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Polyimide/silica hybrid-clay nanocomposites

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Abstract

A hybrid-clay nanocomposite was prepared by dispersing organically modified layered silicates (organoclay) into an organic–inorganic hybrid matrix. Layered silicates were dispersed in a hybrid matrix consisting of an alkoxysilane terminated amide acid oligomer and tetraethoxysilane. Transmission electron microscopy (TEM) and wide angle X-ray diffraction (WXRD) confirmed uniform dispersion and a high degree of predominantly exfoliated layered silicates. Storage modulus of the hybrid film containing 5 wt% exfoliated clay was 300% higher above the glass transition temperature and 30% higher at room temperature. The room temperature tensile strength and elongation to break decreased moderately with increasing clay loading. This approach provided a means of achieving excellent dispersion of predominantly exfoliated clay by reacting hydroxyl groups in the inorganic and organic precursors with hydroxyl groups at the edges of the clay layers.

Keywords: Clay; Organic–inorganic hybrid; Nanocomposite

1. Introduction

The observation that incorporation of clay (i.e. layered silicates) into a polymer matrix imparts unique physical and chemical properties was first reported by the Toyota Research Lab for nylon 6/organoclay nanocomposites [1]. Since then, many literature reports on various polymer-clay nanocomposites have appeared. In many of these reports, the organoclay is only intercalated or partially exfoliated in the matrix and not fully dispersed [2–9]. One of the reasons for the low degree of dispersion is the lack of compatibility between the hydrophilic clay surfaces and the organophilic polymer. Natural clay, such as montmorillonite, is classified as a 2:1 phyllosilicate and is intrinsically hydrophilic. To make them more oleophilic, the natural clays are often modified with small organic functional molecules. These organoclays have been available for many years in the clay industry and often used to aid in intercalating and exfoliating layered silicates in a polymer [10]. A method to enhance the intercalation and exfoliation of organically modified silicates into polymers has involved surface modification of the organoclay with organosilanes [11–17]. These silane modified organoclays have been used as nano-inclusions in rubber [12,15], PAN [14] PMMA [16], and polyimide [17] matrices for mechanical reinforcement.

In general, there are three common methods to disperse organically modified layered silicates into a polymer. The first method involves dispersion of a dilute layered silicate solution in a polymer solution to intercalate and exfoliate the layered silicates by high shear and cavitational forces (ultrasonication), followed by solvent evaporation [18]. This approach is simple, but the exfoliated layered silicates often collapse back to stacked layers during solvent evaporation or thermal cure. The second approach involves in situ polymerization [1,19–21], where a monomer is anchored in the gallery located between the silicate layers and polymerization occurs while the material is under shear. This method, however, is not universally applicable to all polymer types and the polymerization often tends to be incomplete. The third method involves melt blending under high shear [5,22] and is applicable primarily to

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thermoplastic polymers and typically produces preferentially oriented inclusions along the flow direction. Complete dispersion of the clay as individual layered silicates in a polymer matrix has rarely been achieved by these methods due to the intrinsic strong attraction among the clay layers with large surface areas.

The objective of the present study was to provide a unique method to exfoliate and uniformly disperse layered silicates into individual layered silicates in a host polymer by using a reactive organic–inorganic hybrid as the matrix. Hydroxyl groups in the inorganic and organic precursors can react with hydroxyl groups at the edges of the clay layers resulting in hydrogen and/or covalent bonding between the two materials aiding in the exfoliation of the intercalated layered silicates under high shear. It will be shown that this approach prevents the collapse of the individual layered silicates into stacked layers and achieves complete exfoliation and uniform dispersion as individual layered silicates. The chemistry, morphology, and physical properties of the resulting nanocomposites will be described.

2. Experimental

2.1. Materials

The organic precursor was a pendent phenylethynyl imide oligomeric dialkoxysilane (PPEIDS) based on 3,3′,4,4′-biphenyl tetracarboxylic dianhydride, 3,4′-oxydianiline, and 3,5-diamino-4′-phenylethynylbenzophenone and end-capped with aminophenyltrimethoxysilane. It was prepared at a calculated number average molecular weight (M_n) of 5000 g/mol as previously reported [23]. Tetraethoxysilane (TEOS, 98%, ACROS Organics) was used as received as an inorganic precursor. Cloisite 30B (S30B), an organically modified clay, was obtained from Southern Clay Products, Inc. This organoclay consists of a natural montmorillonite modified with a ternary ammonium salt that contains a tallow group. The specific gravity of the organoclay is 1.98 g/cm^3. *N*-Methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co., Inc.) was used as a solvent for the organic–inorganic solution as received. For comparison, PETI-5 (phenylethynyl terminated imide oligomer, (Imitec, Inc.)) [24] or PPEIDS itself was also used as a matrix.

2.2. Hybrid-clay preparation

2.2.1. Organic–inorganic hybrid sol–gel solution preparation

PPEIDS and TEOS were used to formulate a hybrid sol–gel solution at approximately 15% (w/w) in NMP in a beaker equipped with a stir bar. The composition of the sol–gel solution was an 85/15 ratio of PPEIDS to TEOS. Distilled water was added dropwise to the stirred transparent solution at room temperature to hydrolyze the alkoxysilane groups. Addition of water caused immediate formation of a white precipitate, which dissipated within 5 min, forming a transparent, dark brown solution. The transparent sol–gel solution was stirred at least 12 h prior to casting thin films or mixing with the organoclay.

2.2.2. Clay solution preparation

The organoclay, S30B, was added to NMP and sonicated with a ultrasonic bath at 50 kHz at 65 °C for 3 h to intercalate (swell) the inter-layers of the clay affording a light clear yellow solution. The solution was subsequently homogenized with a high-shear homogenizer (Powergen Model 700) for 10 min (750 rpm with a 30 mm diameter flat bottom rotor) to generate a translucent solution with a light yellow tint. The concentration of the clay was 1% (w/w) in NMP.

2.2.3. Hybrid-clay solution preparation

The hybrid solution was prepared in a beaker with the organoclay solution added at the prescribed ratio. The mixture was homogenized with a high-shear homogenizer for 15 min (750 rpm with a 30 mm diameter rotor) at room temperature to disperse the intercalated clay platelets in the sol–gel solution. Homogenization tended to be exothermic, raising the temperature of the solution up to approximately 40 °C. Following homogenization, the solution was sonicated for 1 h at 65 °C to eliminate air bubbles and promote better mixing. The resulting dark-brown transparent solution was fairly stable (no sedimentation observed) for at least up to 3 months at 4 °C. PPEIDS-clay and PETI-5-clay solutions were also prepared using the same procedure as the hybrid-clay solution for comparison.

2.2.4. Film cast

The hybrid and hybrid-clay solutions were cast on clean, dry glass plates and dried until tack-free in a low-humidity chamber at room temperature. The films on glass were cured at 110 and 220 °C for a half hour each, and then at 252 and 371 °C for 1 h each in flowing air. The cured films were retrieved from the glass substrate by immersing the plate in a warm water bath.

2.3. Characterization

Tensile properties of the films were measured with a tensile tester (SINTECH 2000/2w) according to a modification of ASTM D882. The test film dimension was $50\times 5\times 0.050$ mm^3 ($L\times W\times t$). Five specimens were used for each test condition. Dynamic mechanical analysis (DMA, Rheometrics DMTA Mark V) was performed in a tensile mode with a constant dynamic strain amplitude on the film samples in air. Data at 1 Hz were collected for 1.0 °C/min increments. An optical microscope (Olympus BH) was used to examine the macroscopic phase separation between the organic and inorganic phases. Transmission electron microscopy (TEM) was employed with a Zeiss CEM 925 in the bright field mode to assess the dispersion and exfoliation of the layered silicates in the hybrid matrix. The specimen for TEM was sectioned approximately 70 nm thick with an ultramicrotome at room temperature after embedding in an epoxy mold. To examine the degree of exfoliation (delamination) of the layered silicates, wide-angle X-ray diffraction (WXRD) measurements were performed with a Siemens rotating anode wide angle X-ray diffractometer. The X-ray source was Ni-filtered Cu Kα radiation ($\lambda = 1.541838$ Å). The 2θ-scan was performed between 2 and 20° at the rate of 5°/min at room temperature. The structure of the organoclay was studied before and after hybrid-clay nanocomposite synthesis. Specimens were prepared from thin films of the hybrid-clay nanocomposites. For the reference, Cloisite 30B (S30B, organoclay) was used as a powder form.

3. Results and discussion

3.1. PPEIDS/TEOS hybrid matrix

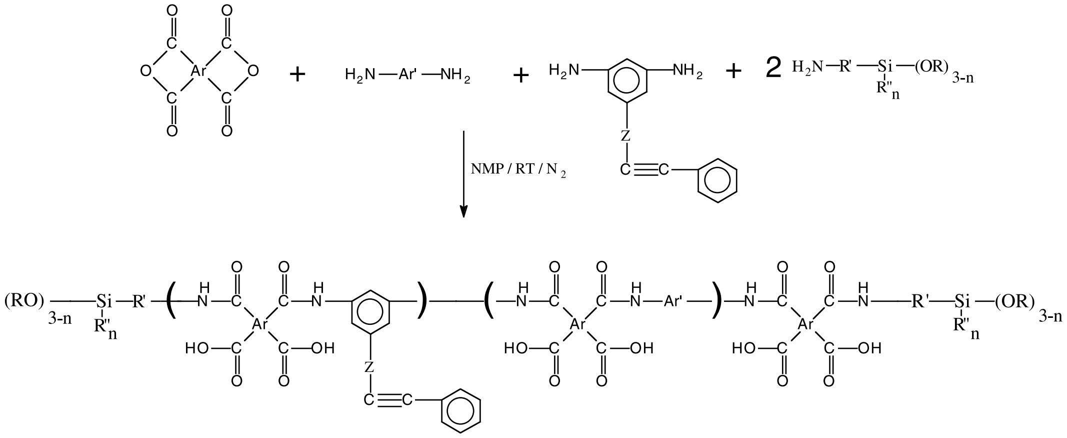
The matrix system chosen to perform this study was based on materials originally developed to improve the hot-wet performance of bonded structures of PETI-5 (phenylethynyl terminated imide oligomer) [23]. The approach involved the use of oligomeric species (PPEIDS) containing terminal alkoxysilane groups and a pendent phenylethynyl group (Scheme 1). Under the appropriate conditions, the alkoxysilane groups can hydrolyze to give the corresponding silanol moieties. These silanol groups can then self condense affording siloxane chains or with hydroxy groups located on the inorganic surface affording oxane bonds. Upon thermal cure to 371 °C, the pendent phenylethynyl groups on PPEIDS would then react with the phenylethynyl groups on neighboring PPEIDS to give a crosslinked matrix.

The PPEIDS described above was mixed with TEOS at various weight loadings and the thin film properties were evaluated [23]. The organic–inorganic hybrid sol–gel solutions of the PPEIDS/TEOS formed transparent hybrid films up to a 90 wt% TEOS loading. The hybrid composition chosen for the present study was a PPEIDS/TEOS ratio of 85/15 based on preliminary assessment of physical and mechanical properties. A thin film prepared from this material was transparent and flexible. The film exhibited room temperature tensile properties of 4.25 ± 0.13 GPa, 145 ± 7.9 MPa, and 6.05% for the Young's modulus, tensile strength, and elongation at break, respectively. No phase separation between the organic and inorganic phases was observed by optical microscopy. No discernible features were observed by TEM of this hybrid film (Fig. 1), indicating the organic–inorganic hybrid was homogeneously mixed at the molecular level.

3.2. Hybrid-clay nanocomposites

Hybrid-clay nanocomposites were prepared by dispersing organically modified layered silicates (organoclays) into the organic–inorganic hybrid (PPEIDS/TEOS(85/15)) matrix at loading levels ranging from 2 to 5 wt%. The same process was used to prepare a PPEIDS/clay nanocomposite with the organoclay loading of 5 wt% for comparison. Fig. 2 depicts a flow diagram illustrating the process used for preparation of the organic–inorganic hybrid-clay nanocomposite. The PPEIDS/TEOS(85/15) hybrid-clay amic acid sol–gel solution was sufficiently acidic (pH = 4.8) to initiate efficient hydrolysis reaction of the alkoxysilane groups to the corresponding silanols, therefore, no additional acid was added to the reaction medium. To ensure complete hydrolysis, water was added to the sol–gel solution and it was stirred for at least 12 h at RT prior to casting films. Hybrid-clay thin films remained optically transparent after thermal cure for clay loadings up to 5 wt%.

Optical microscopy was used to screen the hybrid-clay nanocomposite films for phase separation and agglomeration. No noticeable features were observed, indicating that the organic (PPEIDS) and inorganic phases (TEOS) in the hybrid matrix mixed homogeneously below the visible light



Scheme 1. Synthesis of pendent phenylethynyl imide oligomeric disilane (PPEIDS).

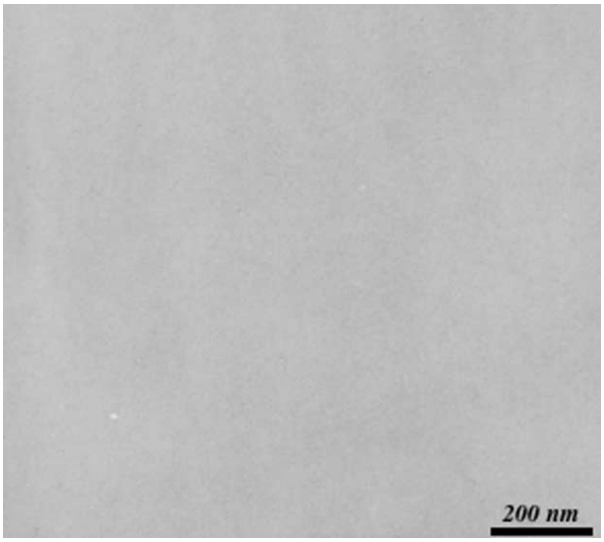


Fig. 1. Transmission electron micrograph of 85PPEIDS/15TEOS hybrid.

range in the presence of the layered silicates, and the layered silicates dispersed homogeneously without optically observable agglomeration. To further examine the dispersion and exfoliation of the layered silicates in the hybrid matrix, TEM was used. TEM micrographs of the hybrid-clay nanocomposite with a 5 wt% clay loading is shown in Fig. 3. The hybrid matrix in the hybrid-clay nanocomposite in Fig. 3 revealed no noticeable phases, indicating that the organic (PPEIDS) and inorganic (TEOS) components were mixed at the molecular level and the miscibility of the two phases was not influenced by the presence of the layered silicates. Fig. 3(a) shows uniform dispersion of predominantly exfoliated layered silicates throughout the hybrid matrix. Most of the exfoliated layered silicate platelets dispersed as individual or double layers; however, a few dispersed multi-layered silicate platelets were observed. Although a few multi-layered silicate platelets are present, no regularly stacked layered silicates were observed in the matrix as seen in Fig. 3(b). The thickness of the dispersed silicate layers in the hybrid-clay in Fig. 3 was approximately 1 nm indicating that the layered silicates were nearly completely exfoliated and delaminated.

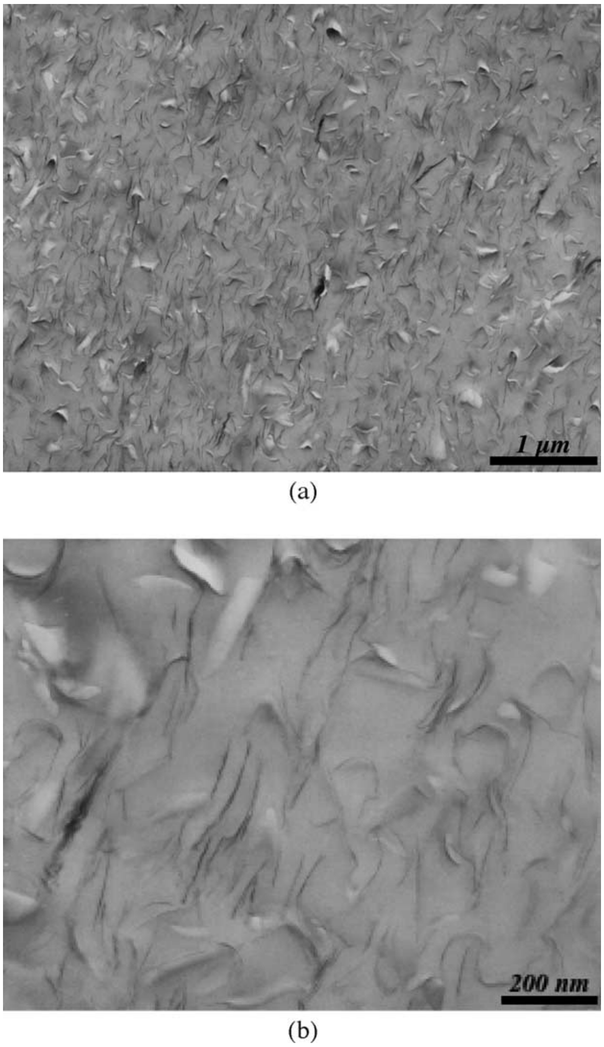


Fig. 3. (a) and (b) Transmission electron micrographs of 85PPEIDS/15TEOS-clay (5 wt%) nanocomposite.

The organic precursor PPEIDS has trialkoxy silane groups at both chain ends as well as pendent phenylethynyl

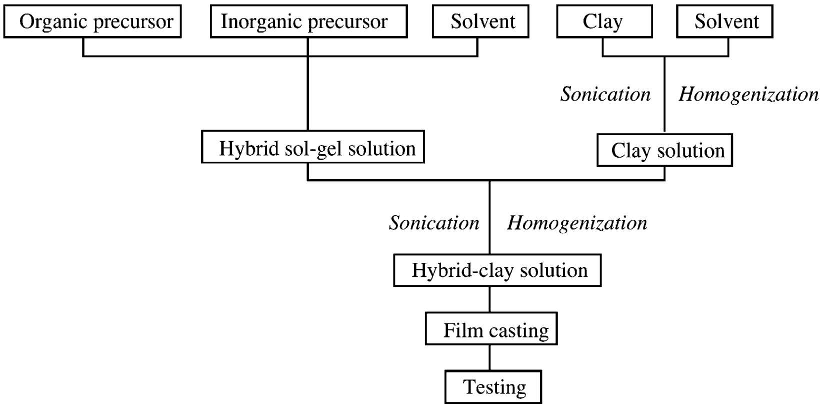


Fig. 2. Flow diagram for preparation of organic–inorganic hybrid-clay nanocomposites.

groups randomly distributed along the backbone with the backbone (Scheme 1) analogous to PETI-5 (phenylethynyl terminated imide oligomer) [23]. When the organoclay (1.5 wt%) was mixed with PETI-5 without any silane moiety, the layered silicates formed micrometer-scale large agglomerates as shown in Fig. 4 and no exfoliation and delamination of the individual layered silicates were observed. The nanocomposite film of PPEIDS-clay prepared with a clay loading (5 wt%) was likewise examined by TEM. As observed in the TEM micrograph of a PPEIDS-clay (5 wt%) nanocomposite film, a uniform dispersion of the layered silicates was achieved as seen in Fig. 5. The PPEIDS has a similar backbone structure to PETI-5, but contains additional alkyl silanol groups at both ends, which provides reactive sites (hydroxyl) with the hydroxyl groups at the edges of the clay platelets. This suggests that the hydroxyl groups in the polymer matrix aided in the dispersion of the layered silicates during the shear mixing. However, exfoliation and delamination of the individual layered silicates were not as complete as the hybrid-clay nanocomposite containing TEOS as part of the formulation. The distance between the layered silicates of the PPEIDS/TEOS hybrid-clay (Fig. 3) appeared shorter than that of PPEIDS-clay nanocomposite at the same clay loading because more layered silicates dispersed as individual silicate platelets. The presence of additional hydroxyl groups afforded by TEOS may have contributed to more efficient delamination of the layered silicates as well as preventing the collapse of the individual layers during the drying/curing treatment.

Fig. 6 shows results of the wide angle X-ray diffraction (WXRD) of the pristine organoclay, PPEIDS-clay, and the hybrid-clay nanocomposites. A strong peak was observed at 4.76° (2θ) for the pure organoclay, corresponding to the (001) plane peak, indicating the interlayer spacing (*d*-spacing) of the organoclay was about 18.6 Å. This value is comparable to the value (18.5 Å) reported by the supplier (Sourthern Clay Products, Inc.). The organoclay studied here is a natural montmorillonite modified with a ternary ammonium salt and has a larger interlayer spacing than a natural montmorillonite (12.4 Å). The (001) plane peak of the layered silicates for PPEIDS-clay (5 wt%) shifted to 2.63° (2θ) indicating significant exfoliation of the inter-layer spacing (33.6 Å), but not complete delamination. On the other hand, the (001) plane peak of the layered silicates disappeared for the hybrid-clay nanocomposites (2 and 5 wt% clay) within the scanned range, which suggests that the layered silicates exfoliated (delaminated) completely or were separated at least more than 8 nm, the measurable limit of the instrument. This result is consistent with observations noted in the TEM micrographs in Figs. 3–5.

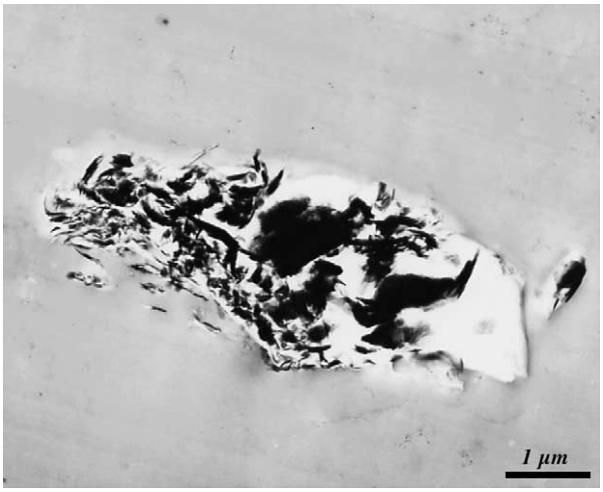


Fig. 4. Transmission electron micrographs of PETI-5/clay (1.5 wt%) nanocomposite.

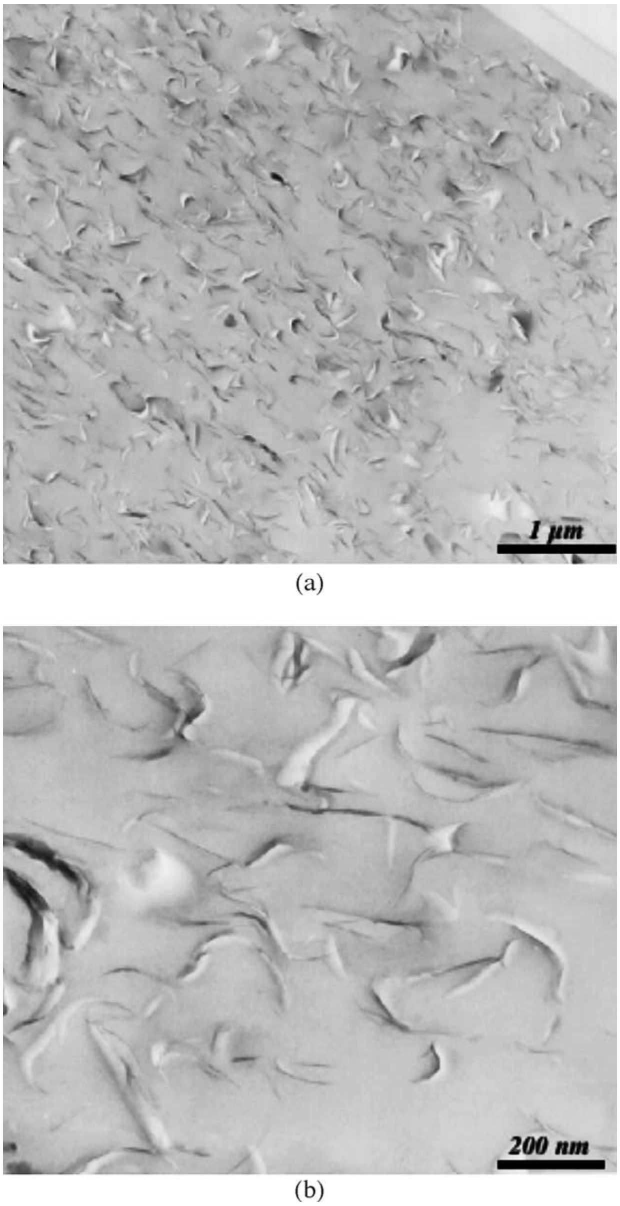


Fig. 5. Transmission electron micrographs of PPEIDS/clay (5 wt%) nanocomposite.

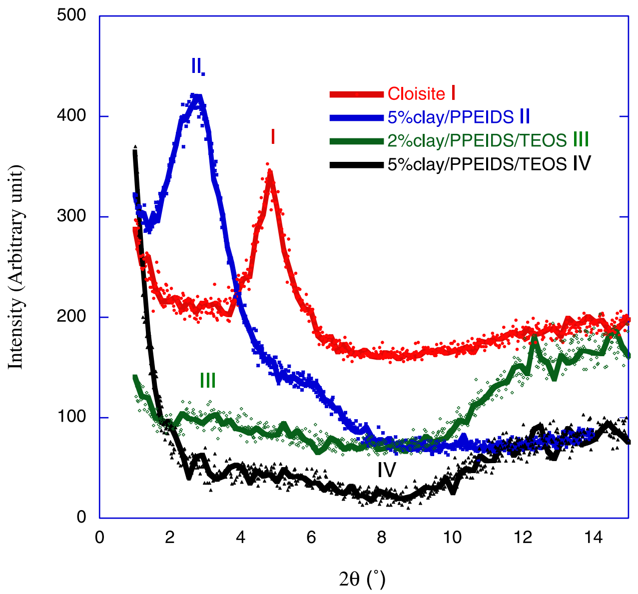


Fig. 6. Wide angle X-ray diffraction of the clay and hybrid-clay nanocomposites.

It is known that 2:1 phyllosilicates (e.g. montmorillonite) do not have appropriate reactive sites (hydroxyl groups) in the inter-layer space and only hydrous alkali silicates (e.g. kanemite and magadiite) and crystalline silicic acids contain silanol groups in the internal surfaces [13]. Accordingly, bonding with the hydroxyl groups of the hybrid matrix is restricted to the hydroxyl groups located on the edges of the layered silicates studied here. Since the ratio of the edge to the surface of the layered silicates is low, application of conventional coupling agents to modify the layered silicate surfaces or to bond with the edges is likely to be inefficient. The low probability of bonding with the edges can be improved by providing additional reactive sites to the matrix. In this study, an inorganic precursor, TEOS, was utilized to generate these sites.

A proposed dispersion process of the individual layered silicates in the hybrid-clay nanocomposite may be described as follows. The silanol groups present in the organic (PPEIDS) and inorganic (TEOS) components react with the hydroxyl groups located at the layered silicate edges and with themselves to form hydrogen and/or covalent bonds as seen in Fig. 7. For simplicity, only the hydrolyzed form of PPEIDS is shown. The covalent bonding between the hydroxyl groups on the edges of the silicate layers and the surrounding matrix aided in disrupting and delaminating the exfoliated layered silicates into individual silicate platelets under high shear by transferring the shear forces to the individual silicate layers independently and more efficiently. The remaining silanol groups react further to form a network structure through self-condensation, preventing the dispersed individual delaminated platelets from collapsing back to a layered structure during thermal imidization. Unfortunately, FTIR spectroscopy was not able to distinguish the two types of bonds. Previous work with polyimide-exfoliated layered silicates without inorganic moieties (silanol groups) often showed that the layers tended to collapse during drying and thermal imidization [25,26].

Room temperature tensile properties of the hybrid-organoclay films are presented in Fig. 8. For increasing clay concentration, the elastic modulus increased while the yield strength and percentage elongation at break decreased as reported in elsewhere [3,5,7,27]. With a 5 wt% loading of the organoclay, the tensile modulus increased approximately 30% as compared to PPEIDS/TEOS(85/15). A comparable modulus to that of the 5 wt% clay/PPEIDS/TEOS could be achieved for the PPEIDS/TEOS film, where TEOS comprised 40 wt% of the composition, and this material was brittle. The room temperature yield strength and percentage elongation at break of the hybrid/clay (5 wt%) nanocomposite were 81 MPa and 1.7%, respectively, while those of the PPEIDS/TEOS(60/40) hybrid were 39 MPa and 0.7%, respectively. The more effective reinforcement effect of the clay inclusion (5 wt%) compared to the inorganic precursor (TEOS) (25 wt%) is likely to be due to the uniform nanometer-scale dispersion of the high aspect ratio layered silicates.

The DMA spectra of the storage moduli and tan delta of the nanocomposites are shown in Fig. 9 and the values below and above T_g are summarized in Table 1. The storage modulus of PPEIDS at room temperature increased by 33% when 15 wt% TEOS was mixed at the molecular level as seen in the TEM micrograph (Fig. 1). As observed for the room temperature tensile modulus, the room temperature storage modulus of the hybrid-clay composites increased moderately with increasing clay loading. For a 5 wt% clay loading, the modulus increased approximately 17% compared to the PPEIDS/TEOS(85/15) and 56% compared to PPEIDS. Above the T_g, the storage modulus increased significantly with the incorporation of clay with respect to PPEIDS/TEOS(85/15) as seen in Fig. 9. More than a three-fold increase in the storage modulus was observed for a 5 wt% clay loading. The tan delta peak for the 5 wt% clay loading was suppressed relative to the other materials as seen in the inset of Fig. 9. This suggests that the relaxation of the polymer in the vicinity of the layered silicate surfaces was suppressed around T_g. Comparable T_gs were observed

Table 1
Summary of the DMA spectra

	E' (GPa) RT	E' (GPa) above T_g	tan δ	Temp. (°C) at tan δ max
PPEIDS	1.98	0.20	0.23	366
PP/TE (85/15)	2.63	0.15	0.25	354
2% Clay/PP/TE (85/15)	2.57	0.25	0.24	352
3% Clay/PP/TE (85/15)	2.73	0.24	0.26	347
5% Clay/PP/TE (85/15)	3.08	0.46	0.17	353

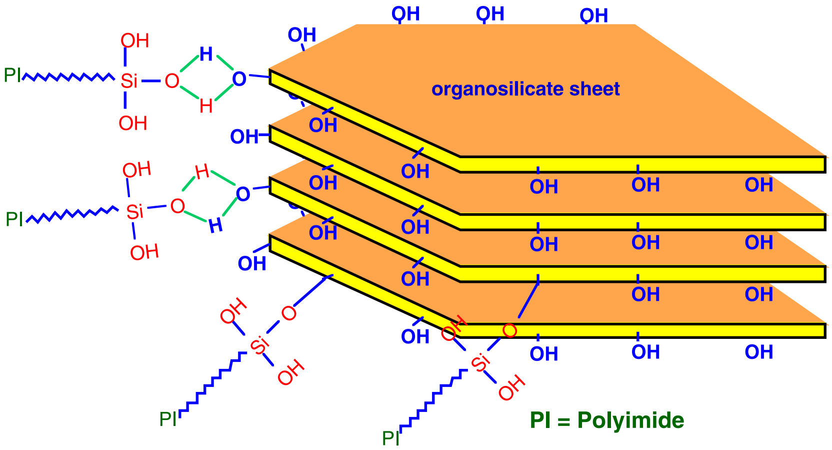


Fig. 7. Reaction between the inorganic precursor and edges of the layered silicates to form hydrogen and/or oxane bonds.

for all of the hybrids regardless of clay loading. The efficacy of clay inclusion reinforcement was pronounced only above T_g in the rubbery state where polymer molecules have a high degree of segmental motion. This result is consistent with reported literatures where significant reinforcement was found mostly in rubber polymers [1,15,27–29] rarely in glassy polymers [3,5,7,20,30,31].

4. Conclusions

A method for achieving a homogeneous dispersion of exfoliated layered silicates as nanometer-thick layers in a polymer matrix was developed. This involved the use of an organic–inorganic hybrid as the matrix to aid in dispersion of the layered silicate inclusions. An inorganic precursor was used to assist in the complete dispersion of the predominantly exfoliated layered silicates with the aid of high shear mixing and sonication. Hydroxyl groups in the inorganic and organic precursors presumably reacted with hydroxyl groups at the edges of the clay layers resulting in hydrogen and/or covalent bonding between the two materials aiding in the exfoliation of the intercalated layered silicates under high shear. The remaining silanol groups subsequently reacted through self-condensation and the phenylethynyl groups reacted to form a crosslinked network structure, thus preventing the exfoliated and dispersed single layers from collapsing during film drying and thermal imidization and cure. Near complete dispersion of exfoliated layered silicates was observed in TEM micrographs and confirmed by WXRD. Storage modulus of the hybrid above T_g was improved three-fold for a 5 wt% exfoliated clay loading. The efficacy of clay inclusion reinforcement was pronounced only above T_g in the rubbery state where polymer molecules have a high degree of segmental motion.

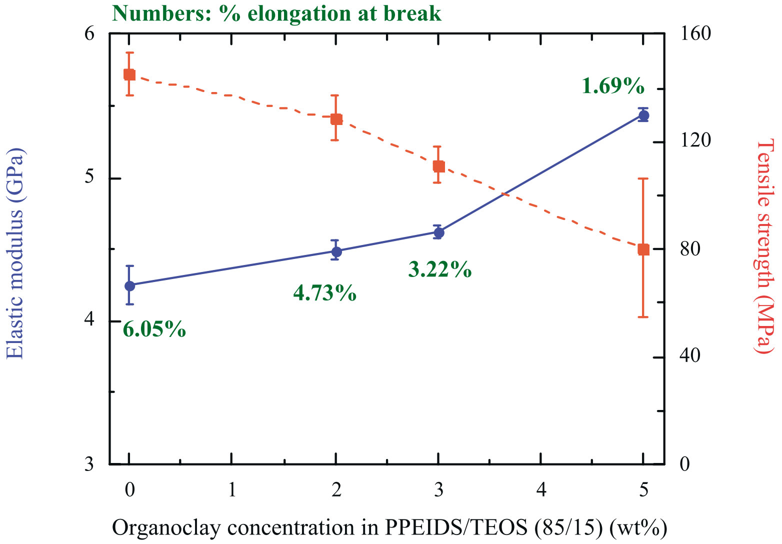


Fig. 8. Room temperature tensile properties of 85PPEIDS/15TEOS-clay nanocomposites as a function of clay concentration.

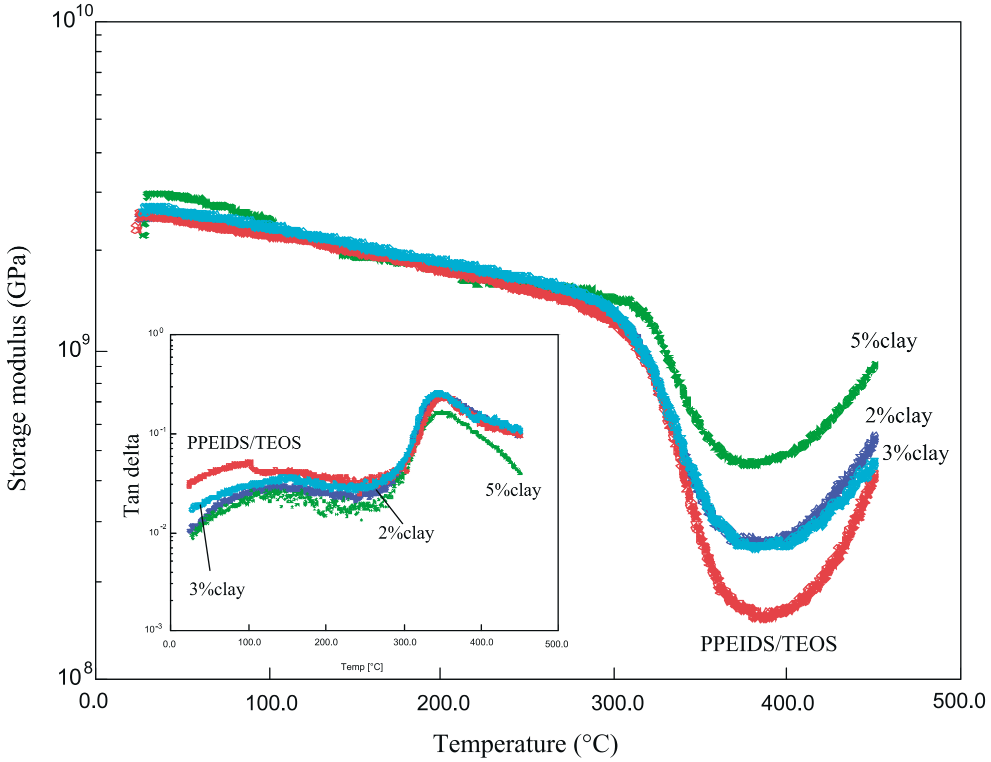


Fig. 9. Dynamic mechanical analysis of 85PPEIDS/15TEOS hybrid and hybrid-clay nanocomposites.

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