



Interfacial interactions of thermally reduced graphene in poly(trimethylene terephthalate)-epoxy resin based composites



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ABSTRACT

Nanocomposites containing thermally reduced graphene (TRG) have been prepared with poly(trimethylene terephthalate) (PTT) plasticized with (bisphenol-A diglycidyl ether) (BADGE), a cross-linkable additive. Morphology of the PTT–BADGE blend was dependent on preference for interaction of TRG with PTT or BADGE and nucleation activity of TRG toward PTT. PTT–TRG and PTT–BADGE–TRG nanocomposites with different BADGE–TRG ratios were prepared by a melt mixing technique facilitated by miscibility of PTT and BADGE. The influence of TRG on crystallization nucleation, kinetics and morphology was measured using differential scanning calorimetry and wide-angle X-ray scattering. Crystallization of PTT caused phase separation of BADGE, though PTT–BADGE remained miscible in PTT amorphous regions. BADGE created increased flexibility of PTT though dynamic mechanical properties were moderated by TRG, both directly as a filler and as a result of enhanced crystallization. Synergistic improvement in modulus was observed at particular compositions attributed to a change in morphology of an immobilized zone consisting of BADGE and TRG within amorphous fractions of PTT. The results are of consequence for design of materials using a semi-crystalline polymer, for applications where simultaneous use of a processing aid, plasticizer and nano-reinforcement.

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1. Introduction

Nano-reinforced semi-crystalline polymers with ease of processing and enhanced flexibility have attracted the attention of the scientific community because self-organizing molecules will play a vital role in next generation materials [1–3]. Polymer crystallization is a typical case of self-organization, where groups of repeat-units/polymer chain segments pass from an amorphous state to an ordered state [2]. The structure and mechanical properties of semi-crystalline polymers undoubtedly depend on the crystallization kinetics [4]. Significant research has been dedicated to their processing, crystallization kinetics and morphology, with a considerable contribution from the theoretical community [1,5,6]. Rastogi et al. [7] showed that slow and careful control of the

melting process can give different entanglements with individually separated chains. Of particular interest is the contribution from Michael et al. [8], where the viscosity and glass transition temperature were evaluated under conditions of minimum extraneous enthalpic or other conditions. This morphology was attained by suspending polystyrene nanoparticles in linear polystyrene followed by its cross-linking. It has been demonstrated that nanoparticles behave as efficient nucleating agents [9,10]. An interesting and important unattended question involves the participation of nanofillers in crystallization kinetics and dynamic properties (storage and loss modulus) in the presence of a low molecular weight additive.

An approach to this situation was made using an engineering thermoplastic, poly(trimethylene terephthalate) (PTT) as the matrix material. The factors favoring its selection involve low cost [11], high resilience (2–3 times greater than that of polyamide-6) [11], and relatively low work of chain folding [12]. Studies show that the amorphous fractions of PTT are miscible with bisphenol-A diglycidyl ether (BADGE) while the crystalline fractions are immiscible

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[13]. Similarly BADGE is reported to behave as a plasticizer for PTT [14,15].

The aim was to blend PTT with BADGE followed by addition of thermally reduced TRG to create the situation envisaged above, where ease of processing, crystallization nucleation, phase separation, reinforcement and plasticization are facilitated. A literature survey revealed that no work has been reported on this system and the present study can provide valuable information. The circumstances encountered as discussed above were analyzed using differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical analysis (DMA), and wide-angle X-ray scattering (WAXS), followed by investigation of degradation kinetics using thermogravimetry (TGA).

2. Experimental

2.1. Materials used

BADGE epoxy resin (Lapox L-12) with an epoxy equivalent between 5.25 and 5.40 eq·kg⁻¹ and viscosity between 1.15 and 1.20 cm² s⁻¹ was obtained from Atul Industries, Gujarat. Poly(trimethylene terephthalate) (PTT or SORONA 3G) with a density between 1.3 and 1.5 g cm⁻³, number average molecular weight (\bar{M}_n) of 22,500 g mol⁻¹ and polydispersity index (PDI) of 2.5 was kindly supplied by DuPont Industries, USA. Details of the materials used [13], and chemical characteristics of the TRG has been discussed elsewhere [16].

2.2. Nanocomposite preparation

Neat PTT and PTT-BADGE-TRG nanocomposites were prepared with a Thermo Fisher Rheomixer at a torque of 10 MPa, and temperature of 245 °C for 15 min. In all nanocomposite blends the ratio BADGE: TRG was fixed and the amount of TRG was taken as 0.1%·w/w of the weight of BADGE. This eliminates possibility of any predominance of plasticizer/nucleating agent on the basis of amount. The weight ratios of PTT, BADGE and TRG used for the study along with the designations used for the nanocomposites are given in Table 1. The nanocomposites blends so prepared were compression molded into sheets by pressing at 245 °C, and at 10 kPa, for 15 min. Nanocomposites so prepared were used for the following analysis.

2.3. Analysis

2.3.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were conducted using a PerkinElmer Diamond DSC. Nanocomposites prepared were subjected to the following measurements:

(a) Glass transition temperature (T_g)

T_g measurements were made on PTT, PTT-BADGE blends and BADGE using a PerkinElmer Diamond DSC. About 2–3 mg sample

was first heated to 260 °C at a heating rate of 10 K min⁻¹ and annealed for 3 min to remove any thermal history, followed by cooling to 20 °C at a rate of 10 K/min. The sample was then again heated to 260 °C at 10 K min⁻¹. Endothermic deviations from the baseline observed during the second heating cycle was recorded as representative of the blend morphology.

(b) Isothermal crystallization studies

Nanocomposites prepared were annealed at annealing temperature (T_a) = 260 °C for 1 min, followed by cooling at a rate of 20 K min⁻¹ to the respective crystallization temperature (T_c) (ranging from 190 to 210 °C) and held until crystallization was complete. The half-time of crystallization ($t_{0.5}$) was determined at $T_c = \text{const}$. The same procedure was applied for determination of the melting temperature. After crystallization for $5t_{0.5}$, samples were heated to 260 °C with a rate of 10 K min⁻¹. This procedure was used for the calculation of crystallization kinetics and equilibrium melting temperature (T_m°) by Hofmann-Weeks method.

2.3.2. Wide angle X-ray scattering studies (WAXS)

WAXS analysis was carried out on PTT and PTT-BADGE-TRG nanocomposites using a Bruker AXS D8 X-ray diffractometer equipped with a High Temperature XRD cell (HTK2000), between 2θ ranges of 10–35°.

2.3.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy studies on PTT and PTT-BADGE-TRG nanocomposites were carried out in attenuated total reflection (ATR) mode using PerkinElmer Spectrum One spectrometer (Lantrisant, UK). FTIR spectra were recorded in transmittance mode over the range of 4000–600 cm⁻¹ by an averaging 16 scans at a resolution of 4 cm⁻¹ in each case.

2.3.4. Dynamic mechanical analysis (DMA)

2.3.3.(i) Rectangular test specimens of dimensions (45 × 8 × 3.5 mm) were subjected to DMA using a PerkinElmer DMA8000, by means of three-point bending mode at a frequency of 1 Hz and oscillation amplitude of 0.05 mm. The nanocomposite specimens were scanned between temperature ranges of 30 °C–250 °C at 2 K min⁻¹.

2.3.5. Polarized optical microscopy

Morphologies of neat PTT and PTT-BADGE-graphene blends nanocomposites were imaged with a Nikon Labophot 2 microscope (Yokohama, Japan) equipped with a Linkam heating/cooling unit (Linkam TM 600/s) (Surrey, UK) with images collected using Leica Q Win software.

2.3.6. Thermogravimetry (TGA)

TG analysis was carried out on PTT, PTT-BADGE-TRG nanocomposites using PerkinElmer TGA7 instrument calibrated with Curie temperature metal standards. Samples were heated from room temperature to 800 °C at different heating rates of 5, 10, 15, 20 and 25 K min⁻¹ in dry nitrogen atmosphere. Results obtained was analyzed with Pyris software.

3. Results and discussion

Glass transition temperature (T_g) that is usually calculated by the half C_p extrapolation method is widely accepted as prima facie indication of extent of miscibility [17]. Changes of T_g upon addition of TRG can be well understood by considering the T_g characteristics of PTT-BADGE blends. Correlation shows that the normalized T_g provided a good fit with the Fox model indicating that the

Table 1
Weight ratios and designations of PTT and PTT-BADGE-TRG nanocomposites synthesized.

BADGE content (%·w/w)	TRG content (%·w/w)	Designation used
0	0	neat PTT
0	0.1 (PTT)	PTT–nanocomposite
5	0.1 (BADGE)	nanocomposite, 95%·w/w
10	0.1 (BADGE)	nanocomposite, 90%·w/w
20	0.1 (BADGE)	nanocomposite, 80%·w/w
30	0.1 (BADGE)	nanocomposite, 70%·w/w

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