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# 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 prac-

tical 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

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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], BDPDA-PDA [13,14] (2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride with *p*-phenylenediamine) BDPDA-ODA-MDA (4,4'-oxydianiline and *m*-phenylenedi-

amine) [14] and PMDA-MMDA (4,4'-diamino-3,3'-dimethyldiphenyl-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-methylethylidene)bis(1,4-phenyleneoxy)]bis-1,3-isobenzofurandiene) and MDA. The hybrid powders (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 crosslinked 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.

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