T_g^{(c)}$ (°C)	54	-16	-
$T_m^{(d)}$ (°C)	227	-	150
$\Delta H_{ref}^{(e)}$ (J·g ⁻¹)	146	-	-
Supplier	DuPont Industries, USA.	Atul Industries, Gujarat, India.	Atul Industries, Gujarat, India.

- (a) Molar mass estimated by gel permeation chromatography (Perkin-Elmer). Polystyrenes with low polydispersity were used as standards.
(b) Information provided by the supplier.
(c) Glass transition temperature as determined by DSC.
(d) Apparent melting temperature for the neat polymer during a first heating scan.
(e) The melting enthalpy of PTT crystals [7].



Diglycidyl ether of bisphenol-A



Poly(trimethylene terephthalate) ($n \neq m$)

Figure 1: Chemical structure of DEGEBA and PTT.

2.2 Blend preparation

PTT with varying amounts of DGEBA (5, 10, 20, 30 %·w/w) were prepared by using a Haake mixer. The blends were heated to 240 °C for 900 s with constant shearing at 80 rpm. After mixing the blends were removed and used for the study.

3. Equipment

3.1. Differential Scanning Calorimetry

Perkin-Elmer DSC7 (Shelton, CT, US), calibrated for temperature with indium and zinc standards, and for enthalpy with indium, was used for the analysis of the blends under a



nitrogen atmosphere. A new sample was used for each DSC experiment. The samples were exposed to different thermal histories:

3. 1. (A) Glass transition temperature determination.

Blends prepared were annealed at $T_a = 260$ °C for 1 min, followed by cooling at a rate of $100 \text{ K}\cdot\text{min}^{-1}$ to -50 °C and held for 1 min. The samples were then reheated to 260 °C at a rate of $10 \text{ K}\cdot\text{min}^{-1}$.

3.1. (B) Samples were annealed at $T_a = 260$ °C for 1 min followed by cooling at a rate of $20 \text{ K}\cdot\text{min}^{-1}$ to the T_c of 205 °C and held until crystallization was complete. The half-time of crystallization was determined at $T_c = \text{constant}$. The same procedure was applied for the determination of the melting temperature. After crystallization sample was heated to 260 °C at a rate of $10 \text{ K}\cdot\text{min}^{-1}$.

3.2 *Infrared Spectroscopy Analysis*

Fourier transform infrared (FTIR) spectroscopic studies were performed on neat polymers and the blends using attenuated total reflection (ATR) using Perkin-Elmer Spectrum One Spectrometer (Lanstrisant UK). FTIR spectra were recorded in transmittance mode over the range of $4000 - 600 \text{ cm}^{-1}$ by an averaging 16 scans at a resolution of 4 cm^{-1} in all cases.

3. 3. *Raman spectroscopy analysis*

Raman spectroscopy analysis was performed on neat PTT and the blends using Perkin-Elmer Raman Station 400F Raman spectrometer.

4. **Results and Discussion**

Miscibility studies using modulated temperature DSC (MTDSC) shows that as the amount of DGEBA in the blends increases the glass transition temperature (T_g) decreases. Experimentally observed T_g values were fitted with the Fox equation and it shows that the blend exhibit a negative deviation from a Fox equation fitting. The experimentally observed T_g values and the Fox equation fitting results are shown in Figure 2.

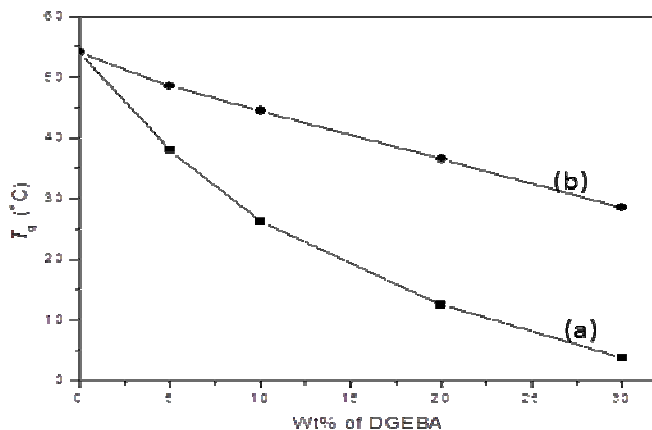


Figure 2: Plot of T_g against DGEBA concentration for PTT-DGEBA blends, (a) represents the experimentally observed values and (b) represents the Fox equation fitting.

The equilibrium melting temperature (T_m°) determined by using Hoffman-Weeks equation shows a regular decrease as the amount of DGEBA in the blends increases indicating that DGEBA can act as a plasticizer. The results of Hoffman-Weeks fitting are tabulated in Table 2.



Table 2: T_m and correlation coefficient (r) for T_m versus T_c relationship in the T_c range of 185-205 °C for PTT-DGEBA blends.

Blend composition	$T_m / ^\circ\text{C}$	α	r
100:0	229.0	0.060	0.899
95:5	227.7	0.043	0.899
90:10	225.5	0.024	0.968
80:20	221.8	0.023	0.999
70:30	221.0	0.035	0.996

The T_m values decreased as the amount of DGEBA increased in the blends. Analysis of the epoxy networks using FTIR spectroscopy is widely followed by researchers and the peak at 915 cm^{-1} is characterized as that of the oxirane ring [8], [9]. In the case of PTT-DGEBA blends it was observed that the peak at 915 cm^{-1} disappeared completely indicating the possibility of chemical reaction between the hydroxyl and carboxylic acid end groups of PTT and the epoxy group of DGEBA. The experimentally observed FTIR spectrum is shown in Figure 3.

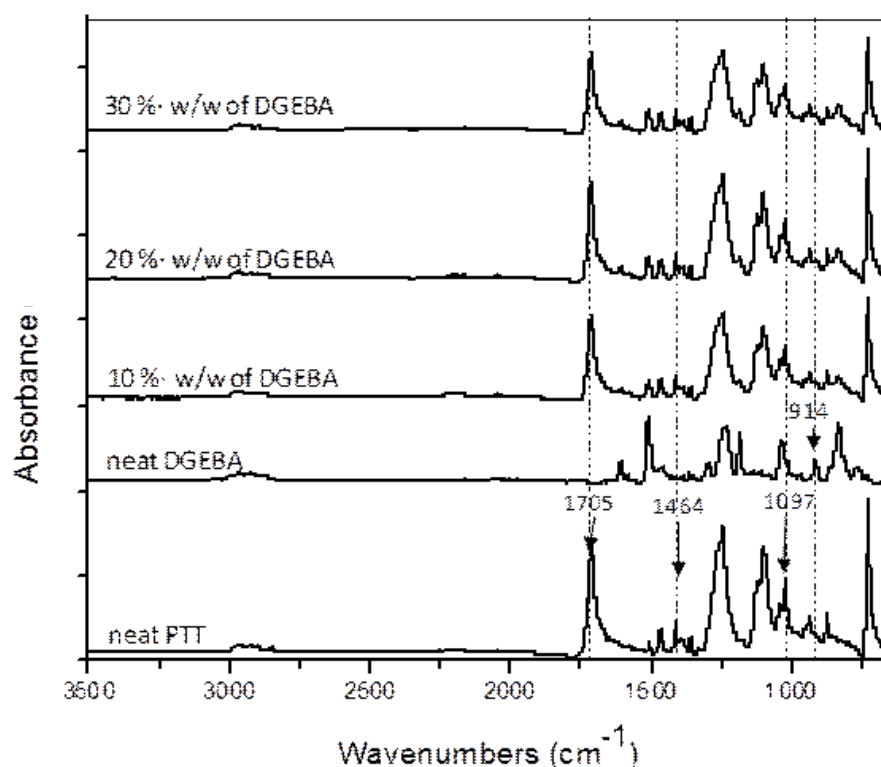


Figure 4: FTIR spectra of the blends, dotted lines represent the areas of interest.

The peak at 1464 cm^{-1} is assigned to gauche $-\text{CH}_2$ group of the crystalline region [10] indicating that the PTT retains its crystallinity in the blends. This possibility of chemical reaction between the end groups of PTT and DGEBA was further confirmed by Raman spectroscopy. Raman spectroscopy is more sensitive to polarizable bonds and less sensitive to polar bonds [11]. Epoxy ring produces two intense peaks at 846 cm^{-1} (epoxy deformation) and at 1259 cm^{-1} (in-plane deformation of the epoxy ring) [11]. The peak at 1259 cm^{-1} corresponds to the breathing mode of benzene rings and so the peak at 846 cm^{-1} is to be considered as the



presence of un-reacted epoxy groups. Raman spectroscopy results show that the peak at 846 cm^{-1} disappear completely confirming a chemical reaction between the end-groups of DGEBA and PTT.

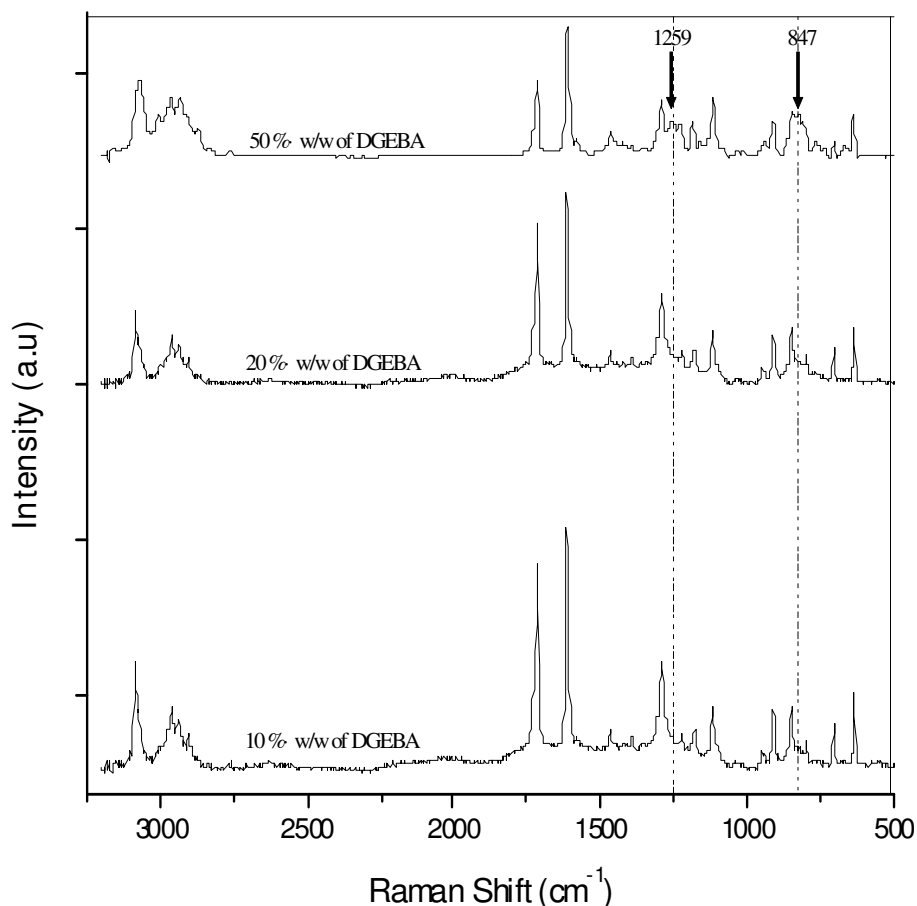


Figure 5: Raman spectroscopy results for PTT-DGEBA block co-polymers.

This shows that when the amount of DGEBA was between 0-30 %·w/w the pH of the medium induced a chemical reaction between the end groups of PTT and DGEBA. The nucleophiles (hydroxyl and carboxylic acid) at the ends of PTT attack the oxirane ring of DGEBA leading to it ring opening. This reaction leads to the formation of a block co-polymer (DGEBA-*block*-PTT-*block*-DGEBA). Further characterization of this novel block co-polymer by NMR spectroscopy was not successful due to practical difficulties.

5. Conclusion

A chemical reaction between the end groups of DGEBA and PTT was followed by using FTIR spectroscopy and Raman spectroscopy. Results showed that a chemical reaction occurred between the terminal hydroxyl and carboxylic acid end group of PTT and the oxirane ring of DGEBA. This chemical reaction was found to be highly sensitive to the amount of DGEBA which in turn can be correlated to the pH of the medium because when the amount of DGEBA was $\geq 40\%$ ·w/w no ring opening reaction was observed. A steady decrease in the T_g as observed in the MTDSC studies shows that the block co-polymer formed follow a negative deviation from the Fox equation fitting. The steady decrease in the T_m° value indicate that DGEBA can act as a plasticizer for PTT. This result has been reported earlier by different researchers. The FTIR and Raman spectroscopy analysis shows that the plasticizing action of DGEBA is due to the formation of a block co-polymer. This novel block co-polymer (DGEBA-*block*-PTT-*block*-DGEBA) can find use in a variety of fields.



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