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Preparation and characterization of polyimide/organoclay nanocomposites

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Abstract

Organically modified montmorrillonite clay, containing a long chain aliphatic quarternary ammonium cation, was used to prepare polyimide/organoclay hybrids. Several approaches were examined in an attempt to achieve fully exfoliated nanocomposites. These included simple mixing of the clay in a pre-made high molecular weight poly(amide acid) solution; simple mixing followed by sonication of the organoclay/poly(amide acid) solutions; and the preparation of high molecular weight poly(amide acid)s in the presence of the organoclay dispersed in *N*-methyl-2-pyrrolidinone (NMP). The best results were obtained using the in-situ polymerization approach. The resulting nanocomposite films (both amide acid and imide), containing 3–8% by weight of organoclay, were characterized by differential scanning calorimetry (DSC), dynamic thermogravimetric analysis (TGA), transmission electron microscopy (TEM), X-ray diffraction (XRD) and thin film tensile properties. A significant degree of dispersion was observed in the nanocomposite films of the amide acid and the imide. After thermal treatment of amide acid films to effect imidization, in both air and nitrogen, the films were visually darker than control films without clay and the level of clay dispersion appeared to have decreased. In the latter case, the separation between the layers of the clay decreased to a spacing less than that present in the original organoclay. These observations suggest that thermal degradation of the aliphatic quarternary ammonium cation occurred likely during thermal treatment to effect imidization and solvent removal. These thermal degradation effects were less pronounced when thermal treatment was performed under nitrogen. The polyimide/organoclay hybrid films exhibited higher room temperature tensile moduli and lower strength and elongation to break than the control films.

Keywords: Nanocomposites; Polyimide; Organoclay

1. Introduction

Certain organically modified clays comprising silicate sheets separated by cations can be homogeneously incorporated into organic polymers to enhance select physical, morphological, and mechanical properties [1–6]. The organically modified clays are prepared by the addition of long chain aliphatic quarternary ammonium cations to sheet mineral inorganic clays such as montmorrillonites and hectorites. An ion exchange process is utilized to displace the inorganic cations (e.g. sodium) with organic cations, thus improving the compatability of the organosilicate with an organic environment. When mixed into the host polymer, exfoliation (breaking apart) of the nanophase organoclay can occur whereby the silicate sheets lose their attraction to each other. A very large increase in surface area occurs and, if the chemistry is properly designed, the polymer chains can become attracted to the clay sheets. A hybrid inorganic–organic material is produced with altered properties that vary depending on the level of dispersion, the ammonium cation, the silicate, and the host polymer [7–26]. One example by Pinnavaia et al. is the incorporation of low concentrations of organically modified silicate sheets (organo-montmorillonite) into a polyimide that improved certain mechanical and thermal properties [7–12]. Visually clear films, indicative of a dispersion of nanometer-sized particles, were obtained with lower coefficient of thermal expansion (CTE), markedly lower gas permeability coefficients, and higher mechanical properties than the pristine material. The lower gas permeability coefficient is attributed to the dispersed clays creating a tortuous path for gas molecules [26]. Other property enhancements such as reduced time and temperature to effect imidization [27] and increased resistance to certain solvents [28] were manifested in polyimide systems with dispersed nanoclays.

Over the past decade, work involving the incorporation of nanometer-sized clay particles as a hybrid medium has involved several polymer families including polyamide [29], polystyrene [30], polymethylmethacrylate [30], polyacrylate [31], polycarbonate [32], and epoxies [33]. The use of nanoclay additives into these materials

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can improve properties such as heat distortion temperature, flammability, toughness, modulus, tear resistance and reduce permeability to moisture and gaseous species. Since the organically modified clays typically contain long chain aliphatic hydrocarbon based cations, incorporation of these materials into high temperature polymers is of concern due to the potential for thermal decomposition of the cation during high temperature processing. Investigations of these organoclays using thermogravimetric analysis (TGA)/mass spectroscopy revealed that long and short chain carbon species evolved at approximately 200 and 300°C, respectively [34].

The work presented herein was focused on developing a method to prepare well-dispersed polyimide/organoclay nanocomposites. Several approaches were evaluated to achieve a high degree of dispersion as evidenced by the characterization of physical and mechanical properties of nanocomposite films. Since the preparation of the films used a high-temperature treatment (i.e. 1 h each at 100, 200 and 300°C in air and nitrogen), it was of interest to investigate the effects of thermal treatment on the physical and mechanical properties as well as morphological changes resulting from the thermal decomposition of the aliphatic organic cation.

2. Experimental

2.1. Starting materials

The organically modified clay (SCPX-2003) used in the preparation of nanocomposite films was donated by Southern Clay Products, Gonzalez, TX and used as received. This organoclay consists of a 2:1 montmorillonite modified with a quarternary ammonium salt that contains a long chain hydrocarbon (tallow) group. Sodium (Na^+) montmorrillonite was obtained from Southern Clay Products, Gonzalez, TX and used as received. The following chemicals were obtained in polymer grade purity from the indicated sources and used as received: 1,3-bis(3-aminophenoxy)benzene [(APB), Mitsui Petrochemical Ind., Ltd, melting point (m.p.) 107–109°C.]; pyromellitic dianhydride [(PMDA), Aldrich, m.p. 283–286°C] 4,4′-oxydianiline [(ODA), Mitsui Petrochemical Ind., Ltd. m.p. 190–192°C]; 3,3′,4,4′-biphenyltetracarboxylic acid [(BPDA), Chriskev Co., Inc. m.p. 295–297°C]; and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride [(BTDA), Allco Chemical Corporation, m.p. 223–225°C]. High purity, anhydrous *N*-methyl-2-pyrrolidinone (NMP) was purchased from Aldrich and used as received.

2.2. Preparation of poly(amide acid)s

The following example is a representative of the procedure used to prepare neat poly(amide acid) solutions.

Into a 100 ml three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and drying tube containing calcium sulfate were placed ODA (6.4926 g, 0.032 mol) and NMP (25 ml). The solution was stirred under nitrogen until the diamine completely dissolved (~0.5 h). BTDA (10.4480 g, 0.032 mol) was then added followed by NMP (25 ml) to adjust the solids content to ~18%. The mixture was stirred at room temperature for ~24 h under nitrogen. The resulting brown solution was clear and viscous. The solution was subsequently used to prepare thin films for characterization.

2.3. Preparation of poly(amide acid)/organoclay hybrids via methods other than in-situ polymerization

The following are two examples of attempts to prepare nanocomposites by mixing previously prepared poly(amide acid) solutions with clay solutions.

Simple mixing: Into a 500 ml three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and drying tube containing calcium sulfate were placed ODA (6.0072 g, 0.030 mol) and NMP (50 ml). The solution was stirred under nitrogen until the diamine completely dissolved (~0.5 h). PMDA (6.5436 g, 0.030 mol) was then added followed by NMP (50 ml) to adjust the solids content to ~11%. The mixture was stirred at room temperature for ~24 h under nitrogen. The resulting brown poly(amide acid) solution was clear and viscous.

Into a 250 ml Erlenmeyer flask containing a magnetic stirbar were placed the organoclay (SCPX-2003, 2.9991 g) and NMP (100 ml). The flask was fitted with a glass stopper. The solution was mixed at room temperature for ~36 h using a magnetic stirrer.

Into a separate 125 ml Erlenmeyer flask fitted with a glass stopper was placed the poly(amide acid) solution (20 g). The clay solution (4.19 g) was subsequently added while stirring continuously with a magnetic stirbar. This solution contained ~5.6 wt% clay relative to the poly(amide acid). The resulting hybrid mixture was visually cloudy indicating significant phase separation. The mixture was subsequently used to prepare thin films that were characterized for mechanical properties.

Simple mixing with sonication: The same procedure was used in the preparation of the poly(amide acid) as previously discussed above. In this method, the organoclay/NMP mixture was placed in a sonic bath for several hours. This slightly cloudy mixture was subsequently added to a poly(amide acid) solution that had been prepared earlier and mixed using magnetic stirring. The resulting mixture was treated in a sonic bath for 1–2 h at temperatures that reached 45–60°C due to the sonication. The mixture's visual clarity showed little change with sonication. The resulting mixture was used to prepare films that were characterized only by visual inspection.

2.4. Preparation of poly(amide acid)/organoclay hybrids via in-situ polymerization

The following example is representative of the procedure

used to prepare poly(amide acid)/organoclay solutions by synthesizing the poly(amide acid)s in the presence of the clay solution.

Into a 100 ml volumetric flask were placed SCPX-2003 (0.5095 g) and NMP (25 ml). The flask was fitted with a glass stopper and placed on a mechanical shaker for ~1 h at room temperature. The solution was cloudy, but no large clusters or clumps of clay were visually observed. Into a 100 ml three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, and drying tube containing calcium sulfate were placed the organoclay solution, ODA (6.4983 g, 0.032 mol) and NMP (25 ml). The solution was stirred under nitrogen until the diamine completely dissolved (~0.5 h). BTDA (10.4572 g, 0.032 mol) and NMP (25 ml) were subsequently added. The mixture was stirred at room temperature for ~24 h under nitrogen. The solution concentration was ~18% solids with a clay concentration of ~3%. The resulting brown solution was clear and viscous. A 3 ml aliquot of this solution was removed and stored at 4°C prior to X-ray diffraction (XRD) analysis. The remaining solution was used to prepare thin films for characterization.

2.5. Unoriented thin films

Thin films were cast from neat (i.e. control) poly(amide acid) and poly(amide acid)/organoclay solutions in NMP. The solution was doctored onto clean, dry plate-glass and dried at room temperature to a tack-free form in a low humidity chamber. The films were subsequently treated under several different drying conditions in flowing air and characterized. The thermal conditions after air drying at room temperature were: (1) 100°C for 1 h; (2) 1 h each at 100 and 200°C; and (3) 1 h each at 100, 200, and 300°C to effect solvent removal and imidization. These thermal conditions were applied in both air and nitrogen. Film samples were removed from the plate glass and characterized. Thin-film tensile properties were determined according to ASTM D882 at room temperature using five specimens.

2.6. Other characterization

TGA was performed on a Seiko SSC/5200 thermal analyzer at a heating rate of 2.5°C/min in air and nitrogen at a flow rate of 50 ml/min. Differential scanning calorimetry (DSC) was performed using a TA instruments DSC 2900 at a heating rate of 10°C/min with the glass transition temperature (T_g) taken at the inflection point of the ΔT versus temperature curve. Transmission electron microscopy (TEM) was obtained using a Zeiss EM109 electron microscope with an 80 kV accelerating voltage. TEM samples were prepared by placing small strips of the sample film in an epoxy resin and curing the resin overnight at 80°C. The samples were then cut using a ultramicrotome and placed on a 200 mesh copper grid for analysis. XRD patterns were obtained on solutions of poly(amide acid) in NMP, poly(amide acid) films, and polyimide films using a Scintag X1 X-ray diffractometer with a Copper Kα radiation source.

3. Results and discussion

3.1. Preparation of polyimide-organoclay hybrids via methods other than in-situ polymerization

When preparing polymer nanocomposite materials, which involve stacked silicate sheets, it is important to take advantage of the clay's ability to expand. The ability of montmorillonite clays to expand beyond their natural dimensions can aid in their dispersion. Recent studies have shown that, by the introduction of a positively charged organic surfactant to the interlayer galleries (i.e. ion exchange), the negatively charged faces separate to distances not found naturally. This replacement of inorganic cations with organic cations leaves the silicate sheets with organic character and therefore facilitates the interaction with other organic substituents such as organic solvents and polymer molecules. Consequently, the once tightly packed, closely oriented clay sheets can now allow entry of polymer molecules into the interlayer gallery (i.e. intercalation) and can expand beyond the point of any interaction with neighboring species resulting in a disordered array of individual clay particles (i.e. exfoliation). Unfortunately, the driving forces required for polymer molecules to enter the interlayer galleries are not generally favorable. In some cases more than one clay particle may be associated with the same surfactant molecule thus making exfoliation more difficult [35]. In order to alleviate this problem the length of the non-polar portion of the surfactant is typically increased in order to increase the separation of clay sheets; thus, long-chain aliphatic quartenary ammonium cations are typically used.

Initially, simple mixing techniques were employed with high molecular weight aromatic poly(amide acid)s and organically modified clay. The mixtures in these cases were not transparent and the films prepared from them contained visually apparent clay agglomerates. If the clay had exfoliated in the poly(amide acid) to provide particles on a nanometer scale, one would have expected a visually clear material. Tensile properties determined on thin films prepared in this manner showed large increases in moduli. In nearly all cases, the films failed at these clay agglomerates, which apparently served as stress concentrators. Thus, the organoclay behaved here much like a conventional micron sized filler.

Consequently, another method to intercalate and exfoliate the clays in a polyimide matrix was investigated. This attempt involved the use of high frequency sound waves created in a sonic bath. The poly(amide acid) and organoclay mixtures were combined with a mechanical stirrer and then placed in a sonic bath for up to 2 h in an attempt to facilitate intercalation of the polymer into the clay galleries.

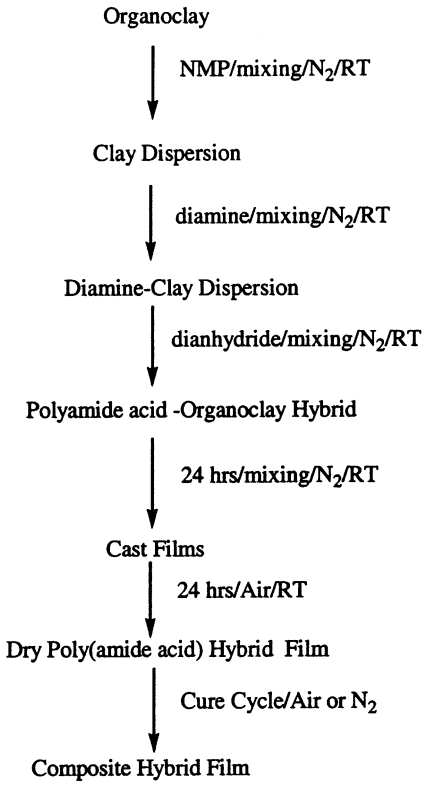

Fig. 1. Flow chart of hybrid preparation.

These efforts proved futile as no further increase in visual clarity of the mixture or the resulting polyimide films were observed.

High shear mixing with shearing forces much greater than those typically encountered with a magnetic stirbar or mechanical stirrer improved intercalation and exfoliation. A Powergen™ homogenizer imparted the high shear on the clay particles. The poly(amide acid) used was an oligomer prepared at a calculated number average molecular weight of 9000 g/mol designated LaRC-8515™. Upon high shear mixing of the hybrid mixtures the visual clarity improved. Thin films were cast and cured to 300°C in flowing air of both the neat polymer and the mixture. Visual inspection as well as TEM and XRD showed significant exfoliation of the clay using this method of mixing. These materials were extremely brittle making mechanical properties impossible to measure, but the materials were examined by Fourier transform infrared spectroscopy and ^{13}C nuclear magnetic resonance [36]. Further work is being conducted which involves this same mixing technique albeit with a higher calculated molecular weight polymer.

The organoclay's retention of an oriented structure in the presence of solvent and in the presence of poly(amide acid) proved to be a problem in the preparation of nanocomposites. It was clear that the two species were incompatible when simply mixed together. A solution to the problem was found with the use of high shearing forces, but it was unclear if this method caused damage (i.e. fracture) to the clay particles or if the molecular weight of the polymer that was used played a role. Thus, it was desirable to investigate alternative methods that did not require the use of special equipment.

3.2. Preparation of poly(amide acid)/organoclay solutions via in-situ polymerization

An improved method for preparing polyimide/clay nanocomposites involved performing the polymerization in the presence of the clay as proposed by Yang et al. [37]. This method was used in the synthesis of hybrid polyimides that were prepared with various organoclays and was reported to afford good dispersions in some cases. Initially, the diamine was combined with the NMP/clay mixture. During this step, the diamine may intercalate into the interlayer gallery of the clay. Subsequent addition of the dianhydride afforded almost transparent solutions that exhibited slight cloudiness. A representative procedure for preparing the hybrid nanocomposites is represented in Fig. 1.

With this approach, at least a portion of the polymer could reside in clay gallery. The growth of the polymer, with its origin being in the gallery, could provide additional aid in forcing the clay layers apart resulting in exfoliation. The chemical structures of the monomers used in this study are depicted in Fig. 2.

The visually clear hybrid solutions were used to cast thin films. The films received several different thermal treatments prior to characterization. These included, air drying at room temperature in a low humidity chamber with no further thermal treatment. In addition, the air-dried films were thermally treated: (1) 100°C for 1 h; (2) 1 h each at 100 and 200°C; and (3) 1 h each at 100, 200, and 300°C. All thermal treatments were performed in a forced air and forced nitrogen ovens. No visual difference between the pristine films and the ones containing 3% clay were observed for APB–BPDA based films treated for 1 h at 100°C in both air and nitrogen. These clay-containing films began to darken after treatment for 1 h each at 100 and 200°C. Films that were thermally treated in air began to turn a light brown whereas the same compositions treated in nitrogen changed to a light yellow. After thermal treatment to achieve solvent removal and imidization (i.e. 1 h each at 100, 200 and 300°C), the films were darker in color when compared to control films treated under the same thermal conditions. Once again, the use of forced air resulted in dark brown films while films thermally treated under nitrogen became yellow. Pristine films thermally treated under nitrogen to effect imidization were less colored than those treated in air. Coloration was more apparent in films containing higher clay-loading levels (i.e. 5 and 8%). The control film obtained from ODA–BTDA was clear and brown after thermal imidization in air, while the film containing 8% clay was considerably darker and nearly black. Thermally imidized films from APB–BPDA exhibited a similar behavior.

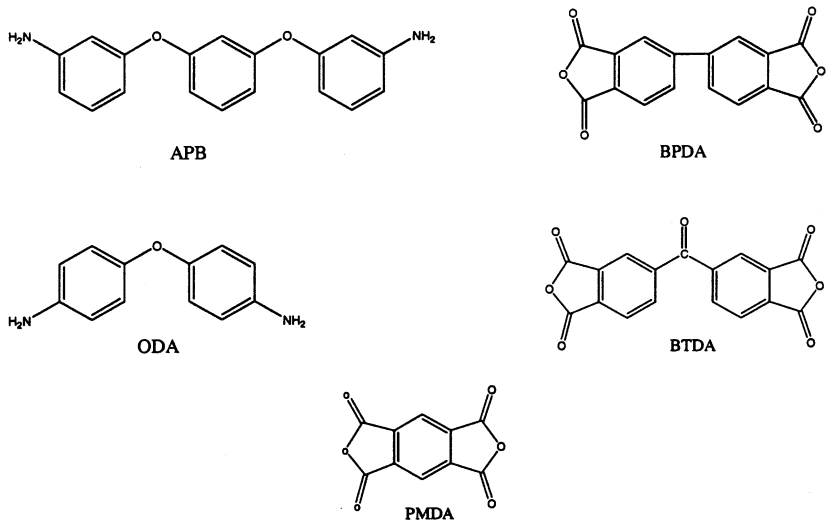

Fig. 2. Monomers used to prepare polyimides.

The white organoclay powder was thermally treated in both air and nitrogen using the same cure cycles as described for the films. After 1 h at 100°C, no visible darkening of the clay powder was observed under either atmosphere; however, after 1 h each at 100 and 200°C in air, the clay powder was light tan. Thermal treatment for 1 h each at 100 and 200°C in nitrogen resulted in a slightly off-white powder. After treating the organoclay for 1 h each at 100, 200 and 300°C it turned black in air and light tan in nitrogen. Thus, the darkening of the films was attributed to the degradation of the long chain aliphatic quarternary ammonium cation. This is consistent with previous reports regarding the thermal stability of aliphatic quarterary ammonium salt modified clays [34]. From these results on the SCPX-2003 organoclay, it appeared that the organic cation is slightly more stable in nitrogen than in air. The neat polyimide films and films containing up to 3% clay were tough and fingernail creasable, while the higher clay content films were brittle and uncreasable. This brittleness may be a consequence of the higher clay loading or the formation of agglomerates as a result of the thermal decomposition of the organic cation.

3.3. Thermal characterization of polyimide/organoclay hybrids prepared via in-situ polymerization

The results of dynamic thermogravimetric analyses performed on the films of the two polyimides containing various amounts of clay in air are presented in Fig. 3. The temperature at which 5% weight loss occurred in air increased with the addition of the clay. The reason for the divergent behavior of the two systems at higher clay loading levels is not apparent.

The TGA curves obtained on the organoclay powder in air and nitrogen are presented in Fig. 4. The clay began to lose mass in air at 150°C, lost approximately 1% at 200°C, 5.5% at 250°C, and 12% at 300°C.

This is presumably due to the loss of the organic cation and more specifically the degradation of the long hydrocarbon tail. The products of this degradation are known to be long hydrocarbon chains near 200°C with the long chain continuing to degrade as the temperature increased [34]. The TGA curve obtained on the organoclay powder in nitrogen is also presented in Fig. 4. The organoclay is more thermally stable when heated under a nitrogen atmosphere. Weight loss data again shows initial loss at 150°C, but only a 4% loss at 250°C, and 9% loss at 300°C. This slightly higher thermal stability may account for the different color obtained for the 3% clay containing APB–BPDA films cured under nitrogen as compared to those thermally treated in air.

The thermal degradation of the organic cation at these temperatures poses concern to the preparation of polyimide/clay nanocomposites via a thermal imidization approach. Alternative approaches involving room-temperature catalyzed cyclodehydration, and thermal imidization in solution are currently under investigation. In the latter approach imidization can be accomplished at temperatures less than 200°C with the use of an appropriate solvent and azeotroping agent. Of course, for either of these methods to be useful, the resultant polyimide must remain soluble after

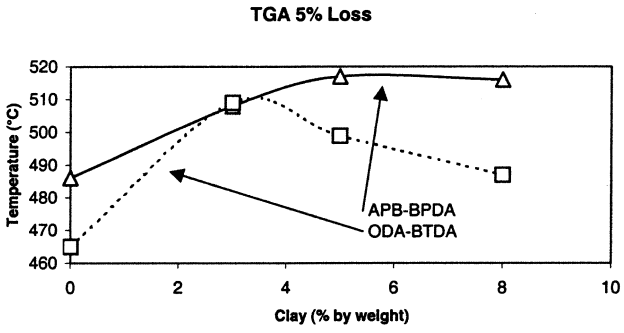

Fig. 3. Temperature of 5% weight loss in air versus clay loading.

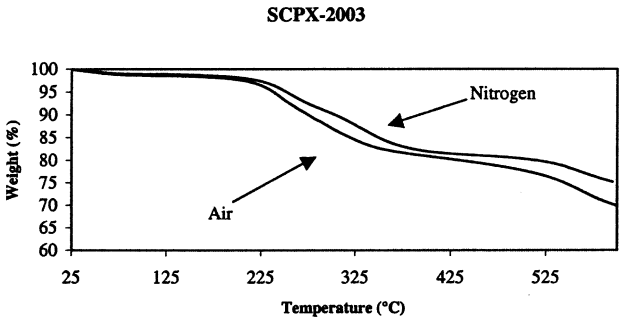

Fig. 4. TGA of quaternary tallow ammonium organoclay in air and nitrogen.

imidization, thus limiting these approaches to soluble polyimides.

Both polyimides are amorphous in their unmodified forms as evidenced by DSC and XRD analyses. DSC was performed on thin film samples. The T_g for the neat APB–BPDA polyimide film was 208°C and was constant within 1°C for the hybrid films. The T_g for the neat ODA–BTDA system was 283°C and remained constant within 4°C for the hybrid films.

3.4. TEM analysis of clay dispersion in hybrid films prepared via in-situ polymerization

TEM was performed on thin film samples of cured 3% clay APB–BPDA polyimide films prepared via in-situ polymerization. Large areas of the films were examined in order to obtain a representative analysis of the degree of exfoliation. The results indicated that a high degree of exfoliation of clay nanometer sized particles, were obtained.

Fig. 5. TEM photo of 3% clay APB–BPDA films showing exfoliated clays.

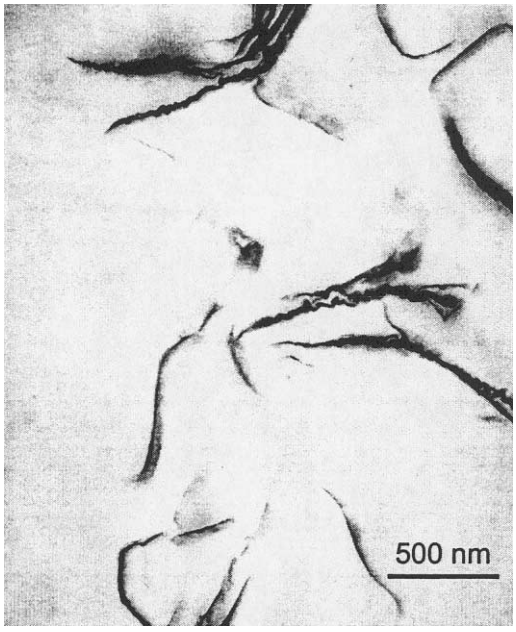

Fig. 6. TEM photo of 3% clay APB–BPDA films showing some collapsed clay.

Representative photomicrographs of different sites on the same polyimide/clay film are presented in Figs. 5 and 6. Although good dispersion was achieved as seen in Fig. 5, Fig. 6 shows larger and thicker clay particles. In the latter case, clay particles have apparently formed agglomerates in some areas of the film during thermal treatment in air. Fig. 6 shows some clay particles that have collapsed. Presumably, some clay particles were not fully wetted by the polymer in these regions and upon thermal degradation of the organic cation, the galleries collapsed. The percentage of dispersion cannot be quantified by examination of these photos but it would appear from Fig. 7 (in which the magnification has been reduced) that exfoliation dominates. These exfoliated particles are ~200–700 nm in length and ~1–10 nm thick.

3.5. XRD analysis of clay samples and hybrid films prepared via in-situ polymerization

Although visually transparent films were obtained through the in-situ polymerization method, both TEM and XRD indicated agglomerates in the thermally imidized films. The XRD data of thermally imidized films cured to 300°C in air prepared from APB–BPDA corresponding to 0, 3, 5, and 8% clay loadings are presented in Fig. 8. The peak at $2\theta = 6.6°$ for the 3% sample corresponds to a *d*-spacing of ~1.34 nm for the 001 reflection. The 5 and 8% peaks shift slightly so that in the 8% sample the *d*-spacing is ~1.36 nm. Broad peaks centered near $2\theta = 4°$ for the 8% clay sample may be the consequence of small, residual amounts of the SCPX-2003 clay whose galleries were not penetrated by monomer and did not collapse (see Fig. 11). Analogous data for thermally imidized hybrid films prepared from ODA–BTDA and cured to 300°C in air are

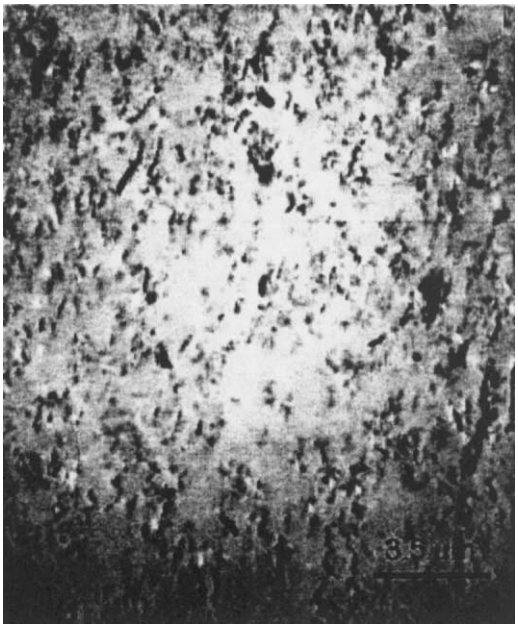

Fig. 7. Reduced magnification photo of 3% clay APB–BPDA films.

presented in Fig. 9. The peak centered at $2\theta = 4°$ appears again in the 8% clay sample while all the samples have a peak near $2\theta = 6.6°$. These results are similar to the APB–BPDA sample but show a slightly smaller *d*-spacing (1.28 nm). This peak indicates the presence of some clay particles close to or even smaller than sodium montmorillonite. In the XRD data from two previous publications, both of which concern polyimides, small peaks appear with similar 2θ values [23,38]. XRD patterns of the organoclay and of sodium montmorillonite are shown in Fig. 10. By XRD, the sodium clay has a *d*-spacing of approximately 1.33 nm. The XRD data for the SCPX-2003 sample indicated that no particles were present with a gallery height close to 1.3 nm in the original organoclay. The fact that there was only one peak corresponding to a *d*-spacing of 2.37 nm and no peaks corresponding to a *d*-spacing of 1.3 nm in the organoclay sample indicated that the closer packed clay particles were formed during preparation of the polyimide films. This was likely due to the decomposition of the aliphatic quarternary ammonium cation of poorly

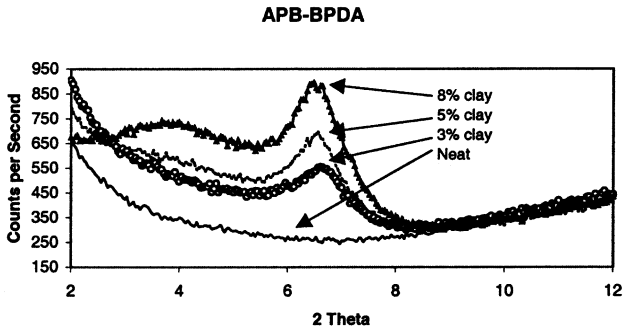

Fig. 8. XRD patterns of air cured APB–BPDA thin film samples.

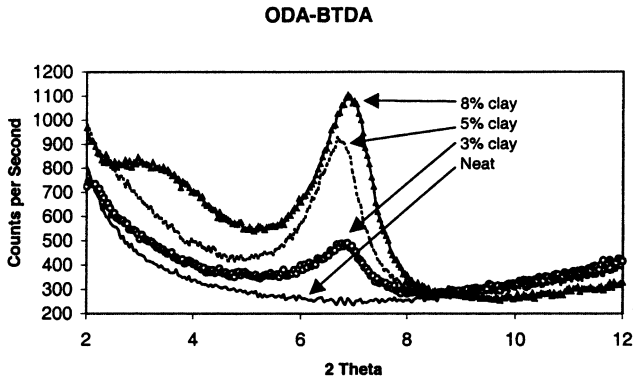

Fig. 9. XRD patterns of air cured ODA–BTDA thin film samples.

wet out or intercalated clay particles during the thermal treatment to 300°C in air to achieve solvent removal and imidization.

3.6. XRD analyses of the effect of thermal treatment on hybrids prepared via in-situ polymerization

Upon observing the collapse of the organoclay to a layer spacing of ~1.3 nm it was of interest to examine the hybrid preparations and the organoclay using XRD after thermal treatment. XRD patterns for the hybrid were obtained for each of the following preparations: (1) the hybrid solution; (2) the film dried to a tack free state in air at room temperature; (3) after thermal treatment at 100°C for 1 h; (4) after thermal treatment for 1 hr each at 100 and 200°C; (5) after thermal treatment for 1 h each at 100, 200, and 300°C for 1 h. The thermal treatments were applied in both air and nitrogen. These thermal treatments were also applied to the organoclay in air and nitrogen.

The 3% clay in APB–BPDA poly(amide acid) preparation was examined by XRD immediately after mixing and again after air drying for 24 h to a tack free state as a thin film on a glass plate at room temperature. The XRD data for these two samples, presented in Fig. 11, exhibited peaks at $2\theta = 4.1°$ (2.15 nm) for the poly(amide acid) solution before drying and at $2\theta = 4.3°$ (2.05 nm) after drying to a tack free state. This indicated that there were some clay

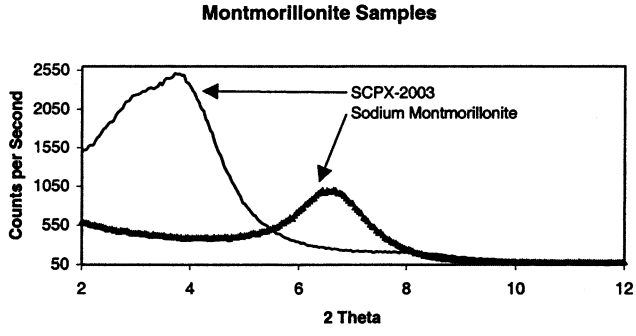

Fig. 10. XRD patterns of sodium montmorrillonite and organoclay (SCPX-2003).

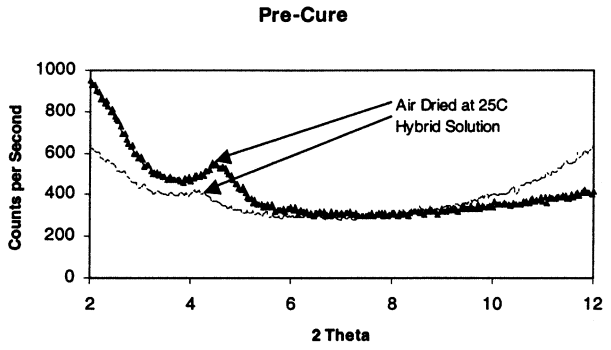

Fig. 11. XRD patterns of 3% clay APB–BPDA poly(amide acid) hybrid solution and film after air drying at room temperature.

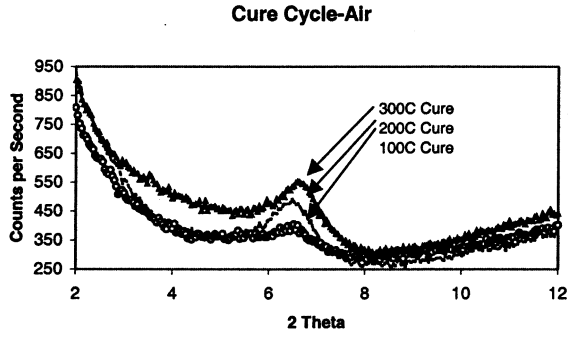

Fig. 12. XRD patterns of 3% clay APB–BPDA films treated at different temperatures in air.

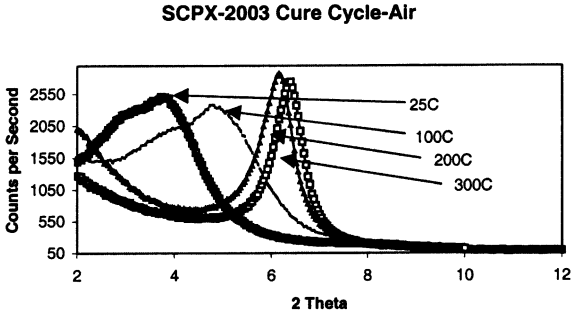

Fig. 13. XRD patterns of organoclay treated at different temperatures in air.

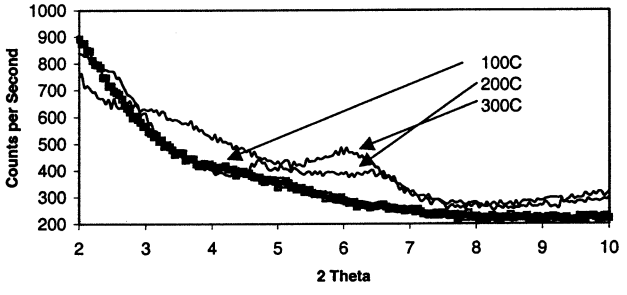

Fig. 14. XRD patterns of 3% clay APB–BPDA films treated at different temperatures in nitrogen.

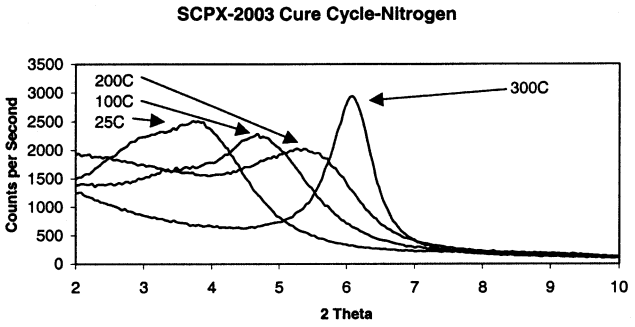

Fig. 15. XRD patterns of organoclay treated at different temperatures in nitrogen.

particles, which were not intercalated or exfoliated in solution. These clay agglomerates apparently retained their original structure, and it is doubtful that they were impregnated by monomer prior to polymerization. XRD data (Fig. 12), collected after each step in the cure cycle in air (100, 200, 300°C) shows the loss of the $2\theta = 4.1°$ and $2\theta = 4.3°$ peaks and the formation of a new peak at $2\theta = 6.6°$. The 001 peak shifted from $2\theta = 4.3°$ (2.05 nm) in the air dried sample to $2\theta = 6.6°$ (1.34 nm) after holding at 100°C for 1 h and increased in intensity as the temperature was increased. Thus, it was apparent that the thermal decomposition of the cation resulted in a collapse of the clay layers reducing the *d*-spacing. Additional data to support the hypothesis that the organoclay had exceeded its thermal resistance are shown in Fig. 13. In this case, the neat clay was subjected to the same thermal treatment as that used for the hybrid films and the XRD patterns were obtained. The 001 peak was observed to shift to the right upon heating resulting from a collapse of the gallery. Assuming, that the organoclay was completely exchanged with the organic surfactant (Fig. 10), a process for the formation of small clay agglomerates in these hybrid films is now described.

A similar analysis was performed on 3% APB–BPDA poly(amide acid) and polyimide films prepared via in-situ polymerization that were thermally treated in nitrogen instead of air. The films were prepared and dried in the same manner as the films discussed above. In Fig. 14 it was apparent that thermal treatment of the thin films in a nitrogen atmosphere delayed the formation of the collapsed layer agglomerates. The 001 peak remained at $2\theta = 4.3°$ (2.05 nm) in the sample held at 100°C for 1 h. After holding a film for 1 h each at 100 and 200°C, the XRD pattern indicated that there was layer spacing that varied from $2\theta = 4.3°$ (2.05 nm) to approximately $2\theta = 6.0°$ (1.47 nm) for the collapsing clay particles. After holding for 1 h each at 100, 200, and 300°C the XRD peak was more defined and had a maximum at approximately $2\theta = 6.0°$ (1.47 nm). The films thermally treated under nitrogen did not show collapsed particles after treatment at 100°C treatment and complete collapse occurred at a higher temperature when compared to samples prepared in air. Fig. 15 shows this same trend in the

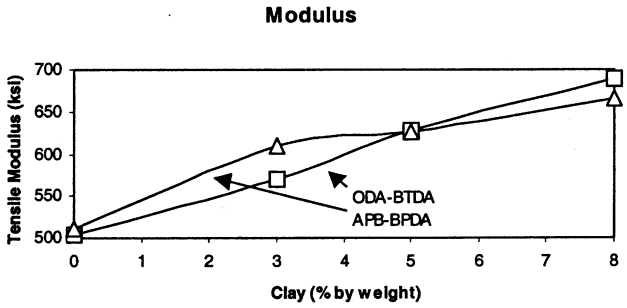

Fig. 16. Tensile modulus versus clay loading of air cured polyimide/organoclay systems.

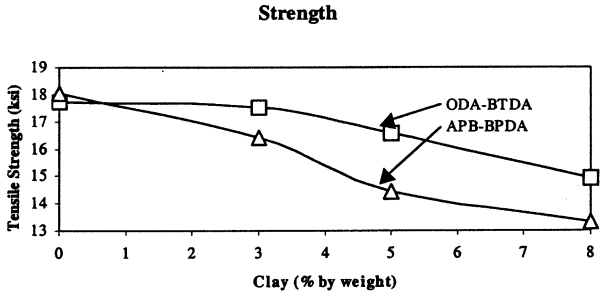

Fig. 18. Yield strength versus clay loading of air cured polyimide/organoclay systems.

organoclay as it was subjected to the same thermal conditions. The organoclay sample that was subjected to a 1 h hold each at 100 and 200°C in nitrogen exhibited a maximum at $2\theta = 5.2°$ (1.70 nm) indicating that the interlayer cation did not completely degrade at this temperature. The peak for the organoclay sample held for 1 h each at 100, 200, and 300°C under nitrogen was centered at approximately $2\theta = 6.0°$ (1.47 nm) which is similar to the peak in the film sample treated in nitrogen but is at a slightly lower value than the samples that were treated at these temperatures in air. The organoclay did not appear to collapse in nitrogen as it did in air indicating that a thermoxidative mechanism is more damaging to the interlayer cation than a mechanism involving nitrogen.

3.7. Mechanical properties of hybrid films prepared by in-situ polymerization

In Fig. 16, the tensile modulus of thin films after imidization in air is plotted against clay concentration. A linear increase in modulus as the clay concentration was increased from a 0 to 8% loading was observed for both the APB–BPDA and the ODA–BTDA systems. This was as expected since the clay particles inherently possess high moduli and if dispersed on the nanoscale level, should also increase the moduli of polymeric systems. This result is typical of polymeric systems in which nanoscale dispersion of the clay is attained. However, Agag et al. found that the modulus increased up to 2% clay loading and that upon further additions of clay lowered moduli were observed. The polyimides used in Agag's work had a more rigid backbone and some degree of molecular ordering [38].

Fig. 17 shows a decrease in percent elongation at break with the addition of organoclay. This may be a consequence of the collapsed clay layer agglomerates present. A decrease in tensile strength shown in Fig. 18 and a corresponding decrease in elongation to break were observed in both systems, and could be attributed to the same reason. It would take only a small amount of the undispersed organoclay on the nanoscale level to create the effects that were observed for elongation and strength. On the other hand it would take a much larger dispersed amount to create the rise in tensile modulus seen in both systems.

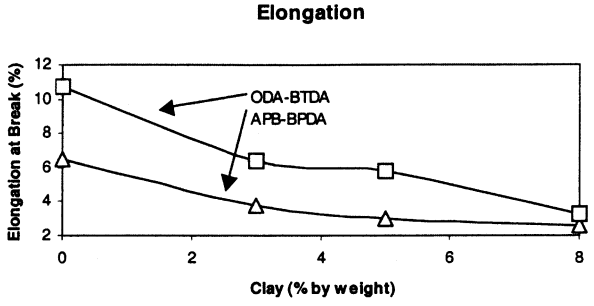

Fig. 17. Elongation at break versus clay loading of air cured polyimide/organoclay systems.

4. Summary

Several approaches were examined in an attempt to prepare well-dispersed polyimide/organoclay nanocomposites. The best results were obtained using an in-situ polymerization technique whereby poly(amide acid)s were synthesized in the presence of the organoclay. Poly(amide acid)/organoclay nanocomposite solutions and films with a significant amount of exfoliation were prepared and characterized. Upon thermal conversion of poly(amide acid)/organoclay films to the corresponding polyimides in air, decomposition of the organic cation occurred resulting in the collapse to some degree of the clay particles into larger agglomerates. In addition, this decomposition caused the films to become visually darker. Thermal treatment under nitrogen allowed the interlayer cation to withstand higher temperatures but did not completely stop degradation from occurring. Even though degradation was present, the resulting polyimide/organoclay nanocomposite films still maintained a large amount of exfoliated clay particles regardless of cure atmosphere. Polyimide/organoclay nanocomposite films exhibited increased tensile moduli, similar strengths and lower elongations to break as compared to control films. It is apparent that organoclays with improved thermal stability are required for the preparation of polyimide/organoclay nanocomposites via a thermal imidization process regardless of cure atmosphere.

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