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Compatibilized polyimide (R-BAPS)/BAPS-modified clay nanocomposites with improved dispersion and properties

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Abstract

There is a need for clay modifiers that will not thermally degrade at elevated temperatures commonly used in polymer processing operations such as extrusion and injection molding. In this context, natural montmorillonite clay (Na-MMT) was organically modified by varying concentrations of 4,4′-bis(4″-aminophenoxy)diphenylsulfone (BAPS) using different chemical dispersion methods to yield new chemically modified clays that are relatively thermally stable at elevated temperatures compared with current commercial modified clays. This paper shows that the Na-MMT chemical modification (BAPS-MMT) was confirmed by XRD that showed a shift of diffraction peak at $2\Theta = 7.3°$ for Na-MMT towards lower $2\Theta = 5.8°$. Thermogravimetric analysis of the samples showed a weight loss of organically modified clay that started at a temperature of 350 °C, corresponding to the degradation temperature of the BAPS monomer. Rheological measurements in combination with XRD data showed clearly that the quality of dispersion of BAPS-MMT type particles in R-BAPS type polyimide and oligoimides strongly depends on the clay surface modification, the specific chemical modification method used, and on the polymer molecular weight. Note that the oligoimides were specifically used as model systems to confirm our expectation of improved chemical compatibility between the BAPS-MMT and the polyimide system. This study may stimulate a better understanding of the effects of rational chemical modification methods on the quality of clay dispersion in polyimide matrices, enhancing our ability to prepare useful polyimide/clay nanocomposites with improved properties for targeted high-temperature applications where current polymer nanocomposite systems are not useable.

Keywords: Polyimide and oligoimide; Nanocomposite; Structure and rheology

1. Introduction

Polymer/clay nanocomposites have attracted great academic and industrial interests in recent years because they exhibit unique microstructure with enhanced mechanical, thermal and barrier properties compared with conventional microcomposite at identical filler concentrations [1–9]. It is noteworthy that chemical modification of nanoparticles such as clay prior to their incorporation into polymer nanocomposites provides a convenient route to improve dispersion and to modify interfacial properties that may in turn improve the properties of the nanocomposites. Polyimide (PI) is widely used in the field of microelectronics and photonics application, because of their outstanding electrical properties, heat resistance, and chemical stability [10–12]. PI/clay nanocomposite has been reported to show relatively low coefficient of thermal expansion, low amount of moisture absorption, and low dielectric constant for improved performance in targeted application areas [13–22]. Yano et al. [13] prepared PI (PMDA–ODA)/clay composite film from solution mixing of polyamic acid (PAA) and dimethylacetamide (DMA) dispersion of clay. They used dodecylamine as the clay modifier and the resulting film showed reduced thermal expansion and gas permeability. However, they did not report the thermal and mechanical properties of the nanocomposite films. Yang et al. [14] fabricated and characterized PI (PMDA–MMDA)/clay composite film.

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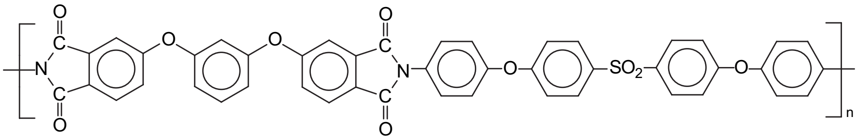
They used hexadecylamine as the clay modifier, and prepared a mixture of PAA with the clay dispersed in DMA followed by subsequent *in situ* polymerization of PAA in the mixture to yield (PMDA–MMDA)/clay composite film. The mechanical and thermal properties of the resulting film just mentioned were improved even in the presence of agglomerated clay particles, as confirmed by TEM image of the film. Delozier et al. [15] reported the morphology of PI/clay nanocomposite film containing clay modified with a long chain aliphatic quaternary ammonium salt. They showed that the modified clay particles were dispersed as stacked silicate layer structures in the polymer matrix. They suggested that the poor exfoliation of the clay particles in the polymer matrix may be due to decomposition of the organic modifier, leading to stacking of the clay particles during thermal imidization. These reported studies indicate that the thermal stability of organic modifiers is very important when modified clay is incorporated into high-performance polymers such as PI that are normally processed at relatively high temperatures.

Compared with the chemical modifiers already mentioned, aromatic ammonium salts are expected to provide improved thermal stability and compatibility between PI matrix and modified clay. To our knowledge, only a few research studies on PI nanocomposites containing clay modified with aromatic modifier have been reported in the literature [16–22]. Tyan et al. [16–18] modified natural clay with selected aromatic ammonium salts having multi-amine functional groups. They prepared PAA and the modified clay in DMA dispersion by solution mixing. The solution mixing involved the reaction between amine groups of the modified clay and anhydride end group of the PAA during the solution mixing. The resulting PI/clay nanocomposite film displayed intercalated and exfoliated structure of modified clay, and showed an increase in thermal and mechanical properties. Vora et al. [19] and Liang et al. [20,21] reported studies on PAA/modified clay dispersion where the clay was modified with aromatic ammonium salts followed by *in situ* polymerization of PAA to yield the corresponding PI/clay nanocomposite film. Campbell and Scheiman [22] prepared nanocomposites of PMR-15 polyimide and a diamine-modified clay where the clay was modified with four types of aromatic ammonium salts having diamine functional groups. While few studies on PI/clay nanocomposites have been reported in the literature, the effects of chemical modification method on dispersion of clay in PI matrix (thermoplastic or thermosetting type) are little studied and poorly understood.

The current study is aimed at understanding the effects of various chemical modification methods on the state of dispersion of clay particles in PI matrix. 4,4′-Bis(4″-aminophenoxy)diphenylsulfone (BAPS) was used as an aromatic modifier to improve thermal stability of montmorillonite (MMT) type clay as compared with commercially modified clay (Cloisite 15A, supplied by Southern Clay Products) used earlier in our previously reported study [23]. In this article we report an efficient method of incorporating organically modified BAPS-MMT particles into a relatively new type of amorphous PI R-BAPS type matrix [26–28] based on diamine BAPS and dianhydride 1,3-bis(3′,4,-dicarboxyphenoxy)-benzene (R):



As previously reported [24–26], this PI R-BAPS type (denoted here as PIR-BAPS) is soluble in aprotic solvents and can be converted into plastic fluid state at temperatures higher than 320 °C, giving the possibility to use different methods such as solution and melt blending for incorporating BAPS-MMT type nanoparticles into the polymer matrix. The influence of molecular weight of this amorphous PI on the rheology and morphology of the pure PI and on the PI filled with BAPS-MMT nanoparticles will be investigated. Special attention will be given to the method of MMT surface modification by BAPS and to different methods of incorporating BAPS-MMT particles into PI R-BAPS matrix such as melt or solvent blending. It is anticipated that the present study will stimulate a better understanding of the effects of chemical modification methods on the quality of clay dispersion in polyimide matrices, enhancing our ability to prepare new PI/clay nanocomposites with improved properties. In addition, the study may provide alternative routes to preparing useful PI/clay nanocomposites such as pre-dispersing of chemically compatible modified clay particles in oligoimides as already mentioned followed by subsequent chemical transformation in the melt state of the oligoimide/clay mixture into PI/clay nanocomposites in a conventional polymer processing equipment such as extrusion and injection molding, making the resulting nanocomposites widely applicable. Further, the study is based on the premise that optimal dispersion of nanoparticles is not trivial and it is a critical necessary precondition to achieve optimal performance properties from polymer nanocomposites in general.

2. Experimental

2.1. Organic treatment of MMT

Natural montmorillonite clay Na-MMT [Cloisite® Na^+, cation exchange capacity (CEC): 92.6 meq/100 g] was obtained from Southern Clay Products, Inc. Hydrochloric acid (concentration: 36.5%) and 4,4′-bis(4″-aminophenoxy)diphenylsulfone (BAPS) were obtained from Fisher Chemical and Wakayama Seika Kogyo Co., Ltd. in Japan, respectively.

Na-MMT was organically modified with BAPS ammonium salts following the steps shown in Fig. 1. A mixture of BAPS

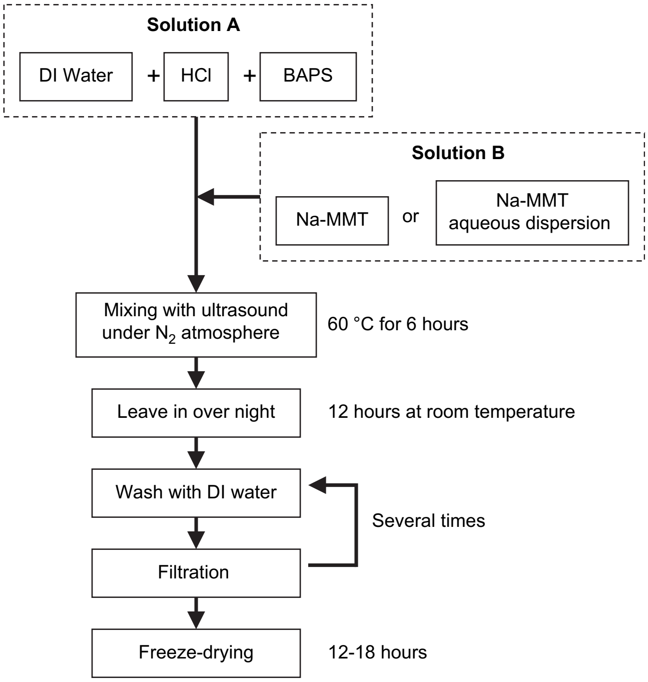


Fig. 1. Elementary steps for modification of natural montmorillonite Na-MMT.

and hydrochloric acid in deionized water (DI water) was prepared. Subsequently, either Na-MMT or aqueous dispersion of Na-MMT that was agitated for 3 h was added to the previously prepared mixture. The resulting mixture was agitated simultaneously with mechanical stirrer and ultrasound at 60 °C for 6 h, and the mixture was then left at room temperature for 12 h. The resulting white precipitate was filtered and washed repeatedly with DI water at 60 °C to remove superfluous ammonium salts and Cl^- ion. Removal of Cl^- ion was monitored by titration with addition of 0.1 N $AgNO_3$ into the filtered liquid (based on whether white precipitation of AgCl appeared or not). The filtered cake was freeze-dried for 12–18 h to yield BAPS-modified clay (BAPS-MMT).

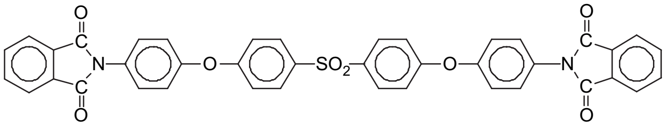
The three different chemical modification methods used are summarized in Table 1. The Na-MMT powder was added to the solution containing DI water + HCl + BAPS to give the modified clay denoted by Clay A. Note that the pH of the resulting Clay A mixture was adjusted to 1.6 after agitation of the mixture. For the modified clays denoted by Clay B and Clay C, Na-MMT was pre-dispersed in DI water with ultrasound for 2 h prior to mixing it with solution A containing DI water + HCl + BAPS and the pH of the resulting Clay B and Clay C solutions was adjusted to 9.7. Note that Clay B and Clay C differed only in the concentration of BAPS used as depicted in Table 1. The ratio of amount of BAPS to CEC of Na-MMT was maintained at 1:1 for Clay A and Clay B and at 2.5:1 for Clay C.

Table 1
Material compositions used in chemical modification of natural montmorillonite clay (Na-MMT)

Modified clay	Solution A			Solution B	
	Water (g)	HCl (g)	BAPS (g)	Water (g)	Na-MMT (g)
Clay A	150	1	0.8	–	2
Clay B	50	1	0.8	100	2
Clay C	50	1	2	100	2

2.2. Preparation of oligoimides with different molecular weights

To understand the effects of molecular weight on dispersion quality, a number of oligoimides (OI) with different molecular weights were synthesized by controlling the ratio of monomers to endcapper (i.e., phthalic anhydride (PA)). Here, poly(amic acid) (PAA) was obtained by polycondensation of 1,3-bis(3′,4,-dicarboxyphenoxy)benzene (R) and 4,4′-bis(4″-aminophenoxy)diphenylsulfone (BAPS) in a 20 wt% solution of *N*-methyl-2-pyrrolidone (NMP) at 25 °C. The polyamic acids (PAA) were subsequently converted to the respective PIs (R-BAPS-PA) by using solution imidization techniques [25,26]. An azeotropic liquid (toluene) was added to the PAA solution to yield an 80/20 ratio of NMP to toluene that was then stirred at ~180 °C under nitrogen. After ~5 h of azeotropic distillation of the water by-product, a yellowish brown, highly viscous solution of PIs with phthalimide end groups was obtained. After cooling, this PI solution was diluted with NMP and slowly added to a vigorously stirred reaction flask containing alcohol. The resulting white powder was filtered, washed with water, and dried in vacuum oven at ~200 °C overnight and subsequently at 250 °C for 2 h to ensure complete imidization. Molecular weight during the synthesis was controlled through stoichiometric offset of the monomers (i.e., dianhydride, diamine and phthalic anhydride). Table 2 summarizes the properties and molecular weights of the R-BAPS-PA type PI and oligoimides S1 and S2 obtained from gel permeation chromatography. The lowest molecular weight of the oligoimide S0 that was synthesized corresponds to the diamine BAPS endcapped by PA (M_n ~ 700 g/mol):



2.3. Sample preparation

2.3.1. Preparation of nanocomposites by solution mixing of OI or PI with clay

Simple solution mixing method was used to prepare a mixture of NMP solution of OI or PI with the modified MMT clay

Table 2
Properties and molecular weights of R-BAPS type PI and oligoimides S1 and S2

Sample	Stoich. offset (%)	T_g (°C)	M_n (g/mol)	M_w (g/mol)	PDI
S1	50	153	3609	11,553	3.2
S2	20	201	8845	23,603	2.7
PI	5	220	18,558	50,133	2.7

Note: T_g is glass transition temperature; M_n is number average molecular weight; M_w is weight average molecular weight; PDI is polydispersity.

as follows. Firstly, the modified clay was dispersed in NMP with the aid of ultrasonic mixer (40 kHz, average sonic power: 45 W) for 1 h. Various amounts of the modified clay were used to obtain the final OI/MMT or PI/MMT mixture containing 3–20 wt% of the modified MMT clay. Subsequently, NMP solution of OI or PI (20 wt% OI or PI concentration) was added to the modified MMT/NMP dispersion, and the combined mixture was stirred with magnetic stirrer for 5 h followed by ultrasonic mixing of same for 1 h. The resulting NMP dispersion of OI or PI with modified MMT was poured on a Teflon-coated metal substrate that was subsequently dried at 100 °C for 1 h, 200 °C for 1 h, and 280 °C for 0.5 h to remove NMP solvent completely (drying was controlled with the aid of TGA). The Teflon coating on the metal substrate greatly facilitated collection of the OI/BAPS-MMT or PI/BAPS-MMT nanocomposites in the form of film or powder after drying.

2.3.2. Injection molding of nanocomposite samples

The PI/clay nanocomposites after solution mixing and evaporation of NMP were injection molded into standard test specimens using a DACA® Instruments MicroInjector. The test specimens had the following dimensions: length = 20 mm, width = 5 mm, and thickness = 1 mm. These specimens were prepared using a barrel temperature of 380 °C, mold temperature of 90 °C and injection pressure of 100 bar.

2.4. Measurements

The polymer molecular weights, molecular weight distributions, and polydispersity indices were determined by size exclusion chromatography (SEC) in DMF at a flow rate of 1.0 mL/min and 40 °C. The equipment used comprises a Waters 515 HPLC pump, Waters 2410 RI detector, Waters 2457 Dual l absorbance detector, column oven, and a Polymer Labs PLgel 5 mm MIXED-C 300 × 7.5 mm column. The column was calibrated with a series of narrow molecular weight distribution poly(methyl methacrylate) standards (obtained from Polymer Laboratories). Data were acquired and analyzed using the Waters Empower computer software package.

The XRD patterns of the modified MMT particles, aqueous dispersion of Na-MMT, and PI/modified MMT nanocomposite were recorded with an X-ray diffractometer (D/MAX Ultema®, Rigaku Co., Ltd.). The X-ray was generated with nickel-filtered Cu Kα ($\lambda = 0.154$ nm) at 40 kV and 44 mA. The samples were scanned at 2Θ angles ranging from 2° to 10° using a scanning rate of 10°/min at room temperature. An increase in the basal layer spacing of organically modified MMTs of the PI/MMT nanocomposites, which was determined from a shift in the (001) peak position, confirmed ion exchange or polymer intercalation between the silicate layers. The corresponding d-spacing value was calculated from the diffraction peak maximum, using Bragg equation: $d = \lambda/2 \sin \Theta$.

Thermogravimetric analysis (TGA) curves were recorded with a comprehensive Perkin–Elmer thermal Analysis 7 system. The TGA measurements were conducted using 5–10 mg samples contained in a platinum crucible with a heating rate of 10 °C/min under a nitrogen atmosphere.

A strain-controlled dynamic rheometer (ARES® from TA Instruments) was used to measure the dynamic and steady shear viscosity of polymers in the cone and plate configuration within a 5% accuracy following standard procedures. The diameter of the plate was 25 mm and the cone angle was 0.1 rad. Nitrogen was used as the heating gas for temperature control. The powdered samples were compacted into discs at room temperature using a compression molding machine. The disk was then subsequently placed between the plates of the rheometer that were preheated to the desired temperature.

The torsion rectangular test fixture of the ARES was used for measuring storage shear modulus G' of the molded nanocomposites with dimensions: length = 20 mm, width = 5 mm, and thickness = 1 mm. The samples were held in tension between the upper and lower tool. Dynamic oscillatory strain frequency sweep experiments were performed at a frequency of 1 rad/s and a linear strain of 0.1%.

3. Results and discussion

3.1. BAPS-modified clay (BAPS-MMT)

The XRD patterns of BAPS-modified MMT (BAPS-MMT) together with that of Na-MMT are shown in Fig. 2. A diffraction peak at around $2\Theta = 7.3°$ corresponding to an interlayer spacing of 1.2 nm was observed in Na-MMT. Diffraction peaks at $2\Theta = 5.8°$ (equivalent to interlayer spacing of 1.5 nm) were displayed by BAPS-MMT regardless of the specific modification method used. These results indicate that modification of Na-MMT with BAPS increases its interlayer spacing, an experimental fact that is consistent with that reported in the literature on clay particles modified with aromatic ammonium salts [19,22]. For example, Vora et al. [19] and Campbell and Scheiman [22] reported a diffraction peak located at $2\Theta \sim 6°$ in the XRD patterns of BAPS-MMT and of

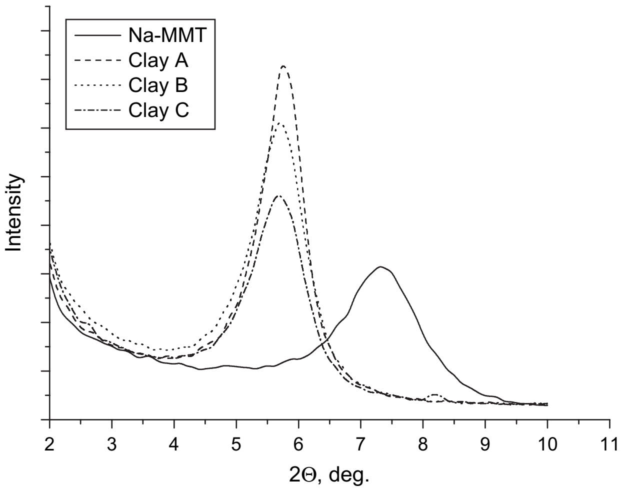


Fig. 2. XRD patterns of modified clay particle and natural montmorillonite clay particle (Na-MMT). See text for sample nomenclature.

clay modified with various diamine such as *p*-phenylene diamine, methylene dianiline, 4,4′-(1,4-phenylene-bismethylene)-bisaniline, and 4,4′-bis(4-aminobenzyl)diphenylmethane.

The TGA data of the respective clays are shown in Fig. 3 together with that of the pure BAPS monomer for comparison. Significant onset of weight loss of BAPS-MMT is evident at about 350 °C, and can be ascribed to the loss of BAPS monomer that is known to thermally decompose at these temperatures (Fig. 3). The weight loss of BAPS-MMT at temperatures ranging from 350 °C to 800 °C was found to be 14 wt%, 13 wt%, and 32 wt% for Clay A, Clay B, and Clay C, respectively. If all of the BAPS monomers used were chemically (ionic) bonded with Na-MMT, the weight loss of the modified MMT should be 28.6 wt% for Clay A and Clay B, and 50 wt% for Clay C depending on the amount of BAPS used during the chemical modification (see Table 1). The appearance of two thermal degradation steps in the TGA data (clearly evident for Clay C but less clearly evident for Clay A and Clay B) (Fig. 3) is thought to be connected with the presence of BAPS type monomers in the BAPS-MMT powder that is chemically unreacted with the platelet surface of MMT. Additional supporting evidence for the presence of unreacted BAPS type monomer (i.e., not ionically bonded with MMT) can be seen in the X-ray data (Fig. 4) for Clay C in the range of $2\Theta = 17-22°$, where the crystalline form of BAPS has strong reflections at $2\Theta = 17.8°$ and 18.2°. Because these reflections are only observed for Clay C and not observed for Na-MMT, it can be concluded that a portion of the BAPS monomer exists in the BAPS-MMT powder in the crystalline form that is not ionically bonded with MMT platelets.

3.2. Dispersion of BAPS-MMT particles in NMP solvent

For the processing of PI/BAPS-MMT nanocomposites by solvent casting method, it is crucial to determine optimal conditions for efficient dispersion of the nanoparticles in aprotic solvents such as NMP that is commonly used for dissolving R-BAPS type PI. To investigate the feasibility of formation of homogeneous nanodispersion of BAPS-MMT in NMP, we used the rheology method that was shown previously [23,27] to be an effective method for characterizing the exfoliation of clay or silicate nanotubes in a suitable solvent. Homogenous dispersion of nanoparticles in a suitable solvent leads to gelation of the solution that exhibits a shear- and time-dependent (thixotropic) behavior that is ascribed to the formation of a percolation type network at some critical concentration of the nanoparticles used. Therefore, the efficiency of the chemical modification of MMT by BAPS and its subsequent role in dispersing the modified particles in NMP can be reliably monitored indirectly by comparing the gelation process of the dispersions as a function of modified clay concentration.

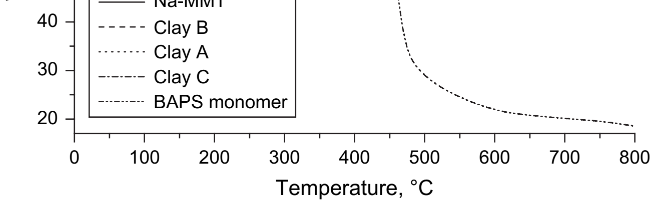


Fig. 3. TGA scans for Na-MMT, modified clay particles, and BAPS monomer obtained at a heating rate of 10 °C/min under nitrogen (see text for sample nomenclature).

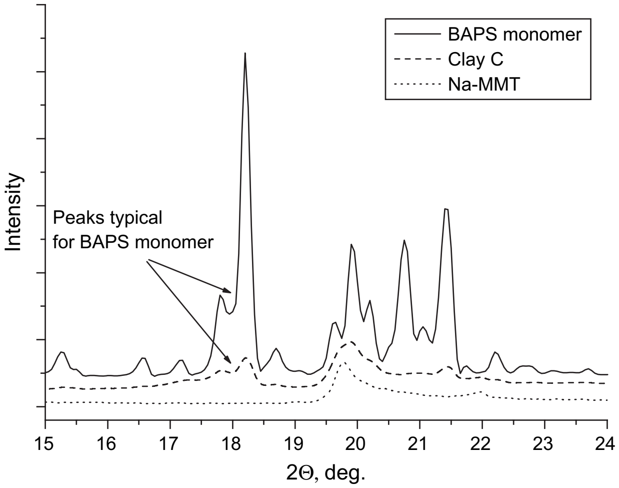


Fig. 4. XRD patterns of BAPS type monomer, modified particles (Clay C) and natural montmorillonite clay particle (Na-MMT). See text for sample nomenclature.

The dispersions of different BAPS-MMT concentrations (from 1 to 20 wt%) in NMP solvent were typically prepared in separate beakers that were subjected to ultrasonic mixing for 1 h in an ultrasound bath (VWR, ultrasonic cleaner model 50HT, frequency: 40 kHz, average sonic power: 45 W). The resulting translucent BAPS-MMT dispersions were used to perform rheological measurements. Note that all the solutions exhibited, at appropriate concentration of BAPS-MMT particles depending on type of chemical treatment (i.e., Clay A, B or C), typical gel-like behavior and a gel structure that was observed to be very stable for a long period of time (≥1 week) in a closed bottle.

Dynamic frequency sweeps with a linear strain of 1% at room temperature in the cone/plate geometry were used to characterize the equilibrium state of the nanodispersions of BAPS-MMT in NMP as shown in Fig. 5. Three measurements were made at one frequency to ensure that solvent evaporation did not occur during the experiment. Fig. 5 shows the dependence of complex viscosity on weight concentration of the BAPS-MMT particles in NMP. Clearly, dramatic increases in the viscosity of the Clay B/NMP and Clay C/NMP

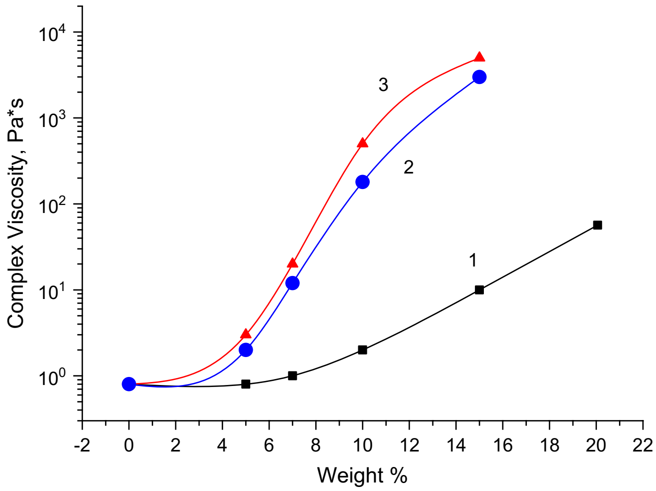


Fig. 5. Dependence of complex viscosity of NMP dispersions of Clay A (1), Clay B (2) and Clay C (3) on their weight percent in NMP solvent. Temperature = 25 °C, frequency $\omega = 1$ rad/s, strain $\varepsilon = 1\%$. See text for sample nomenclature.

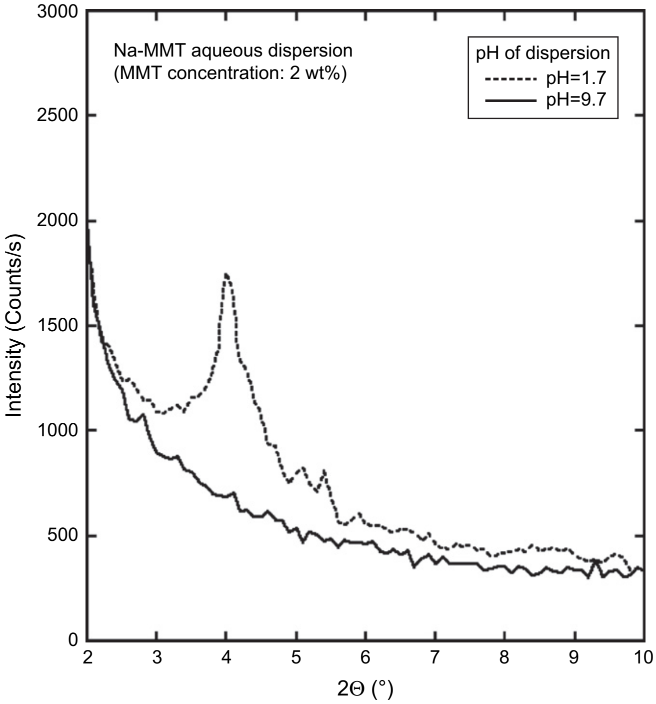


Fig. 6. XRD patterns of 2 wt% Na-MMT aqueous dispersion at different pH values (pH = 1.7 and 9.7).

nanodispersions are evident at approximately the same weight fraction of the MMT type particles (~5–7 wt%). This concentration is remarkably close to that obtained from Cloisite®-15A (or 20A)/xylene nanodispersions as previously reported elsewhere [23,28]. In contrast, the viscosity increase of the Clay A/NMP nanodispersion occurred at relatively high concentrations of the BAPS-MMT particles (~12–15 wt%), indicating a significantly lower dispersibility of Clay A in NMP compared to that of the Clay B and Clay C nanodispersion in NMP.

In an effort to find an explanation for the obvious differences in the quality of dispersion of Clay A and Clay B in NMP solvent, the role of pH was explored by measuring the XRD pattern of an aqueous solution of Na-MMT with varying pH and constant concentration of Na-MMT. Fig. 6 shows the XRD patterns of 2 wt% aqueous dispersion of Na-MMT at different pH (i.e., acidic and basic conditions). The 2 wt% of Na-MMT was added to DI water of pH = 1.5 and 7.0, respectively. After agitating the dispersions using ultrasonic mixing for 3 h, the pH increased from 1.5 to 1.7 and from 7.0 to 9.7, respectively, due to well-known basic properties of Na-MMT in water. It is clear from Fig. 6 that aqueous dispersion of Na-MMT at pH = 9.7 did not show any diffraction peak, suggesting that the Na-MMT particles are well exfoliated in DI water. On the other hand, the aqueous dispersion of Na-MMT at pH = 1.7 exhibited significant diffraction peak at around $2\Theta = 4.1°$, indicating that the Na-MMT particles exist as stacked silicate layer structures in the DI water of pH = 1.7. Note that during the preparation of Clay A, Na-MMT powder was added into solution A (see Table 1 and Fig. 1) having a pH = 1.5. Under this low pH condition, Na-MMT does not exfoliate. Therefore, in this case MMT is modified by the BAPS salts while the stacked silicate layer structures are preserved. In contrast, Clay B is prepared by dispersing Na-MMT in DI water of pH = 7 resulting in a mixture with a pH of 9.7 after agitation with ultrasonic mixing for 3 h. Based on the results shown in Fig. 6, it is reasonable to expect that Na-MMT is well exfoliated in the DI water of pH = 9.7. Therefore, when the aqueous dispersion of Na-MMT (solution B) and solution A including BAPS are combined, exfoliated Na-MMT particles are homogeneously modified with the BAPS salt. This experimental fact supports the conclusion that finely dispersed structure of BAPS-MMT in Clay B and Clay C is preserved even after washing, filtering, and freeze-drying as already described in Section 2. The pH effects just described are expected to explain the difference in the possibility to give homogenous dispersion in NMP for Clay A, Clay B and Clay C. Based on the above findings, Clay B was selected for melt processing the nanocomposites with PI type R-BAPS and for OIs by using the solvent casting method. This selection of Clay B is consistent with the fact that Clay B shows good dispersibility in NMP as compared with Clay A, and that the content of BAPS monomer in Clay B is approximately twice lower than that in Clay C.

3.3. Dispersion of BAPS-MMT particles in R-BAPS-polyimide (PI) and R-BAPS-oligoimide (OI)

It was previously reported [23] that application of strong shear flow in an extruder is crucial to good dispersion of MMT-15A (Cloisite 15A, Southern Clay Products) in the melt of R-BAPS-oligoimides (OIs). The significant viscosity increase exhibited by the OI/MMT nanocomposites after application of the strong shear flow fields was attributed to the partial exfoliation of the MMT-15A particles and formation of a percolating (network) structure at ~10 wt% of MMT-15A particles in the OI melt [23]. It will be shown later that the present BAPS-modified MMT (BAPS-MMT) can be readily dispersed in polyimide nanocomposites without the need of applying strong shear flows as in the case of MMT-15A/oligoimide nanocomposites reported previously [23].

In the present study, BAPS-MMT is dispersed in solutions of OI or PI in NMP solvent due to the good dispersibility of Clay B (and Clay C) in NMP solvent as already described (see Section 3.2). Fig. 7 shows the dependence of complex viscosity (frequency $\omega = 1$ rad/s, strain $\varepsilon = 1\%$) for BAPS-MMT/OI or BAPS-MMT/PI nanocomposites prepared as already described in Section 2. The complex viscosity of the BAPS-MMT/PI and BAPS-MMT/OI nanocomposites was measured at 360 °C and 260 °C, respectively. Note that the respective temperatures were chosen because they correspond to the fluid state of the OI or PI used in this study. Clearly, Fig. 7 shows a significant increase of viscosity by about four decades for the oligoimide S1/Clay B or oligoimide S2/Clay B nanocomposites at a concentration of 5−10 wt% of nanoparticles. This experimental result is in good agreement with the result reported in Ref. [25], with the important difference that in Ref. [25] the gelation (or solidlike behavior) of the OI/MMT samples occurred only after melt blending with the application of strong shear flows. In contrast, gelation occurred for the present samples after simple solution mixing of the OI and BAPS-MMT particles and subsequent evaporation of the NMP solvent. Similar trends in the viscosity of the PI/Clay B were obtained in the same nanoparticle concentration range as before but with a relatively lower increase in viscosity (i.e., two decades increase) (Fig. 7). It is noteworthy that gelation is not observed for the OI/Na-MMT nanocomposite (curve 4 in Fig. 7), indicating that the dispersibility of pure Na-MMT particles in OI is poor compared with that of chemically modified Clay B particles which is homogenously dispersed in the polymer volume even without the application of shear deformation and flow as already discussed.

While the results of the rheology experiments just described suggest partial exfoliation of Clay B particles in polymer volume that is consistent with a significant increase of the viscosity at clay concentrations near the percolation threshold, it is worthy to note that the X-ray data (Fig. 8) does not show evidence of complete exfoliation for the PI/Clay B and OI/Clay B samples at clay concentration of 10 wt%. This suggests that some of the clay platelets especially in the samples with relatively high concentration of MMT particles (i.e., >5 wt%) may aggregate after NMP solvent evaporation during processing of the OI or PI/MMT nanocomposites. This hypothesis is consistent with the observed XRD peak at $2\Theta = 6.5°$ ($d = 1.35$ nm) which may be regarded as an indirect evidence of the aggregation of the clay platelets. Note that the intensity of this peak decreases slightly with decreasing molecular weight of the polymer used (i.e., from PI to OI molecular weight). In addition, it can be seen in Fig. 8 that this peak is not observed for the OI sample with the lowest molecular weight (i.e., S0 sample) filled with 10 wt% of Clay B, indicating the absence of such type of clay aggregation in this sample. Note that the oligoimide (S0) has very similar chemical structure to the BAPS monomer as already mentioned. From the preceding experimental results, it can be concluded that chemical compatibility of the clay surface treatment with the polyimide matrix together with relatively low molecular weight of the polyimide matrix are necessary prerequisites for obtaining enhanced dispersion of the clay nanoparticles. This interesting result can be exploited in future studies to yield useful polyimide nanocomposites via processing of relatively low molecular weight prepolymers of the IDA type obtained from melting of the appropriate dianhydride and diacetyl derivatives of aromatic diamine, and subsequently followed by a chemical transformation at 300 °C into PI in the processing equipment as we previously reported for PI bonded magnets [29,30]. Therefore, the synthesis and processing routes to useful polyimide nanocomposites reported in the current article is expected to be widely applicable to a range of polyimide nanocomposite systems that cannot be processed using traditional methods.

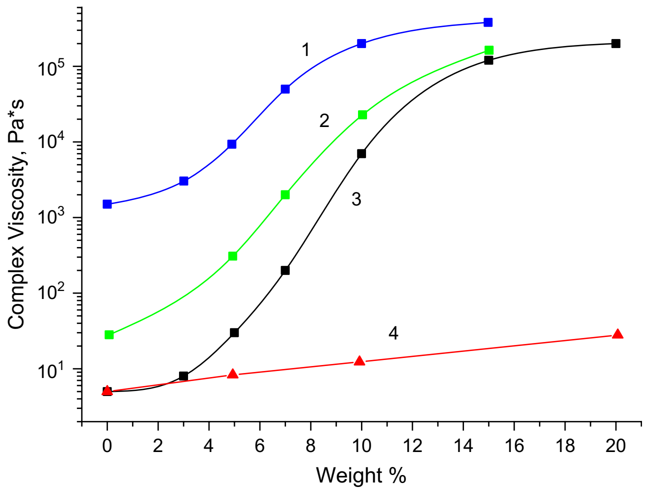


Fig. 7. Concentration dependencies of complex viscosity nanocomposites prepared from NMP: 1 − PI/Clay B, $T = 360$ °C; 2 − S1/Clay B, $T = 260$ °C; 3 − S2/Clay B, $T = 260$ °C; 4 − S2/Na-MMT, $T = 260$ °C. Frequency $\omega = 1$ rad/s, strain $\varepsilon = 1\%$. See text for sample nomenclature.

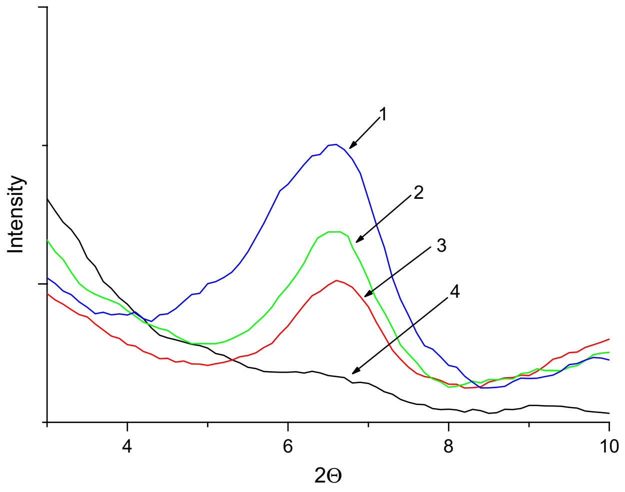


Fig. 8. XRD patterns of nanocomposites containing 10 wt% Clay B prepared from NMP: 1 − PI/Clay B; 2 − S1/Clay B; 3 − S2/Clay B; 4 − S0/Clay B. See text for sample nomenclature.

The clay concentration dependence of storage shear modulus G' obtained from the injection molded samples of PI/Clay B and PI/Na-MMT (Section 2.3.2) is shown in Fig. 9. It is clearly evident from this figure that the modulus increases with increasing clay concentration in both cases. However, the increase in modulus is more significant for the PI/Clay B than for the PI/Na-MMT samples. The increase of shear modulus for the PI/Clay B nanocomposite was estimated to be ∼0.07 GPa/wt% MMT, a value that is larger than that (∼0.03 GPa/wt% filler) of PI/Na-MMT. This modulus increase is also larger than that reported elsewhere by others for conventional composites containing plate-like fillers [18]. The results depicted in Fig. 9 are consistent with relatively good dispersion of Clay B type particles in PI that was confirmed by the XRD and rheology measurements as already described, supporting our expectation that useful PI/BAPS-MMT nanocomposites with enhanced modulus can be prepared using the experimental protocol described in this article.

4. Conclusions and outlook

Natural montmorillonite clay (Na-MMT) was organically modified successfully with 4,4′-bis(4″-aminophenoxy)diphenylsulfone (BAPS) as confirmed by X-ray diffraction and TGA measurements. The TGA showed a weight loss of organically modified clay starting at 350 °C that corresponds to the degradation temperature of the BAPS monomer used. This relatively high degradation temperature should make it possible for the first time to use this organically modified clay BAPS-MMT for the fabrication of nanocomposites from PI matrix or other high-temperature and high-performance polymers that must be processed at elevated temperatures. It is worthy to note that current commercial clay nanoparticles are not useable at such elevated processing temperatures because they thermally degrade at relatively lower temperatures. The chemical modification of the MMT particles to yield BAPS-MMT particles using the special method described in this study significantly enhances the compatibility and dispersion of the polyimide (R-BAPS type) nanocomposite constituents, as well as, their mechanical properties. In addition, homogeneous dispersion of BAPS-MMT nanoparticles in NMP solvent that is suitable for dissolving R-BAPS type PI leads to gelation of the solution at some critical concentration of the nanoparticles used to an extent that depends on the method and efficiency of the chemical treatment of the clay. The results showed that the method of pre-dispersing Na-MMT in DI water before chemical modification with aromatic ammonium salts is the most efficient method to significantly improve the dispersibility of the BAPS-MMT particles in both NMP and R-BAPS type PI. Further, the decrease of molecular weight from polyimides to oligoimides is preferable for optimal clay dispersion in the polymer volume using the solution mixing method. The benefit of using relatively low molecular weight oligoimides is thought to be important because it may be useful for melt processing useful PI nanocomposites from low molecular weight prepolymers and BAPS-MMT particles followed by subsequent chemical transformation of the prepolymer into PI via an *in situ* chemical reaction in the melt carried out in the processing equipment. This study may stimulate a better understanding of the effects of rational chemical modification methods on the quality of clay dispersion in polyimide matrices, enhancing our ability to prepare useful polyimide/clay nanocomposites with improved properties for targeted high-temperature applications where common polymer nanocomposite systems are not useable.

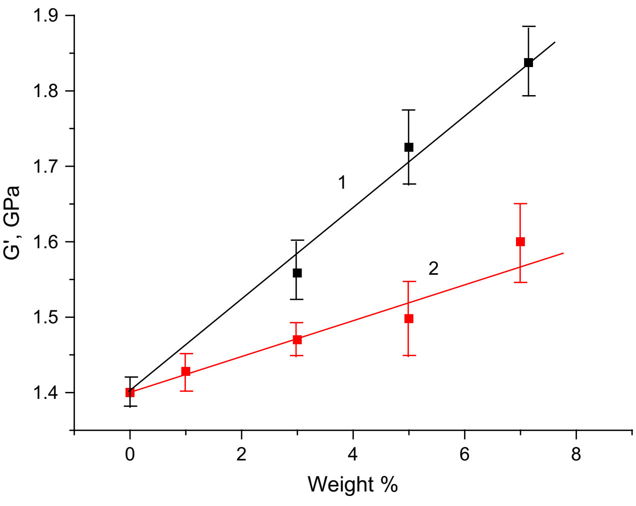


Fig. 9. Dependence of storage shear modulus for PI/Clay B (1) and PI/Na-MMT (2) nanocomposites on clay concentration.

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References

[1] Ray SS, Okamoto M. Prog Polym Sci 2003:1539.
[2] Giannelis EP. Adv Mater 1996;8:29–35.
[3] Giannelis EP, Krishnamoorti R, Manias E. Adv Polym Sci 1999;138:107.
[4] LeBaron PC, Wang Z, Pinnavaia TJ. Appl Clay Sci 1999;15:11.
[5] Vaia RA, Price G, Ruth PN, Nguyen HT, Lichtenhan J. Appl Clay Sci 1999;15:67.
[6] Biswas M, Ray SS. Adv Polym Sci 2001;155:167.
[7] Xu R, Manias E, Snyder AJ, Runt J. Macromolecules 2001;34:337.
[8] Bharadwaj RK. Macromolecules 2001;34:1989.
[9] Kojima Y, Usuki A, Kawasumi M, Fukushima Y, Okada A, Kurauch T, et al. J Mater Res 1993;8:1179.
[10] Bessonov MI, Koton MM, Kudryavtsev VV, Laius LA. Polyimides: thermally stable polymers. New York: Plenum Publishing Corp.; 1987.
[11] Wilson D, Stengenberger HD, Hergenrother PM. Polyimides. New York: Chapman & Hall; 1990.
[12] Sroog CE. In: Ghose MK, Mittal KL, editors. Polyimides: fundamentals and applications. New York: Marcel Dekker; 1996. p. 1.
[13] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. J Polym Sci Part A Polym Chem 1993;31:2493.
[14] Yang Y, Zhu Z-K, Yin J, Wang X-Y, Qi Z-E. Polymer 1999;40:4407.
[15] Delozier DM, Orwoll RA, Cahoon JF, Johnston NJ, Smith Jr JG, Connell JW. Polymer 2002;43:813.

[16] Tyan Horng-Long, Liu Yau-Cheng, Wei Kung-Hwa. Chem Mater 1999;11:1942.

[17] Tyan Horng-Long, Leu Chyi-Ming, Wei Kung-Hwa. Chem Mater 2001;13:222.

[18] Tyan Horng-Long, Wei Kung-Hwa, Hsieh Tsung-Eong. J Polym Sci Part B Polym Phys 2000;38:2873.

[19] Vora Rohit H, Pallathadka Pramoda K, Goh Suat Hong, Chung Tai-Shung, Lim Yong Xiong, Bang Toong Kiang. Macromol Mater Eng 2003; 288:337.

[20] Liang Zhu-Mei, Yin Jie, Xu Hong-Jie. Polymer 2003;44:1391.

[21] Liang Zhu-Mei, Yin Jie. J Appl Polym Sci 2003;90:1857.

[22] Campbell Sandi, Scheiman Daniel. High Perform Polym 2002;14:17.

[23] Yudin VE, Divoux GM, Otaigbe JU, Svetlichnyi VM. Polymer 2005;46:10866.

[24] Svetlichnyi VM, Zhukova TI, Kudriavtsev VV, Yudin VE, Gubanova GN, Leksovskii AM. Polym Eng Sci 1995:1321.

[25] Nesterov VV, Kudryavtsev VV, Svetlichnyi VM, Gazdina NV, Bel’nikevich NG, Kurenbin OI, et al. Polym Sci Ser A 1997;39: 953.

[26] Polotskaya GA, Kuzhnetsov YuP, Anikin AV, Lukashova NV, Zhukova TI, Svetlichnyi VM, et al. Polym Sci Ser A 1992;34:437.

[27] Yudin VE, Gladchenko S, Otaigbe JU, Olson BG, Nazarenko S, Korytkova EN, et al. Polymer 2007;48:1306.

[28] Zhong Y, Wang S-Q. J Rheol 2003;47:483.

[29] Yudin VE, Otaigbe JU, Bui TX, Svetlichnyi VM. J Appl Polym Sci 2006;100:478.

[30] Yudin VE, Otaigbe JU, Bui TX, Svetlichnyi VM. J Appl Polym Sci 2003;88:3151.