Morphology controls of the melt blending in a novel highly crosslinked bismaleimide system

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Abstract

A novel bismaleimide of 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane (BMIP) with a broad working-temperature-range for the melt blending was successfully synthesized. BMIP possesses a considerably broad working-temperature-range from 75 °C to 250 °C, prior to undergoing cure reactions to form a highly crosslinked network. The morphology types of cured BMIP/clay hybrids can be controlled by varying the shearing temperatures and the contents of the clay. The conditions necessary for achieving an exfoliated or an intercalated BMIP/clay hybrid were thoroughly investigated via X-ray diffractometry, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). All the uncured samples prepared at different shearing temperatures and with an adequate amount of MMT-C (above 3 phr) exhibited an intercalated form of morphology. However, the crosslinking reactions for specified samples prepared at relatively elevated shearing temperatures (above 120 °C) and with a relatively low content of clay (below 15 phr) resulted in morphology changes from the intercalated form to the exfoliated form of morphology. There exists an isotropically mechanical property for the cured matrix of the exfoliated hybrids whereas there exists an anisotropically mechanical property for the cured matrix of the intercalated hybrids.

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1. Introduction

An intercalation is one of the most effective approaches to prepare polymer/clay hybrids, including solution intercalation, melt intercalation and intercalation polymerization [1]. The most practical and promising technique is the melt intercalation of the polymer into the interlayer gallery region of the clay, because melt intercalation can avoid problems associated with the search of appropriate solvents and their recovery in the solution intercalation and intercalation polymerization.

Although the melt intercalation was already applied in many thermoplastic polymers, most polyimides, including condensation types (linear polymers) and addition types (network polymers), were
still subject to solution intercalation. This is due to the fact that most condensation types of polyimides exhibit rigid structures and hydrogen bonding, resulting in non-thermoplasticity, and due to that some monomers for polybismaleimide networks do not provide the broader temperature range needed for melt intercalation. The working-temperature-range for melt intercalation is the temperature range between the melting temperature and curing temperature of the monomer. Taking 4,4'-bismaleimidodiphenylmethane (BMI) as an example for the addition types of polyimides, the working-temperature-range for melt intercalation is in the range of 160–165°C [2,3]. This working-temperature-range of 5°C is too small to facilitate melt intercalation.

Aromatic polyimides (PI) exhibit outstanding dielectric and mechanical properties at elevated temperatures [4]. Aromatic polyimides are one of the most frequently used polymers in microelectronic. Many condensation types of polyimides have been considered for the preparation of polymer/clay nanocomposites via the solution intercalation process [5–14], or via monomer solution intercalation polymerization [12,15]. Yano et al. [5] reported the synthesis and properties of PI/clay hybrid films with various lengths of clay and investigated the effect of the size of clay minerals on the properties of the hybrids. A pre-polymer of poly(amic acid) (PAA) was prepared from the polymerization of 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in dimethylacetamide (DMAc) solvent. The organoclay modified by the ammonium salt of dodecylamine was poured into the PAA solution and subsequently stirred vigorously. Then it was cast into film and dried by thermal treatment to remove the DMAc solvent so it could undergo imidization and produce the PI/clay hybrids. The same method as mentioned above was also applied by the other researchers, except that in some cases they utilized different types of dianhydride, and/or diamine, and/or surfactant. The mixing stage of the PAA solution and the organoclay plays an important role in the solution intercalation process. Polymer components in the PI/clay hybrids include PMDA-ODA [5,6,12], BTDA-ODA [7] (3,3',4,4'-benzophenone tetracarboxylic dianhydride with 4,4'-oxydianiline), BPDA-PDA [8,9,14] (3,3',4,4'-biphenyl-tetracarboxylic dianhydride with p-phenylenediamine), BPDA-APB (1,3-bis(3-aminophenoxy)benzene) [10,11], BPDPDA-PDA [13,14] (2,2-bis(4-(3,4-dicarboxyphenoxy) phenyl)propane dianhydride with p-phenylenediamine) BPDPDA-ODA-MDA (4,4'-oxydianiline and m-phenylenediamine) [14] and PMDA-MMDA (4,4'-diamino-3,3'-dimethylidiphenyl-methane) [15].

Delozier et al. [12] had examined several approaches in the PMDA-ODA system to achieve fully exfoliated nanocomposites. These approaches included simple mixing of the clay in a pre-made high molecular weight PAA solution, simple mixing followed by sonication of the organoclay/PAA solution, and the in situ polymerization in the presence of the organoclay dispersed in N-methyl-2-pyrrolidinone (NMP) solvent. It should be pointed out that all of these approaches were conducted in the solution condition.

Incidentally, Delozier and Working [16] prepared polyetherimide (PEI)/organoclay nanocomposites via in situ polymerization followed by melt processing. Polymer components in the PEI/clay hybrid are BPADA ([1-methylethylidienebis(1,4-phenyleneoxy)]bis-1,3-isobenzofurandiene) and MDA. The hybrid powers (polyetherimide (PEI)/organoclay) prepared via thermal imidization in solvent were dried and processed by melt mixing and extrusion. The clay dispersion of the PEI/clay powders was generally poor but was enhanced after melt mixing and extrusion. It should be pointed out that melt mixing and extrusion for this condensation type of PI were conducted at an elevated temperature (above 325°C).

These condensation types of polyimides and the corresponding hybrids are neither soluble nor fusible because of the high rigidity and conjugation of the polyimide backbone. This causes difficulties in fabrication via the melt intercalation and may limit their applications. On the other hand, most monomers of poly-bismaleimide (addition type of polyimide) usually do not exhibit the broader working-temperature-range necessary to fabricate a PI/clay hybrid via the melt blending process. To our knowledge, no report in the literature shows cross-linked PI/clay hybrids.

The objectives of this work are to synthesize a bismaleimide with a broader working-temperature-range, thereby facilitating melt blending in order to obtain a novel highly crosslinked PI/clay hybrid, and to control the morphologies of these hybrids by varying the shearing temperatures and the contents of the clay. The working-temperature-range of this bismaleimide should be broad enough to vary the temperature for shearing the clay into the melt bismaleimide before being cured. The conditions to achieving an exfoliated or intercalated bismaleimide/clay hybrids were thoroughly investigated.
2. Experimental

2.1. Materials

Maleic anhydride (MA) (Sigma, USA), 4,4’-(4,4’-isopropylidenediphenyl-1,1’-diyl)oxy) dianiline (DOPO) (Aldrich, USA), 4,4’-bismaleimidodiphenylmethane (BMI) (Aldrich, USA), acetic anhydride (TEA) (Aldrich, USA), nickel (II) acetate tetrahydrate (Riedel-deHaen, USA), and N,N-Dimethylformamide (DMF) (Tedia, USA) were used as purchased. Montmorillonite PK805 with a cation exchange capacity of 98 meq/100 g (MMT) (Pai-kong, Taiwan) served as the clay, and cetylpyridium chloride (CPC) (Sigma, USA) was used as a surfactant to modify the clay.

Chemical structures of DOPO, MA, BMI, CPC are shown below:

DOPO:

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{O} \\
& \quad \text{C} \\
& \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
\text{O} & \quad \text{H}_2\text{N} \\
& \quad \text{NH}_2
\end{align*}
\]

MA:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{O}
\end{align*}
\]

BMI:

\[
\begin{align*}
\text{N} & \quad \text{C} \\
& \quad \text{H}_2\text{N} \\
& \quad \text{N} \\
& \quad \text{O}
\end{align*}
\]

CPC:

\[
\begin{align*}
\text{O}^\ominus & \quad \text{H}_2\text{O} \\
& \quad \text{CH}_3(\text{CH}_2)_2\text{CH}_3
\end{align*}
\]

2.2. Instrumentation

(1) Differential scanning calorimetry (DSC): Samples approximately 3–6 mg in weight were sealed in hermetic pans and scanned in a differential scanning calorimeter (Perkin-Elmer DSC-7) calibrated with an indium standard. A stream of nitrogen at a flow rate of 20 mL/min was used to purge the DSC cell.

(2) Fourier-transform infrared (FTIR) spectra were recorded on a Digi-Lab FTS-40 FTIR spectrometer. The samples were mixed with dried KBr powder and pressed into pellets. Spectra were obtained in an optical range of 400–4000 cm\(^{-1}\) by averaging 32 scans at a resolution of 8 cm\(^{-1}\). (3) The molecular structure of the synthesized bismaleimide monomer was characterized by the chemical shifts in the \(^1\)H NMR spectrum (Varian UNITY INOVA-500) using CDCl\(_3\) as a solvent and TMS (tetramethylsilane) as the internal standard. (4) Constituents of the synthesized bismaleimide monomer were analyzed by an Elemental Analyzer (EA) (Elementar Vario EL 111, Germany). (5) The morphology of the fracture surfaces of the hybrid was observed with a JEOL 5610 scanning electron microscopy (SEM). (6) Wide-angle X-ray diffraction (XRD) spectra of the polyimide nanocomposites were recorded using a Rigaku, Dmmax-B diffractometer (Japan) with Ni filtered CuK\(_\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)) at a scanning rate of 1 °C/min over the range 2–10 °2\(\theta\), and an accelerating voltage of 40 kV and a 30 mA current. (7) Transmission electron microscopy (TEM) was performed with a JEOL JEM-2100F instrument using an accelerating voltage of 100 kV on ultra-thin samples (typically 60 nm) microtomed from polyimide nanocomposites, using an Ultracut-E Reichert Jung ultramicrotome. (8) Samples approximately 5–10 mg in weight were placed in platinum pans and scanned in a thermogravimetry analyzer (TGA) (TA Instrument TGA 2960) at a heating rate of 20 °C/min. A stream of nitrogen at a flow rate of 110 ml min\(^{-1}\) was used to purge the TGA chamber. (9) Storage moduli (\(E’\)) were determined through measurement of Perkin-Elmer dynamic mechanical analyzer (DMA-7) equipped with a thermal mechanical analyzer (TMA). Temperature was calibrated with an indium standard. Temp/time scan mode in tree-point bending method was used. The frequency, amplitude, and tension were set 1 Hz, 8.5 μm, and 100%, respectively. A stream of nitrogen at a flow rate of 30 mL/min was used to purge the DMA cell. The change of storage moduli (\(E’\)) were measured over the temperature range of 40–350 °C at a heating rate of 10 °C/min, thickness ca. 30 μm were used for measurement.

2.3. Synthesis of 2,2-bis[4-(4-maleimidophenoxy)-phenyl]propane (BMIP)

Takeda et al. [17] reported on the preparation of various bismaleimides containing ether bonds. A few simple modifications were made in this work to synthesize 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane (BMIP). A 1000-mL three-neck reactor was charged with 1.10 mol maleic anhydride (MA) and 200 mL DMF solvent, with the anhydride...
being completely dissolved. Another completely dissolved solution of 0.5 mol DOPO in 450 mL DMF solvent was slowly added into the flask over a period of 1 h at room temperature under a nitrogen atmosphere, and the mixed solution in the flask was stirred for 24 h at room temperature. Subsequently, the catalyst mixture of 1.5 mol AA, 0.25 mol TEA and 0.005 mol nickel (II) acetate tetrahydrate in 350 mL DMF solvent was slowly added into the flask and stirred for another 24 h. The resultant mixture was slowly poured into an excess amount of cold water. The pale-yellow precipitates were collected and washed in sequence with sodium bicarbonate solution (0.01 M), aqueous methanol solution (0.01 M) and pure water to remove the acetic acid and the unreacted reagents until the pH value was 7. The precipitates were re-dissolved and precipitated again, and again washed as described above. The purification cycles were repeated for several times. The final product (BMIP) was dried at a temperature of 60 °C for 24 h. The complete synthesis paths are illustrated in Scheme 1.

2.4. Characterization of 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane (BMIP)

The synthesized BMIP monomer was characterized by its FTIR spectrum, 1H NMR spectrum and elemental analysis (EA). The FTIR spectrum of the BMIP monomer is shown in Fig. 1A(a) and B(a), demonstrating the characteristic absorptions at 3100 cm⁻¹ (=C–H), 2973 cm⁻¹ (C–H), 1712 cm⁻¹ (C=O), 1397 and 1150 cm⁻¹ (C–N–C), 1240 cm⁻¹ (–O–), 686 cm⁻¹ (=C–H bending vibrations of maleimide moiety), 829 cm⁻¹ (out-of-plane bending of the =C–H group of maleimide moiety) [2,18]. These characteristic absorptions indicate the structure of the BMIP monomer.

The BMIP monomer is further evidenced by the 1H NMR spectrum. An analysis of the 1H NMR spectrum was conducted to identify the structure of the BMIP monomer and to quantify the purity of the produced precipitate (BMIP), as shown in Fig. 2. Each chemical shift was individually assigned and associated with the identified hydrogen atoms in the BMIP monomer, whose structure was inserted above spectrum. Among the characteristic chemical shifts, 1.69 ppm is attributed to the hydrogen atoms of the methyl groups (6 H). It should be noted that the produced precipitate (BMIP) was of considerable purity judging by the 1H NMR spectra (Fig. 2).

The structure and purity of the produced precipitate (BMIP) were also supported by the results of the elemental analysis (EA). The experimental values of C/N/O/H are equal to 73.00/4.85/16.82/4.70 in wt%, closely approaching the theoretical values of 73.70/4.90/16.80/4.60.

2.5. Curing behaviors of pristine BMIP

Dynamic DSC tests are a prerequisite in order to make sure that the working-temperature-range of the BMIP monomers should be broad enough to vary the shearing temperature of the clay into the melt bismaleimide before the cure reaction takes place. DSC runs for curing pristine BMIP and 1,1’-(methylene-4,1-phenylene) bismaleimide (BMI) were conducted for comparison at a heating rate of 20 °C/min, as shown in Fig. 3. BMI is one of the most frequently used bismaleimides. The DSC thermogram for neat BMI illustrates that the curing reaction occurs immediately after the temperature of the complete melting is reached, implying that BMI cannot be employed to the melt blending pro-
cess. By contrast, the DSC trace for the pristine BMIP illustrates that BMIP possesses a considerably broad working-temperature-range from 75 °C (endothermic peak, melting temperature) to 250 °C, prior to undergoing cure reactions. Cure reactions proceed from 250 °C to 380 °C (exothermic peak). When compared to BMI, the pristine BMIP shows a relatively low melting temperature ($T_m$) and a small endothermic enthalpy, which can probably be attributed to the effect of the ether linkage on the packing of molecules.

The DSC scan for BMIP shows an exothermic peak from 250 °C to 380 °C (shown in Fig. 3), indicating cure reactions occur, and complete cure is achieved after 380 °C. These cure reactions can be illuminated by the corresponding FTIR spectrum. Shown in Fig. 1 curves (a) and (b) are the FTIR spectra of BMIP monomer prior to being cured and the cured BMIP, respectively. The characteristic absorptions of the $\equiv$C–H bending vibrations of
It should be mentioned that the melt blending method for addition type polymers (network polymer), such as polybismaleimides, is restricted to the samples with a broader working-temperature-range.

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