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Synthesis and rheological properties of oligoimide/montmorillonite nanocomposites

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Abstract

We report a facile strategy for preparing polyimides (PI)/montmorillonite (MMT) nanocomposites at moderate temperatures that avoids thermal degradation of organically-modified MMT (organo-MMT) that is commonly observed during conventional melt-blending of organo-MMT with commercial high molecular weight PI at elevated temperatures. Novel polyimides of low molecular weight (oligoimides) based on 1,3-bis(3′,4,-dicarboxyphenoxy)benzene and 4,4′ bis(4″-aminophenoxy)diphenylsulfone were synthesized and subsequently melt-blended at temperatures ranging from 150 to 250 °C with special organically-modified montmorillonite clay nanoparticles to form new polyimide/organo-MMT nanocomposites with special combination of physical and chemical properties for diverse applications such as microelectronic components where chemical inertness, high temperature stability, low dielectric constant, mechanical toughness and processability are primary requirements. It was found that application of a strong shearing flow near the glass transition temperature of the oligoimide to the oligoimide/organo-MMT nanocomposite melt blend containing 6 ± 2 vol% of the organo-MMT resulted in three orders of magnitude increase in the viscosity. Partial exfoliation of the organo-MMT together with constrained deformation of the polymer between the rigid nanoparticle layers (as evidenced by formation of the network structure or fractal gel) are thought to be responsible for this observed viscosity behavior. The viscosity behavior is typical for model xylene/MMT system where the MMT particles were dispersed in xylene solvent homogeneously via ultrasonic mixing. This study suggests that the rheological methods used here may provide a valuable analytical tool to accelerate efforts to develop useful polyimide nanocomposites from synthetic oligoimides containing ceramic nanoparticles having different shapes and sizes. Further, because of their facile synthesis and desirable characteristics these polyimide/MMT clay nanocomposites are expected to be excellent model systems for exploring feasibility of new routes for driving organic polymers to self-assemble into useful nanocomposites.

Keywords: Nanocomposite; Montmorillonite; Polyimide and oligoimide

1. Introduction

Polymers reinforced by montmorillonite (MMT) represent a relatively new class of reinforced plastics i.e. nanocomposites formed by dispersing MMT (often in relatively small concentrations throughout a polymer matrix) throughout a polymer matrix. These nanocomposites have received much attention in both scientific and industrial areas due to their enhanced mechanical, barrier properties and flame resistance [1]. Special interest is given to polyimide (PI) based composites because of their excellent heat resistance, chemical stability, and superior electric properties [2–4]. It has been reported that PI/MMT nanocomposites exhibit increased modulus and strength, high heat distortion temperature, decreased thermal expansion coefficient, reduced gas permeability, and increased solvent resistance compared to pristine polymer [5–10]. A number of methods, such as solution mixing, melt blending, and in situ polymerization, for preparing PI/MMT nanocomposites have been reported [11–13]. However, there are a number of significant limitations in the case of melt blending that is the most commonly used method [14–17]. These limitations include particularly the relatively low thermal stability of the organically modified MMT (organo-MMT) compared to that of the high melting temperature of PIs. Consequently, there is a need to develop a method for preparing polyimides (PI)/MMT nanocomposites at moderate temperatures that avoids thermal degradation of organically-modified MMT that is commonly observed during conventional melt-blending at elevated temperatures of organo-MMT particles with commercial high molecular weight PI. In addition, the basic knowledge of

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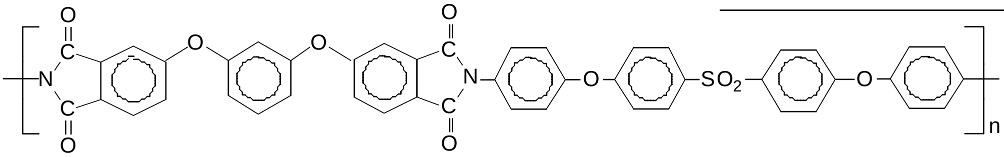
the microstructure evolution during melt blending and its effect on the rheology is a prerequisite for realization of the maximum potential of these interesting materials in diverse application areas such as the aerospace industry and microelectronic components where chemical inertness, high temperature stability, low dielectric constant, mechanical toughness and processability are primary concerns.

Strong shearing flows such as the ones encountered in extrusion and injection molding can be used to completely dissociate and homogeneously disperse the MMT layers in the polymer/MMT nanocomposites [18]. It is noteworthy that both polymer melt intercalation and application of strong shear flows are two important conditions that are needed in the preparation of 'exfoliated' polymer/MMT hybrids. Because of its reported tendency to provide individual MMT sheets with very high aspect ratios, exfoliation or a high level of intercalation is thought to be crucial in producing polymer/clay nanocomposites to an extent that depends on the targeted application of the nanocomposites [19–21].

In this article we describe a method of incorporating MMT nanoparticles into a new type of amorphous PI matrix with low molecular weights (oligoimides) to significantly improve processability with MMT particles at relatively low melt-blending temperatures. The relatively low melt viscosity of the oligoimides compared with that of commercial high molecular weight PI together with the favorable polymer-filler interactions are expected to facilitate dispersion of the MMT particles in the resulting nanocomposites. The chemical structure of the new amorphous PI used in this study is given below:



The influence of molecular weight of this amorphous PI on the rheology and structural behavior of the pure PI and the PI filled with organically modified MMT was investigated for the first time. The results point to the fact that useful PI/MMT nanocomposites with improved properties can be prepared in comparison to reported work in the literature involving a direct physical mixing of clay or other inorganic nanoparticles with high molecular weight polymers, making an important contribution to the current academic and industrial research interests in polymer nanocomposites. The nanocomposites of this study are expected to find many uses in microelectronic and packaging applications where heat resistance, chemical stability and superior electrical properties are important requirements. The favorable chemical interactions between the polymer and the MMT will enhance the mechanical properties of the PI for the targeted applications, making the present nanocomposites useful model materials for exploring feasibility of new routes for driving organic polymers to self-assemble into useful nanocomposites.

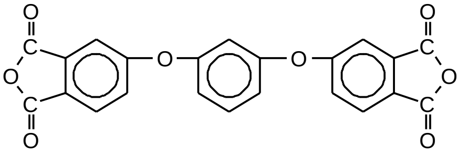
2. Experimental

2.1. Organic treatment of MMT

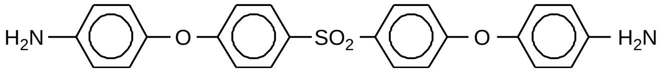
The organically treated montmorrilonite clay {Cloisite 15A (MMT-15A)} was generously provided by Southern Clay Products, which is a Na+ type montmorillonite (Na–MMT) modified with a quaternary ammonium salt. After such a cation exchange modification, the MMT-15A is hydrophobic with low surface energy, making it compatible with the polymer matrix. TGA measurements described later were used to confirm that the organic modifier of MMT-15A is thermally stable up to 240 °C, making the MMT-15A suitable for melt blending with the polymer at temperatures ≤240 °C.

2.2. Preparation of oligoimides with different molecular weights

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 diamine BAPS was supplied by Wakayama Seika Co., Ltd (Japan).

A number of oligoimides with different molecular weights was synthesized by controlling the ratio of monomers to endcapper phthalic anhydride (PA) according to the Carother's equation [22]. The various polyamic acids (PAA) were converted to the respective PIs (R–BABS–PA) by using solution imidization techniques [23,24]. 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 phtalimide 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.

2.3. Melt blending

A HAAKE MiniLab® Micro Compounder was used for melt-mixing of oligoimides with MMT-15A particles. The materials were dried for a minimum of 6 h at 80 °C. Five grams mixtures of oligoimides and MMT-15A particles were extruded using the HAAKE MiniLab® Micro Compounder to obtain blends having concentrations of 3, 5 and 10 wt% MMT in the oligoimides. Using the material densities (1.30 g/cm^3 for oligoimide and 1.66 g/cm^3 for MMT-15A), the corresponding volume concentrations of MMT in the nanocomposites were found to be 2.4, 4 and 8 vol%. The melt compounding was carried out in the temperature window ranging from 140 to 240 °C depending on molecular weight of the oligoimide used. Note that the micro compounder has a single heating zone that is preset to the desired temperature prior to extrusion.

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 was comprised of a Waters 515 HPLC pump, Waters 2410 RI detector, Waters 2457 Dual l absorbance detector, column oven, and a PolymerLabs 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 PolymerLabs). Data were acquired and analyzed using the Waters Empower computer software package. Standard infra-red spectroscopy was used to confirm the formation of PIs via the characteristic absorption peaks occurring at 1780, 1720, 1380, 725 cm^{-1} (not shown) that are typical for aromatic PIs [2].

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 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. Prior to the measurements, the sample was allowed to equilibrate at the desired temperature for approximately 5 min.

Thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) 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 under a nitrogen atmosphere. DSC was performed on 3–6 mg samples contained in a platinum crucible with a heating rate of 10 °C/min under a nitrogen atmosphere.

Small angle X-ray scattering measurements on crushed consolidated samples were performed using a Philips XRG 3100 diffractometer with Cu Kα ($\lambda = 1.54$ Å) radiation and an accelerating voltage of 40 kV/170 mA was maintained throughout the measurements. The step size and the scanning speed were 0.02° and 0.5 s/step. The spectral window ranged from $2\Theta = 1$ to 10°. An increase in the basal layer spacing, which was determined from a shift in the (001) peak position, indicates ion exchange or polymer intercalation between the silicate layers. Disappearance of the (001) peak indicated an exfoliated morphology. The corresponding *d*-spacing value was calculated from the diffraction peak maximum, using the Bragg equation:

$$d = \frac{\lambda}{2 \sin \Theta} \tag{1}$$

3. Results and discussion

3.1. Mixture of MMT-15A with xylene as model system

According to [25], xylene can be used as model matrix for comparing efficiency of different organically treated MMT particles in forming percolating structure during mixing in a liquid media. A 30-min sonication was used for dispersion of the MMT-15A particles in xylene. The volume concentrations of MMT-15A in xylene were 0.5, 1, 2, 3, 4, 5, 7 and 10%. These xylene/MMT-15A nanodispersions were used in the present study as model systems for studying the state of exfoliation of the MMT-15A in xylene, as well as, for visualizing the maximum extent of structural network formation among the individual silicate plates.

Optimal use of nanoparticles in polymer nanocomposites requires an understanding of the rheology of the polymer/nanoparticle dispersions and of how processing conditions influence the ultimate properties of the nanocomposites. Because of the large specific surface area of MMT nanoparticles upon exfoliation, a percolating network structure may form at very low volume fraction of MMT in a liquid (xylene) or polymer media, leading to a significant increase in the melt viscosity of the xylene/MMT nanodispersion and polymer/MMT nanocomposite.

Fig. 1 shows the concentration dependence of the shear storage modulus (G') of xylene/MMT-15A dispersion. A steep rise in the G' was observed in the concentration range of 2–6 vol% that is ascribed to formation of an elastic (fractal) gel [25]. This gel is thought to be consistent with partial exfoliation and a formation of a percolating network structure. The frequency dependence of the complex viscosity reveals a decrease in viscosity as the frequency is increased (Fig. 2). XRD analysis of a 5 vol% MMT-15A/xylene dispersion did not show evidence for complete exfoliation of the clay but a significant increase in the interlayer distance of the clay from 3.15 to 5.28 nm ($2\Theta = 1.67°$) was observed (Fig. 3). This increase in the interlayer distance is consistent with formation of a percolating network structure as already mentioned. Based on the results just described we selected the MMT-15A as the optimal nanofillers in the investigation of the influence of the nanoparticles on the thermo-rheological behavior of thermoplastic PI/MMT blends.

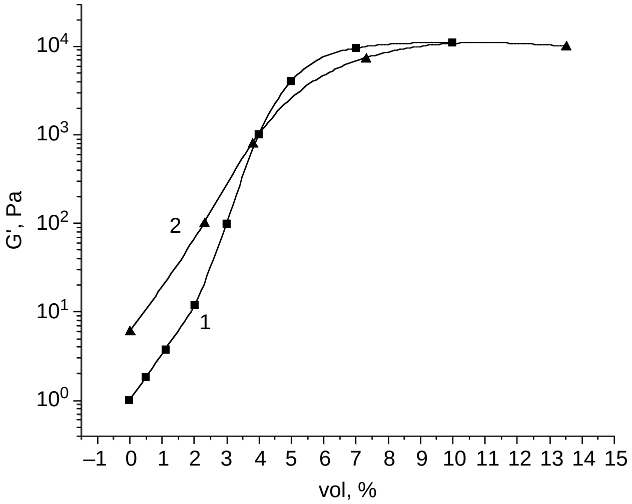
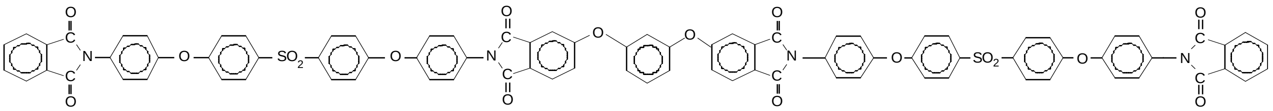


Fig. 1. Dependence of shear storage modulus on volume fraction of MMT-15A in xylene (1) and in nanocomposite s10/MMT-15A (2). Measurements for xylene was at $T=25$ °C and for nanocomposite s10+MMT-15A at temperature $T=220$ °C. Frequency $\omega=1$ Hz, strain amplitude $\varepsilon=1\%$.

3.2. Influence of molecular weight on thermal and rheological behavior of R–BAPS polyimide

To investigate thermal and rheological behavior of thermoplastic PIs, we synthesized a number of R–BAPS–PA oligoimides with varying molecular weights. Molecular weight during the synthesis was controlled through stoichiometric offset of the monomers as dianhydride, diamine and phthalic anhydride. Table 1 summarizes the properties and molecular weights of the R–BAPS–PA polymers obtained. The lowest molecular weight of the oligoimide that was synthesized correspond to the s10 sample having the following chemical structure:



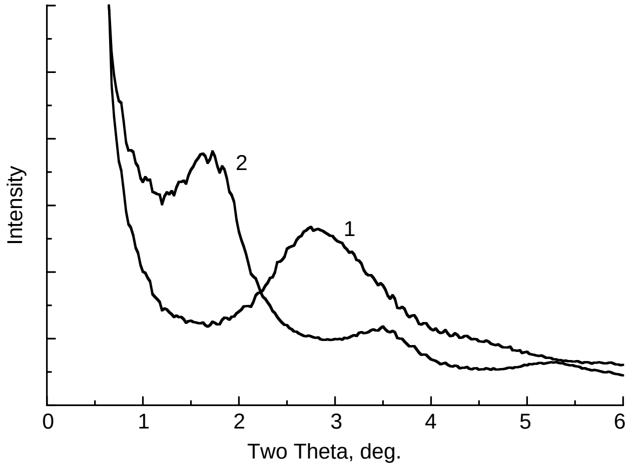


Fig. 3. XRD curves of nanoparticles MMT-15A (1) and mixture of xylene +5 vol% MMT-15A (2).

The number and weight average molecular weights (M_n and M_w, respectively) obtained from gel permeation chromatography and the melt viscosities of the samples are given in Table 1. Using the data in Table 1, we plotted the dependence of viscosity on average weight molecular weight as Fig. 4 shows. From this figure a critical molecular weight M_{cr} of about 15,000 g/mol was obtained. The M_{cr} is the critical molecular weight for entanglement at which the slope of the curve of Fig. 4 changes from 1 to 3.4, and is believed to indicate the macromolecule chain length at which different chains in a melt entangle, leading to a steep rise in viscosity as the figure shows.

The temperature dependence of the complex viscosity of the R–BAPS–PA oligoimides is shown in Fig. 5. The data of this figure was obtained in a reverse temperature program mode where the sample was cooled in a specified cooling rate from the melting to the glass transition temperatures. As expected, the sample with the highest molecular weight (s95 sample) gave the highest viscosity at elevated temperatures that is facilitated by the formation of physical network (or entanglement) between the macromolecules. Therefore, the s95 is unsuitable for preparing blends with MMT-15A, because it needs high (more than 240 °C) temperatures to give a viscosity that is sufficiently low for optimal melt blending. Based on the preceeding results only the oligoimides (s10, s60, s40 and s80) were used in the melt blending experiments described in the following section.

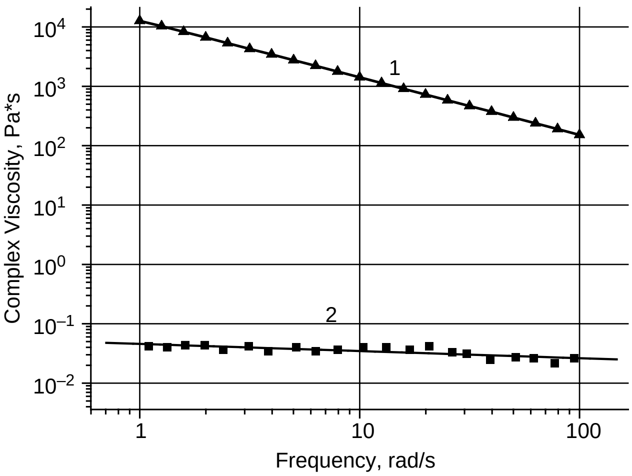


Fig. 2. Frequency dependence of complex viscosity at room temperature for mixture of xylene +5 vol% MMT-15A (1) and for pure xylene (2). Strain amplitude $\varepsilon=1\%$.

3.3. Melt blending of MMT-15A with oligoimides

Prior to melt blending the oligoimides powder with the MMT-15A particles, the two components were physically

Table 1
Properties and molecular weights of R–BAPS–PA

polymer	Stoich. offset (%)	T_g (°C)	M_n (g/mol)	M_w (g/mol)	PDI	η (Pa s)
s10	–	153	3609	11,553	3.2	3 (280 °C)
s40	60	166	3324	12,009	3.6	3.2 (280 °C)
s60	40	177	4850	17,355	3.5	5 (300 °C)
s80	20	201	8845	23,603	2.7	22 (320 °C)
s95	5	220	18,558	50,133	2.7	2500 (360 °C)

Note: T_g is glass transition temperature; M_n is number average molecular weight; M_w is weight average molecular weight; PDI is polydispersity; η is melt viscosity of oligomers and polymers at temperatures indicated in brackets.

mixed in the dry powdered state. The resulting mixture was then melt blended in a HAAKE MiniLab Micro Compounder equipment for 5 min at 240 °C as already described in the experimental section. At temperatures up to 240 °C there is no chemical reaction between oligoimides and MMT-15A particles. A screw rotational speed $N=200$ rpm and mixing time of 10 min were found to yield optimal mixing of the MMT-15A particles with oligoimides as well as gave reproducible results. The concentration dependence of the oligoimide/MMT-15A nanocomposite was found to be consistent with that predicted by the classical Thomas equation [26] as shown in Fig. 6. The Thomas equation is given by:

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2 + A\exp(B\phi) \tag{2}$$

where ϕ is volume fraction of particles; $A=0.0273$ and $B=16.6$. This modest increase in viscosity with increasing ϕ up to 15 vol% depicted in Fig. 6 is somewhat similar to that observed for polyimide bonded magnets filled with 75–100 μm size Nd–Fe–B as reported elsewhere [27].

After melt homogenization of s10/MMT-15A mixture at 220 °C for 10 min in the micro compounder the temperature of the sample was reduced to 150 °C followed by application of shear deformation in the micro compounder for a residence time that was determined by the maximum viscosity (or torque) that the micro compounder can withstand. This melt blending procedure was found to yield s10/MMT-15A nanocomposite with unusual and interesting melt viscosity behavior. Fig. 7 shows the temperature dependence of viscosity for the s10/MMT-15A nanocomposite prepared according to procedure just described with different volume fraction of particles before and after application of shear in the micro compounder. It is clear from this figure that after shear deformation, a gelation (or solidlike behavior) of the sample occurs as evidenced by the significant increase in viscosity (about three decades) especially at elevated temperatures (Fig. 7). This gelation or solidlike behavior of s10/MMT-15A nanocomposite is not reversible, i.e. once formed the stress-sustaining structure has a constant viscosity that is not affected by subsequent heating and cooling cycles. Because there is no chemical reaction of oligoimides in the temperature range of 150–240 °C, it is reasonable to ascribe the stress-sustaining structure to formation of physical cross-links that is possibly akin to the formation of a percolating network of MMT nanoparticles in the polymer matrix.

Fig. 1 shows the nanoparticle concentration dependence of shear storage modulus of the s10/MMT-15A nanocomposite prepared in the HAAKE MiniLab at $T=150$ °C and a screw speed of $N=200$ rpm. A comparison of curve 2 with curve 1 (xylene/MMT-15A dispersion) discussed earlier shows the same trend in the G' versus volume percent MMT-15A behavior. The greatest increase in G' occurs at 4–5 vol% MMT-15A that is probably close to the percolation threshold of the nanoparticles toward network formation. Similar trends in

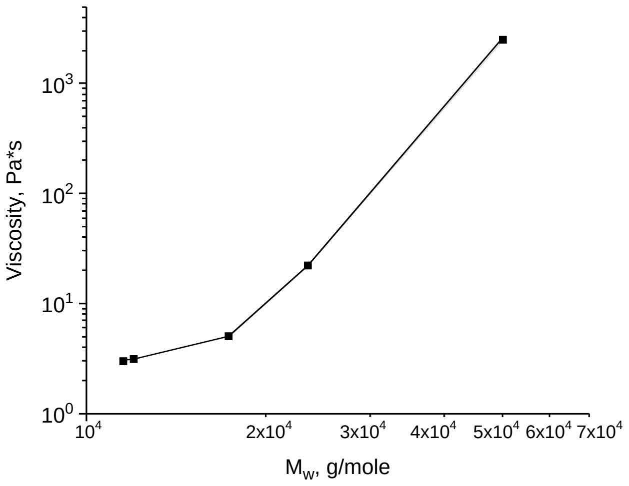


Fig. 4. Dependence of viscosity of R–BAPS–PA oligoimides on their weight average molecular weights. Shear rate is 0.01 s^{-1}. The temperatures are indicated in Table 1.

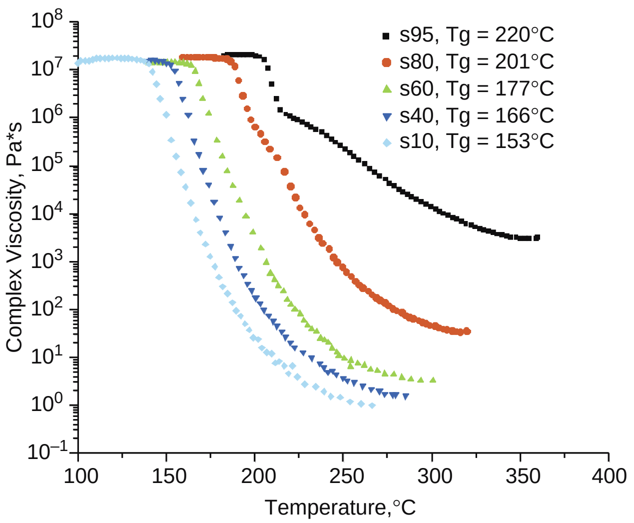


Fig. 5. Dependences of complex viscosity on temperatures for R–BAPS–PA oligoimides. $\omega=1$ Hz, $\varepsilon=1\%$.

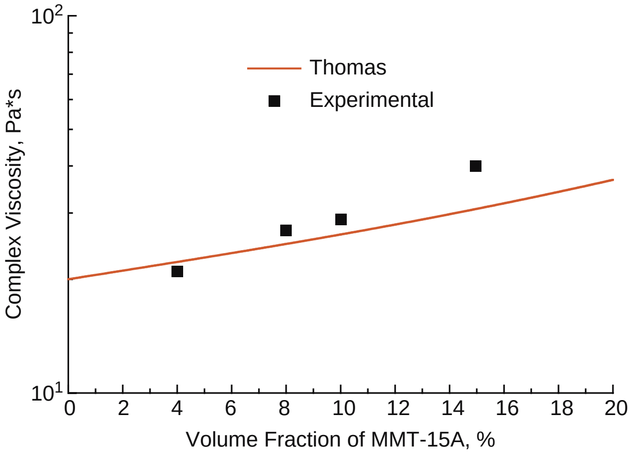


Fig. 6. Dependence of oligoimide s10 viscosity at $T = 240$ °C on volume fraction of MMT-15A particles. $\omega = 1$ rad/s, $\varepsilon = 1\%$.

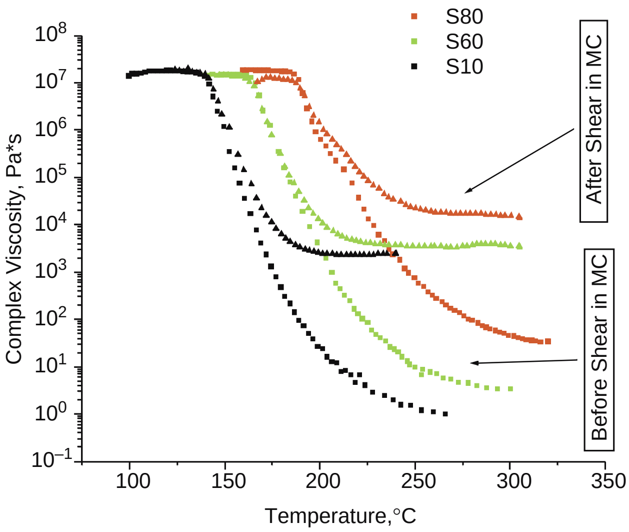


Fig. 8. Dependencies of complex viscosity on temperatures for nanocomposites R–BAPS–PA + MMT-15A (8 vol%) prepared with the aid of HAAKE MiniLab. $\omega = 1$ Hz, $\varepsilon = 1\%$.

behavior were obtained with s60/MMT-15A and s80/MMT-15A nanocmposites that were melt-blended in the micro compounder at 180 and 210 °C, respectively (Fig. 8). Melt blending of the S95 sample with MMT-15A particles at $T \geq 240$ °C was not possible because the MMT-15A thermally degraded at around 240 °C. As already discussed, at $T < 240$ °C the viscosity of pure s95 is too high and intractable to be processed as described above.

Because of the sensitivity of the viscosity of the nanocomposites to shear deformation, we measured the frequency dependence of complex viscosity of s10/MMT-15A mixture before (curve 1, Fig. 9) and after (curve 2, Fig. 9) formation of a percolating network as already discussed. Fig. 9 shows that a significant increase in the viscosity (three orders of magnitude) of s10/MMT-15A blend is obtained after its pre-shearing at 150 °C. As before, this increase in viscosity is ascribed to the formation of a percolating network or critical gel. In addition, the slope of the curve 2 in Fig. 9 is also observed to be increased by pre-shear and its value is analogous to the exponent or shear-thinning index ***n*** in the power law equation [28]:

$$\eta^* = K\omega^{-n} \tag{3}$$

The increase of ***n*** from ∼0.5 (curve 1, Fig. 9) to 1 (curve 2, Fig. 9) is thought to be due to an enhanced structural organization that is strongly sensitive to shear, leading to delamination of the nanoparticles from the matrix especially at high frequencies.

To test this hypothesis we performed XRD analysis on the s10/8 vol% MMT-15A nanocomposite that was pre-sheared at 150 °C as before. The result obtained is shown in Fig. 10. This figure suggests that the nanocomposite is only partially exfoliated because the intensity of d_{001} peak decreases. It is believed that the pre-sheared s10/MMT-15A blend after partial exfoliation is comprised of clay tactoids that may be susceptible to complete exfoliation by using higher shear equipment than the one used in this study. This study shows that a stress sustaining structure such as a percolating network

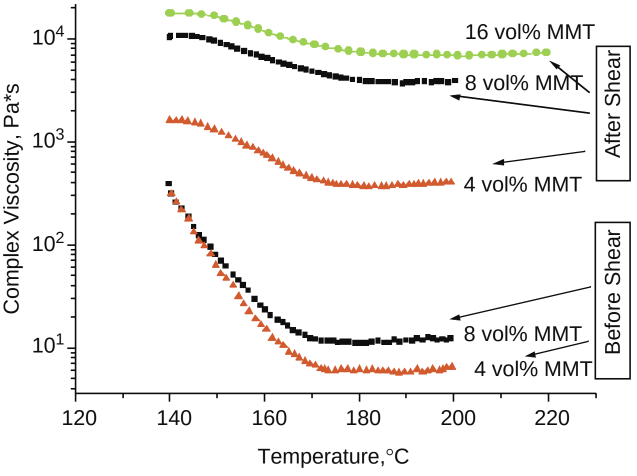


Fig. 7. Temperature dependence of viscosity for S10/MMT-15A mixtures before and after applying a shear at 150 °C in HAAKE MiniLab Micro Compounder. $\omega = 1$ rad/s, $\varepsilon = 1\%$.

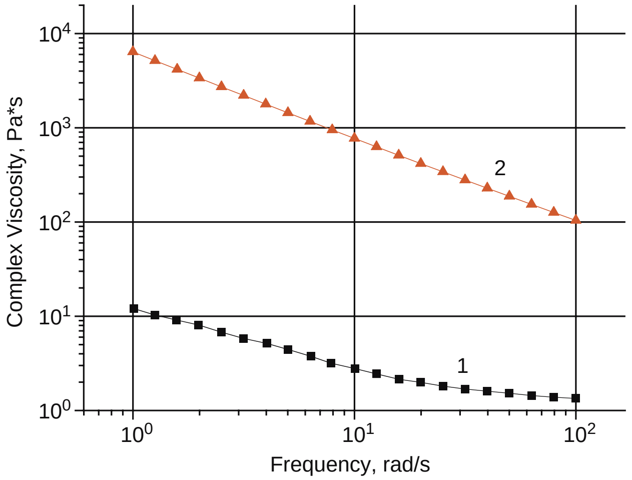


Fig. 9. Frequency dependence of viscosity at $T = 220$ °C for s10/8 vol% MMT-15A mixture: (1) before applying of shear; (2) after applying of shear. $\varepsilon = 1\%$.

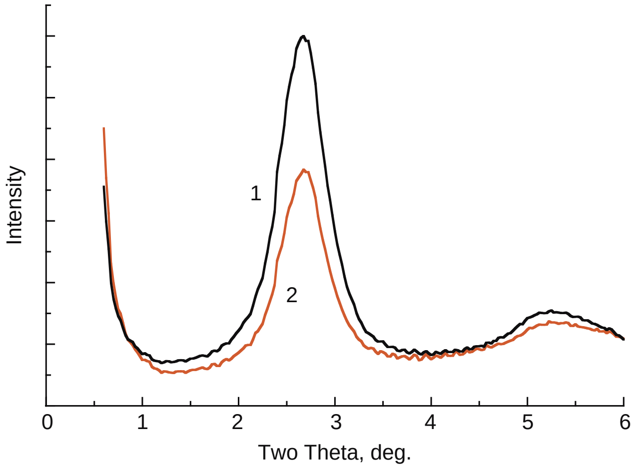


Fig. 10. XRD curves for s10/8 vol% MMT-15A mixture before (1) and after (2) applying of shear at 150 °C.

structure comprising of partially exfoliated MMT nanoparticles can be formed in the PI/MMT blends of this study; the resulting significant increase in the observed melt viscosity cannot be explained by the classical dependence of viscosity on volume fraction of small particles (Eq. (2)), indicating that a more complicated theory that explicitly takes the intrinsic physicochemical interactions (e.g. polymer-filler interaction via hydrogen bonding), concentrations, size distributions, and shear sensitivity of the nanoparticles into account may be necessary for a quantitative description of these nanocomposites [29]. This will be investigated in future proposed research.

4. Conclusions

We have demonstrated that polyimides of the R–BAPS type with relatively low molecular weights ($M_n \leq 100{,}000$ g/mol) can be melt-blended in a micro compounder with organomodified MMT particles to yield nanocomposites with enhanced benefits. Simple mixing in a micro compunder at 220 °C of the organo-modified clays with low molecular weight R–BAPS oligoimide melt leads to the formation of micro-composite with a particle concentration dependence of viscosity that is consistent with the classical Thomas equation. Application of a strong shear field in the micro compounder at relatively low temperatures close to the T_g of the respective oligoimide resulted in a nanocomposite with a significant increase in viscosity (nearly three orders of magnitude increase) that cannot be interpreted by existing theories in the literature. The significant viscosity increase exhibited by the oligoimide/MMT nanocomposites after application of the strong shear flow fields may be attributed to the partial exfoliation of the organo-MMT particles and formation of the percolating (network) structure at 6 ± 2 vol% of MMT in oligoimide melt. It is hoped that the interesting results of the present study may stimulate a better understanding of the influence of the morphological evolution on the rheology and processability of the polyimide/MMT clay nanocomposites. Because of their facile synthesis and desirable properties for a number of applications in protective coatings and films for microelctronic applications and flammability reduction, these low molecular weight polyimide/MMT clay nanocomposites are expected to be excellent model systems for future studies.

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