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Synthesis, Characterization and Dynamic Mechanical Properties of Polyimide-Polyurea-Polysilsesquioxane Block Terpolymers

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ABSTRACT

A novel type of polyurea-*b*-polyimide(PUI)-LPS terpolymer containing ladder like polysilsesquioxane (LPS) hybrid thin film was successfully prepared by coupling ladder-like polysilsesquioxane (LPS) with polyurea-*b*-poly(amide acid), followed solution film casting and thermal imidization. The LPS composed of mercapto and fluoride side groups was synthesized by sol-gel and monomer self-assembly methods. The structure and properties of the resulting PUI-LPS thin films were affected by the reaction conditions. Dynamic contact angles (DCA) and dynamic mechanical analysis (DMA) were used to study the surface energy and mechanical properties of PUI-LPS thin films. The presence of LPS containing fluoride and mercapto side groups significantly increased the extent of cyclodehydration (imidization) process at a relatively low temperature of about 150°C. The surface energy of the hybrid thin films was remarkably decreased as LPS concentration increased. The dynamic mechanical properties of the hybrid thin films were determined by dynamic mechanical analysis (DMA). Fourier transform infrared spectroscopy (FTIR) and Wide-angle X-ray diffraction (WAXRD) methods were used to study the composition and structure of the hybrid thin films.

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Received: April 21, 2022; **Accepted:** May 06, 2022; **Published:** May 12, 2022

Keywords: Polyimide, Polyurea, Ladder-Like Polysilsesquioxane, Thermomechanical Properties, Surface Energy

Introduction

Polyimides have received intense attention and they are widely used in the aerospace and other industries since 1960s because of their excellent mechanical properties, thermal stability, high glass-transition temperature (T_g) and dielectric properties [1-6]. However, polyimides have certain limitations such as moisture absorption, relative low adhesion and high surface energy which limit their application in microelectronics, aerospace and sustainable energy technologies [7-9]. Additionally, their high processing temperature makes polyimide an expensive polymeric material [10]. To satisfy growing commercial and technical requirements, some silicon-containing polyimide composites and copolymers have been explored [11]. For examples, the copolymerization of polysiloxane with polyimide has shown encouraging waterproof property, decreased surface energy as well as reduced imidization temperature [12-14]. However, the incorporation of polysiloxane usually significantly reduces the onset decomposition temperature and glass transition temperature, T_g , and thereby reduces its service temperature, because polysiloxanes have very low T_g of about -123°C [12, 15]. Due to the thermodynamic incompatibility between polyimide and polysiloxane blocks, phase separation occurs and results in imide-rich hard domains and siloxane-rich soft domains [9]. The incorporation of silica (SiO_2) or clay into polyimide has been effective in the enhancement of thermal stability and modulus, but drastically decreases the damping, flexibility and adhesion of polyimides [2, 16-18].

The drawback inherent in polyimide-*b*-polysiloxane can be overcome by coupling onto polyimide chain a ladder-like polysilsesquioxane (LPS) which is a double-stranded polysiloxane with low surface energy, excellent thermal stability and superior mechanical properties [19-21]. According to the study carried out by, it was shown that thermal degradation of the copolymers occurs only at temperature $> 400^\circ\text{C}$ [21]. Additionally, decomposition produced about 70% residue spread over a wide temperature range 400-700 °C. Successfully increased both decomposition temperature and the char retention of polyimide by coupling LPS onto the polyimide main chain [22]. LPS possesses high T_g and thermal decomposition temperature than linear polysiloxanes have been investigated in the past several decades since they were first reported in literature by [23]. Synthesis of ladder and semi-ladder polymers requires precise configuration control during the polymerization of multifunctional monomers [24]. Otherwise, cyclization and gelation reactions will lead to the formation complicated products such as cyclic ladder, cage and cross-linked structure [25]. Zhang, et al. used a novel synthesis method named ‘supramolecular architecture-directed stepwise coupling and polymerization’ and produced a series of ordered LPSs [26-28]. Later, a more convenient three-step approach (monomer self-organization, lyophilization and surface-confined polymerization) was also reported by this group [29]. Recently, ladder-like polysiloxanes were reported to show photo-induced aligning capability, which makes them suitable for use optoelectronic application such as light emitting diodes and solar cells [30-32].

In this paper, the copolymerization of rigid polyurea (PU) with Kapton polyimide (PI) is carried out by using environmentally friendly 4,4'-oxydianiline and N-methyl-2-pyrrolidinene (low volatile organic compound). The presence of hydrogen bond (H-bond) donor atom and H-bond acceptor atom in PUI copolymer can lead to the desirable thermomechanical, interfacial and surface properties [33, 34]. FTIR and WAXD were used to investigate the structure of LPS and the terpolymers. The effect of LPS on the thermomechanical properties of PUI copolymers was studied by DMA. It shows the variation in T_g , storage modulus at the glassy and rubbery plateau regions and damping ability. The surface energy was calculated from contact angle measured by using dynamic contact angles (DCA). The variation of the degree of imidization with varying LPS concentration was determined by using FTIR.

Experimental

Materials

Pyromellitic anhydride (PMDA), 4,4'-Oxydianiline (ODA), 4,4'-methylenbis(phenyl isocyanate) (MDI), N-Methyl-2-pyrrolidinene (NMP), Triethylamine (TEA) and Diiodomethane (99%, contains copper as stabilizer) were purchased from the Sigma-Aldrich Co. (USA). (3-Mercaptopropyl)-trimethoxysilane (MPTMS), (3,3,3-trifluoropropyl)-trimethoxysilane (FPTMS) and 3-Aminopropyl triethoxysilane (3-APTES) were purchased from Gelest Co. (USA). Toluene and tetrahydrofuran (THF) were purchased from Fisher Scientific Co. (USA). Distilled water (DI water) was purchased from TEDIA Co. (USA).

Synthesis

Preparation of Ladder like Polysiloxane (LPS)

The LPS composed of mercapto and fluoride side groups was synthesized via sol-gel and self-assembly methods (Figure 1). 4.5947 g FPTMS (0.02 mol) was dissolved in 40 ml toluene in a conical flask with magnetic stirring. Subsequently, 10 ml distilled water was added dropwise with a speed of 2 drops/min. After 10 min stirring, 4.1335 g MPTMS (0.02 mol) was added into the solution, followed by additional 10 min of stirring. 0.2 g TEA was then added into the solution. The flask was then fitted with a condenser and heated up to 100 °C in an oil bath for 48 hours with refluxing and stirring. After sol-gel reaction, the reaction mixture was separated into an organic solvent phase and an aqueous phase. The lower aqueous layer was removed with a funnel attached to the bottom of the flask and the organic layer was collected. The collected organic solution was washed with ultra-pure water until PH of 7 was achieved. To remove toluene, LPS solution was dried at 60 °C for 5 hours under vacuum, followed by dissolution in THF.

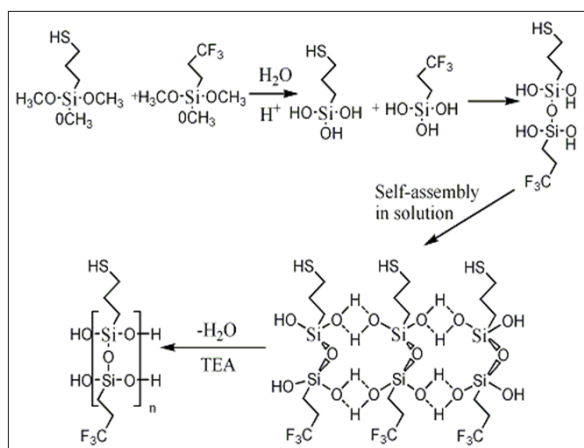


Figure 1: Synthesis of LPS containing fluoride and mercapto side groups

Synthesis of Polyimide-b-Polyurea (PUI) Copolymers Containing LPS

Anhydride terminated poly (4,4'-oxydiphenylene-pyromellitic acid) (PAA) solution was synthesized by condensation polymerization. 15.4824g ODA (0.075mol) was added into 300ml of NMP with mechanical stirring under nitrogen atmosphere at room temperature. After 30min of stirring, ODA was completely dissolved in NMP. 17.0334g PMDA (0.07575mol) was then added into the solution and cooled to 10°C by circulating coolant from a refrigerated cooling system. After 2 hours, anhydride terminated PAA solution was obtained. Isocyanate terminated poly (4,4'-oxydiphenylene-methylenebisphenylurea) (PU) solution was also prepared by step polymerization. 25.5495g MDI was added into a 300ml NMP solution of 20.6535g ODA under a nitrogen atmosphere with stirring, and then the mixtures were stirred for 12 hours. 48ml, 96ml and 192ml of isocyanate terminated PU solutions were added into 128ml anhydride terminated PAA solution, respectively, to obtain PUI33-EX, PUI50-EX and PUI67-EX copolymers. After 0.5h of stirring, 0.01g ODA was added into mixture solution and stirred for additional 3h. 1 ml 3-APTS was hydrolyzed by distilled water and then added dropwise into poly(amic acid)-polyurea solution for 30 min with mechanical stirring, followed by the addition of 10 mol% and 20 mol% LPS, respectively, and mechanically stirred for additional 3 hours. Then PUI and PUI-LPS thin films were obtained by solution casting onto a properly cleaned glass, followed by thermal curing. The step-wise thermal curing scheme is: 75°C for 1.5h, followed by heating at 100°C for 0.5h, followed by heating at 120°C for 2h and finally the curing temperature was raised to 150°C for 5h. PUI and PUI-LPS freestanding thin films were obtained after thermal curing.

Characterizations

Nicolet 6700 FT-IR instrument equipped with a Smart Orbit ATR accessory with diamond crystal was used to determine the chemical composition of the samples. ATR was performed over a wavenumber range between 4000 cm^{-1} and 400 cm^{-1} . Wide angle X-ray diffraction (WAXD) was used to study the crystallization and structure of the samples. X-ray diffraction tests were carried out by using a Cu-K radiation source at a wavelength of 1.54 Å. WAXD test was carried out from a diffraction angle, 2-theta, of 3–35°. The cross-sectional morphology of the films was studied by using the Environmental Scanning Electron Microscopy, model FEI XL30 FEG ESEM. ESEM samples were prepared by immersion in liquid nitrogen and then fractured using a pair of tweezers to expose the cross-sectional area. A Polaron SC7640 sputter coater was used to coat the samples with silver in order to improve their conductivity. Dynamic Mechanical Analysis was used to study the variation of storage modulus and $\tan \delta$ of neat polyimide, neat polyurea and PUI copolymers films with temperature. Dynamic mechanical analysis was performed by using DMS6000, Seiko Instruments Inc. The test was performed under tensile loading mode at a heating rate of 10 °C/min and a frequency of 1 Hz. Dynamic Contact Angle Analyzer was performed by DCA-322, CAHN Instruments, Inc. DI water and diiodomethane were used as the probing liquids for contact angle.

Results and Discussion

Structure of Ladder-like Polysilsesquioxane

FTIR was used to determine the chemical structure of LPS because it is a powerful technique for studying organic compounds containing Si-O-Si bond. Differentiated between network and ladder-like structures of silsesquioxane by using FTIR [35]. The ladder-like Si-O-Si absorbance was distinguished from network Si-

O-Si absorbance by the lower intensity of the symmetric stretching absorbance (1059 cm^{-1}) and a stronger intensity of the asymmetric stretching absorbance (1134 cm^{-1}). As shown in Figure 2, the observed Si-O-C stretching absorbance (1076 cm^{-1}) in FPTMS and MPTMS monomers is not shown in LPS and it is replaced by the Si-O-Si symmetric and asymmetric absorbances at 1059 and 1134 cm^{-1} , respectively. This strongly indicates the success of the condensation reaction by sol-gel method. The stronger intensity of LPS in asymmetric and lower intensity in symmetric absorbance peak suggests that the resulting LPS has a ladder-like structure and not random network.

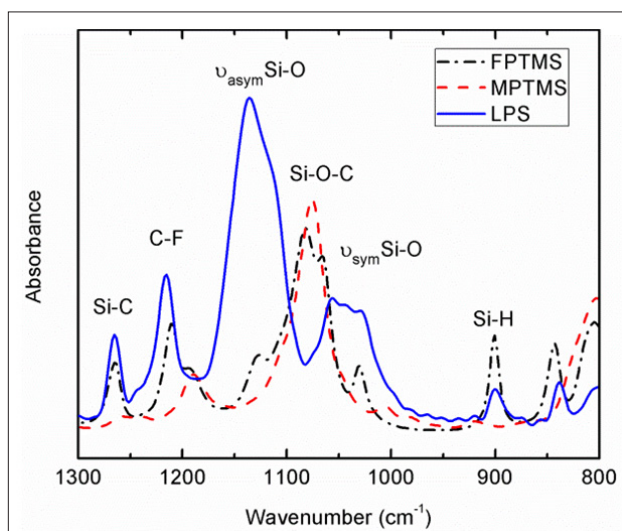


Figure 2: FTIR spectra of LPS and its monomers (FPTMS and MPTMS)

The ladder-like lattice structure in LPS was studied by using WAXD method. Two Bragg peaks are observed, shown in Figure 3. According to investigations of Liu, Zhang, et al, the observed two peaks is the indicator of an ordered ladder-like organization of siloxane bonds, which coincide with the simulated molecular width and thickness (or intermolecular spacing between the ladder) of the ladder chain [26,29]. By following Bragg's Law, the width of each double-chained LPS was calculated as 11.5 Å , and the spacing of 4.3 Å indicates the average thickness of LPS.

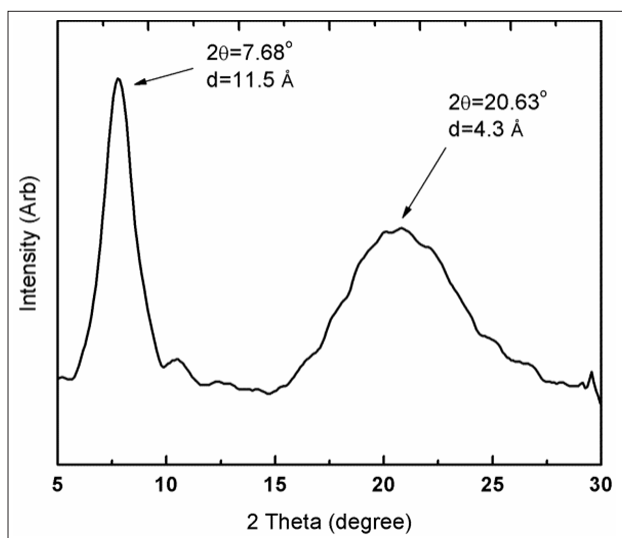


Figure 3: XRD pattern of LPS Structure of PUI/LPS Hybrid Films

Figure 4(a)~(c) show the WAXD spectra of PUI copolymers containing varying LPS mole fraction. As shown in Figure 4(a), two broad peaks at 2θ of 5.68 and 7.24° , corresponding to the d-spacing of 15.5 and 12.2 Å , respectively, were observed in PUI33-10 mol% LPS. As the LPS concentration was increased to 20 mol%, the positions of these two peaks shifted to higher angle, 2θ of 6.08 and 7.48° , corresponding to smaller d-spacing of 14.5 and 11.8 Å , indicating the well-exfoliation and dispersion of LPS. The WAXD spectra of PUI50-LPS are given in Figure 4(b). A diffraction peak at 2θ of 7.46° which corresponds to the d-spacing of 11.7 Å is observed in both PUI50-10 and 20 mol% LPS. As the LPS mole fraction increased from 10 to 20 mol%, the intensity increased. The significant expansion of the interlayer spacing for LPS is believed to be due to the well-exfoliation and dispersion of LPS. In PUI67-LPS, a diffraction peak at 2θ of 7.47° which corresponds to the d-spacing of 11.8 Å was observed in PUI50-10 mol% LPS. Further increase in the LPS mole fraction to 20 mol%, resulted in increased diffraction peak, 2θ to 7.61° and decrease in the d-spacing to 11.6 Å . The presence of two shifted diffraction peaks in PUI33-LPS indicates that enhancement in dispersion and exfoliation were achieved in the block copolymer with high PI concentration. Decreasing the LPS mole fraction in PUI-LPS resulted in decreased d-spacing, indicating the improvement in the dispersion and exfoliation of LPS (Figure 4(a)~(c)).

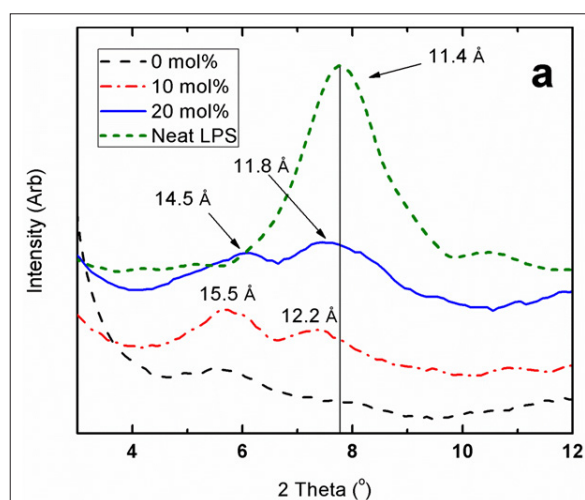


Figure 4(a): WAXD spectra of PUI33 containing 0, 10, 20 mol% LPS and neat LPS

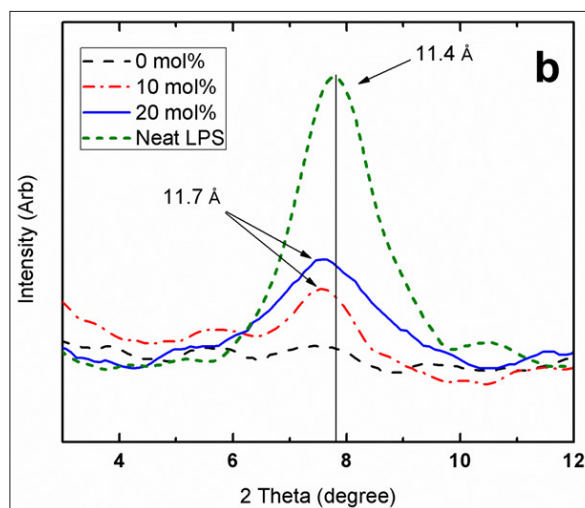


Figure 4(b): WAXD spectra of PUI50 containing 0, 10, 20 mol% LPS and neat LPS

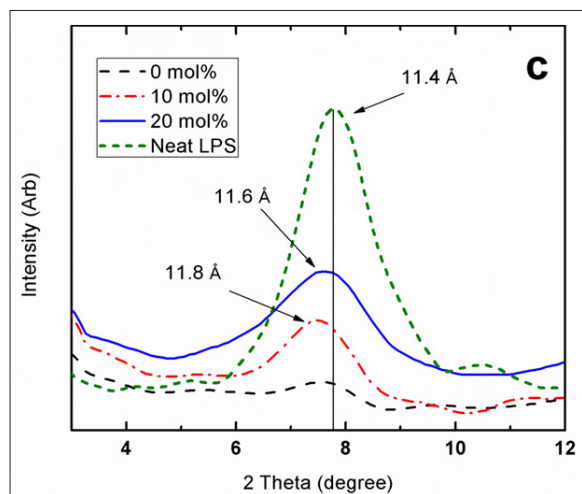


Figure 4(c): WAXD spectra of PUI67 containing 0, 10, 20 mol% LPS and neat LPS

Dynamic mechanical Properties of PUI/LPS Hybrid Films

Glass Transition Temperature

The glass-transition temperature (T_g) is the temperature at which a polymer changes from glassy to rubbery behavior [12]. In dynamic mechanical analysis (DMA), T_g is identified as the temperature corresponding to the $\tan \delta$ peak for α -transition. T_g of LPS identified by α -transition peak in $\tan \delta$ curve, is observed at -19.5°C (Figure 5). Due to the rigidity of ladder-like structure and H-bond interaction, the T_g of LPS is significantly increased as compared with linear polysiloxanes, such as polydimethylsiloxane with a T_g of -123°C [36].

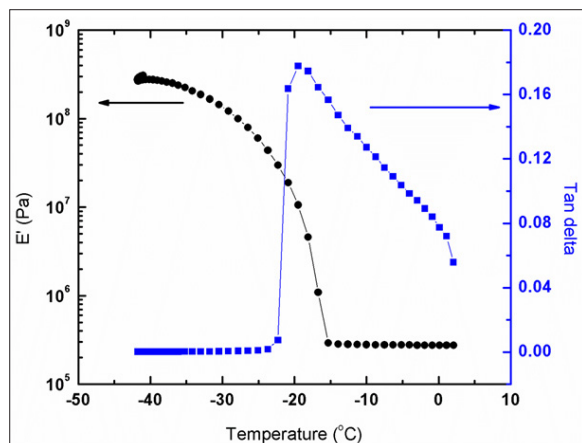


Figure 5: Dynamic mechanical spectra for neat LPS at 1 Hz

The observed two glass-transition temperatures (T_g^a and T_g^b) associated with the PU-rich and PI-rich phases, respectively, are attributed to the micro-phase separation of PU and PI blocks. T_g^a and lower T_g^b are measured from $\tan \delta$ peak located below 250°C and above 300°C , respectively. Temperature depended storage modulus (E') and $\tan \delta$ curves of PU33-LPS, PUI50-LPS and PUI67-LPS thin films are given in Figure 6~8. The variations of T_g^a and T_g^b for PUI copolymers with varying LPS concentration are given in Table 1. For PUI33-LPS, a decrease of about 7.1°C has been observed in T_g^b with the incorporation

of 10 mol% LPS. Further increase in the LPS concentration to 20 mol%, 14.3°C , resulted in additional decrease in T_g^b . However, increasing LPS concentration leads to an increase in T_g^a . About 3.4 and 17.6°C increase in T_g^a were obtained by increasing LPS concentration to 10 and 20 mol%, respectively. For PUI50-LPS, the incorporation of 10 mol% LPS resulted in 6.8°C decreases in T_g^b . However, further increase the LPS concentration to 20 mol%, resulted in only a 1.4°C decrease in T_g^b . A slight decrease of about 6.5 and 12.1°C in T_g^a were observed and are due to the addition of 10 and 20 mol% LPS, respectively. A decrease of about 6.6°C is observed in PUI67-LPS containing 10 mol% LPS and an additional decrease of 5.1°C was shown in PUI67-LPS containing 20 mol% LPS. Increasing LPS concentration to 10 and 20 mol%, led to about 3.3 and 9.3°C decrease in T_g^a , respectively. A similar behavior was reported by Li et al for epoxy/ladder-like polyphenylsilsesquioxane nanocomposites [37]. According to Tsai and Leu et al in polyimide/polysilsesquioxane nanocomposites, the slight reduction in T_g^s is believed to be due to an increase in free volume resulting from the addition of stiff LPS with steric hindrance as well as the interaction between the PUI copolymer and low- T_g LPS [38,39].

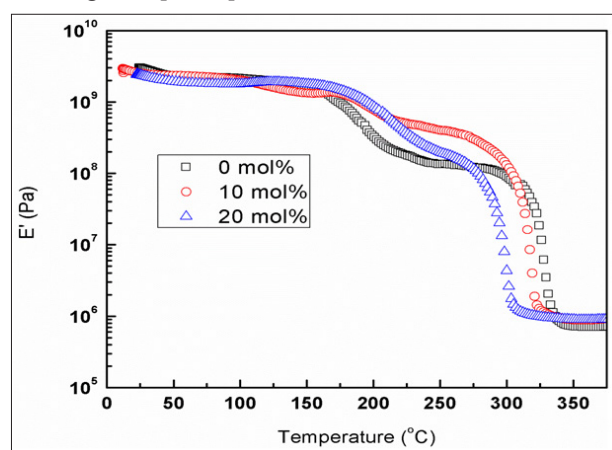


Figure 6(a): Dynamic mechanical spectra for PUI33 containing 0, 10 and 20 mol% LPS at 1 Hz

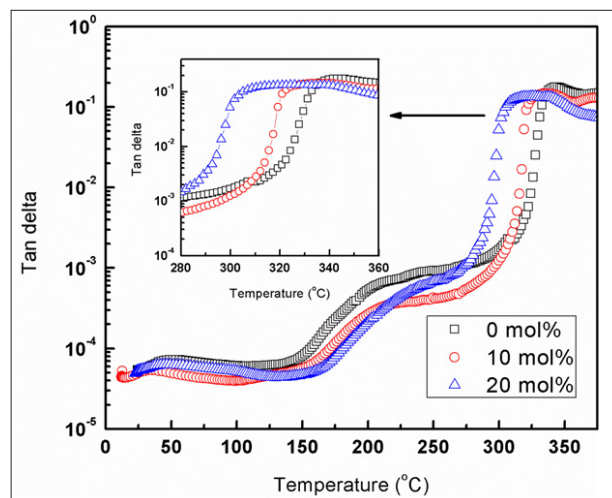


Figure 6(b): Damping behavior for PUI33 containing 0, 10 and 20 mol% LPS at 1 Hz

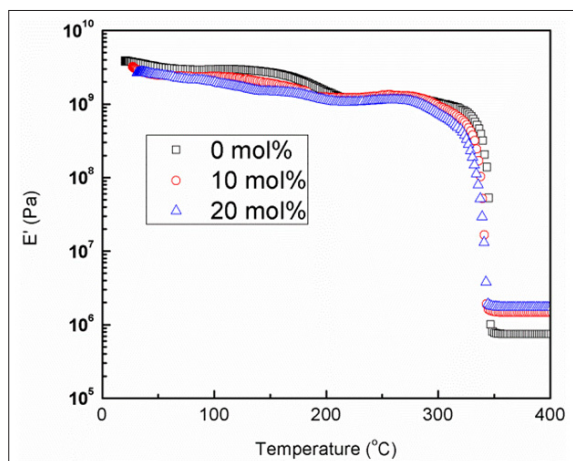


Figure 7(a): Dynamic mechanical spectra for PUI50 containing 0, 10 and 20 mol% LPS at 1 Hz

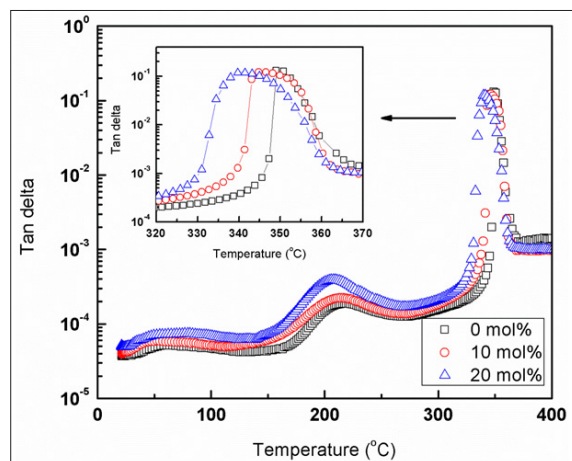


Figure 8(b): Damping behavior for PUI67 containing 0, 10 and 20 mol% LPS at 1 Hz

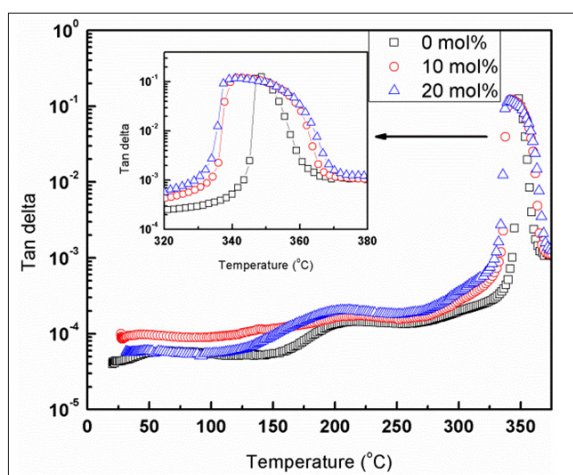


Figure 7(b): Damping behavior for PUI50 containing 0, 10 and 20 mol% LPS at 1 Hz

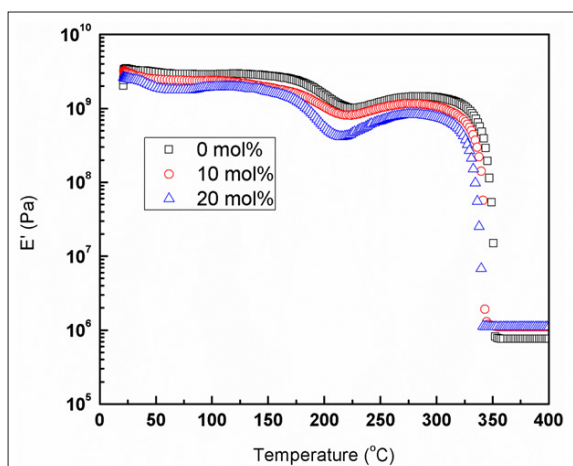


Figure 8(a): Dynamic mechanical spectra for PUI67 containing 0, 10 and 20 mol% LPS at 1 Hz

Table 1: Variations of T_g^a and T_g^b with LPS concentration for PUI copolymers

LPS content (mol%)	PUI33		PUI50		PUI67	
	T_g^a (°C)	T_g^b (°C)	T_g^a (°C)	T_g^b (°C)	T_g^a (°C)	T_g^b (°C)
0	235.2	342.6	218.1	349.1	216.3	351.8
10	238.6	335.5	211.6	342.3	213.0	345.2
20	252.8	321.2	206.0	340.9	207.0	340.1

Damping Ability

The area under the α -transition peak is related to the energy dissipated during deformation, because it is associated with polymer molecular motion and dissipation energy [40,17]. Thus, the tan δ peak area for the α -transition is often correlated with damping ability of a material. Tan δ peak area for the α -transition was calculated for polyimide, polyurea and their copolymers by using equation 1 [17]:

$$Area = \int_{T_0}^{T_1} (\tan \delta) dT \quad (1)$$

Where T_0 is the onset of the glass-rubbery transition; T_1 is the final temperature when α -transition peak is completed. Due to the presence of two T_g , tan δ versus temperature curves for PUI copolymers show two maxima, associated with the tan δ peak from 120 to 270 °C and the tan δ peak from 270 to 380°C. The variations of the total tan δ peak areas for PUI-LPS with increasing LPS concentration are given in Figure 9(a). The sum of the area for the two transition peaks significantly increases with increasing LPS mole fraction. For PUI33-LPS, the tan δ peak area show a sharply increase at a low LPS concentration, followed by a saturation region where little change in tan δ peak area occurred with increasing amount of LPS. In PUI50-LPS, increasing the LPS concentration drastically increased the tan δ peak area. About 71% increase was observed as the LPS concentration was increased to 10 mol%. Further increase in the LPS concentration to 20 mol%, resulted in a remarkable increase in the tan δ peak area of about 136 %. For PU67, increasing LPS concentration to 20 mol% led to about 95% increase in tan δ peak area. Ye, Leu et al reported that the incorporation of polysilsesquioxane led to a significant increase in free volume due to the insertion of polysilsesquioxane into polyimide chains, thereby decreasing the interaction between polyimide chains [39,41]. According to the WAXD analysis (Figure 4), the obtained increase in damping

ability is believed to originate from the increase of free volume and decrease of interaction between PUI copolymer chains caused by the incorporation of LPS.

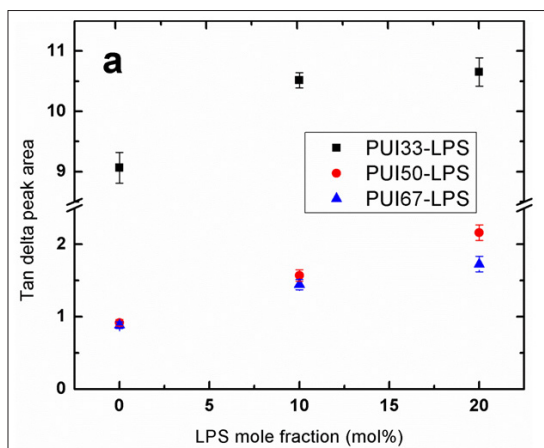


Figure 9(a): The variation of tan δ curve area with varying LPS mole fraction

Rubbery Plateau Modulus

The rubbery plateau region is characterized by a rubber-like softening and reduction in the modulus [17]. The modulus of the rubbery plateau region can increase significantly by increasing molecular weight and crystallinity due to increased entanglements and physical cross-linking [17]. The rubbery plateau modulus is identified as the storage modulus above T_g in the case of PUI and PUI-LPS films. As shown in Figure 6(a), 7(a) and 8(a), increasing amount of LPS significantly increases the storage modulus at rubbery regions above T_g , indicating remarkable enhancement in thermal dimensional stability of PUI-LPS films. The variation rubbery plateau modulus with varying LPS concentration is given in Figure 9(b). For PUI copolymers without LPS, no significant increase in the rubbery plateau modulus occurred. However, with increasing LPS concentration, a drastic increase occurred in PUI50-LPS films. Terpolymers PUI33-LPS and PUI67-LPS, showed only a moderate increase in rubbery plateau modulus with increasing LPS concentration. In general, it was observed that the rubbery plateau modulus increased sharply initially, followed by a saturation region with little change. With the incorporation of 10 mol% LPS into PUI50, a remarkable enhancement in rubbery plateau modulus of about 96.2 % occurred. This enhancement is much more than the enhancements of (26.6 % and 45.1 %) obtained from PUI33 and PUI67, respectively. Increasing the mole fraction of LPS to 20 mol% sharply increased the enhancement in rubbery plateau modulus for PUI50 by about 129.5 % while no significant increase was observed in PUI33 and PUI67. The remarkable increase in modulus above T_g is believed to be due to the enhancement in hydrogen bonding, resulting in a strong chain interaction and physical crosslinking. Due to the presence of hydrogen bond donors and acceptors in both LPS and PUI copolymers, such as the fluoride, F and thio, SH groups in LPS, as well as the carbonyl, C=O and secondary amine, NH groups in polyimide and polyurea, hydrogen bonding may result in strong interactions and physical cross-linking between the polymer chains. Increasing LPS concentration significantly increases the storage modulus at rubbery plateau region and thermomechanical stability of PUI-LPS films.

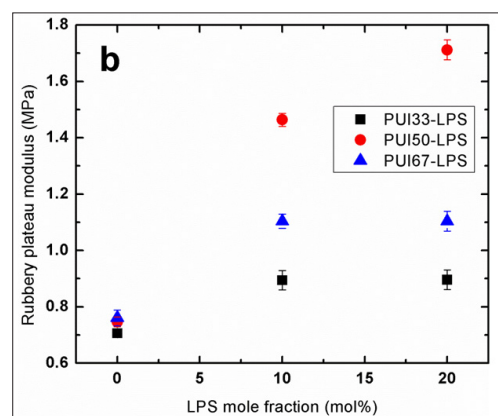


Figure 9(b): Variation of the rubbery plateau modulus for PUI-LPS with varying LPS concentration

Effect of LPS Content on Degree of Imidization

The catalytic effects of siliceous materials on imidization have been widely reported, such as polysiloxane and clay [10,14]. Tyan et al used FTIR to study imidization of poly(amic acid) [10]. They normalized the area of imide C-N bending (725 cm^{-1}) absorbance by dividing it with the area of the absorbance at 1011 cm^{-1} and calculated the degree of imidization by using the equation 2:

$$\alpha_{T^\circ\text{C}} = \frac{\left(\frac{A_{725}}{A_{1011}}\right)_{T^\circ\text{C}}}{\left(\frac{A_{725}}{A_{1011}}\right)_{300^\circ\text{C}}} \times 100\% \quad (2)$$

Where $\left(\frac{A_{725}}{A_{1011}}\right)_{T^\circ\text{C}}$ is the normalized the area of imide C-N bending absorbance arising from the samples cured at temperature 'T';

$\left(\frac{A_{725}}{A_{1011}}\right)_{300^\circ\text{C}}$ is the normalized the area of imide C-N bending

absorbance arising from samples cured at 300°C . The effect of LPS concentration on degree of imidization was studied by following the same method. By normalizing the reference peak at 1011 cm^{-1} , the change in the imide characteristic absorption peak at 725 cm^{-1} was used to detect the variation of imidization degree with varying LPS concentration. As shown in Figure 10(a), the peak area of imide C-N bending drastically increased with increasing LPS concentration. By using equation 2, the variations of imidization degree for PUI-LPS with varying LPS concentration determined and plotted as shown in Figure 10(b). The reference samples were cured at 300°C for 5 hours to approach full imidization. The incorporation of LPS remarkably increased the degree of imidization in all PUI-LPS samples cured at low temperature (150°C). The concentration of LPS and PU also significantly influenced the kinetics of imidization. For instance, the degree of imidization for PUI33-LPS approached 95% by adding only 5 mol% LPS. Further increase in LPS concentration to 10 mol% resulted in full imidization (100%) in PUI33-LPS terpolymer. In PUI50, increasing the LPS mole fraction from 0 to 10 mol% significantly increased the degree of imidization from 63% to 84 %. Full imidization was achieved by increasing the mole fraction of LPS to 20 mol%.

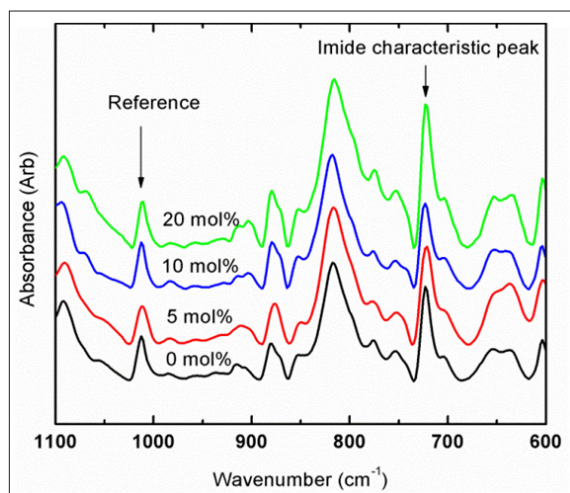


Figure 10(a): FTIR spectra of PUI50 and PUI50 containing 5 mol%, 10 mol% and 20 mol% LPS

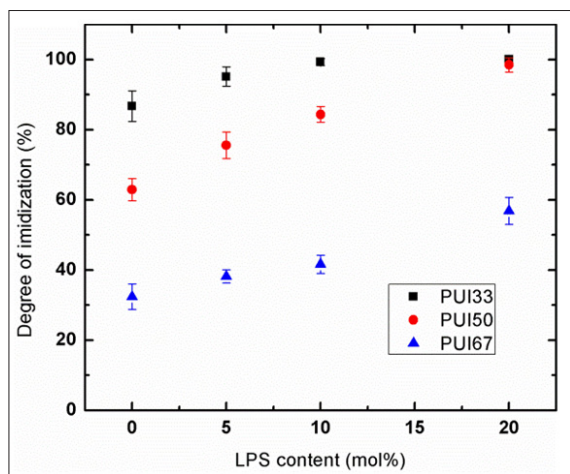


Figure 10(b): Dependence of the degree of imidization on LPS mol% and PUI composition

Effects of LPS on Surface Energy

The contact angle of PUI-LPS terpolymer thin film was measured by using the dynamic contact angle analyzer (DCA). By using equations 3 and 4, the surface energy was calculated from contact angle.

$$\frac{(1+\cos(\theta))\gamma_{lv}}{2(\gamma_l^d)^{1/2}} = (\gamma_s^d)^{1/2} + \frac{(\gamma_s^p)^{1/2}(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}} \quad (3)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (4)$$

where θ is contact angle, γ_{lv} was total surface energy between liquid and vapor, γ_l^d is the dispersive surface energy of liquid, γ_l^p is the polar surface energy component of liquid, γ_s^d is the dispersive surface energy of solid, γ_s^p is the polar surface energy component of solid, γ_s is the total surface energy of solid. The variations of surface energy with varying LPS mole fraction for PUI copolymers are given in Figure 11. Increasing LPS concentration, resulted in significant decrease in the surface energy (γ_s) in all PUI-LPS samples. For PUI33 and PUI67, the reduction in surface energy with addition of LPS followed two stages: (i) initially, the surface energy decreases sharply with incorporation of small amount of LPS (up to 10 mol%); (ii) the second stage is a saturation region

where little change in surface energy occurred with increasing LPS concentration. However, only one stage was observed in PUI50: the surface energy decreases gradually but continuously with increasing LPS concentration. An ultra-low surface energy of about 24 mJ/m² was approached by incorporating 20 mol% LPS into PUI50.

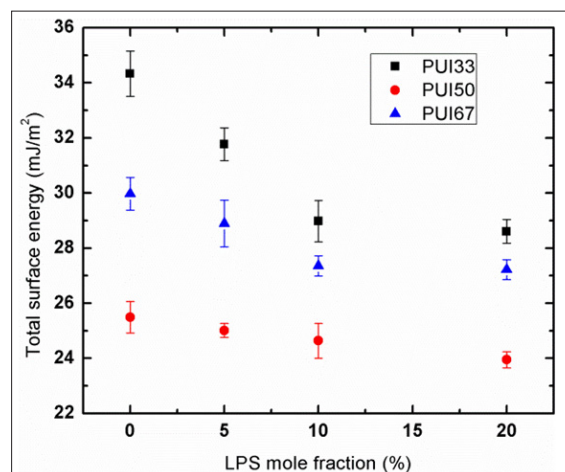


Figure 11: Variation of total surface energy with varying LPS concentration for PUI copolymers

Morphology

Figures 12(a)~(c) show the SEM micrographs of a cross-section of PUI33-LPS containing 0, 10 and 20 mol% LPS. The neat PUI33 has a continuous ‘coral-like’ nanostructure constituted of network and ‘rod-like’ structures mixed by interlacing. With the incorporation of 10 mol% LPS, the aspect ratio of ‘rod’ decreased and a ‘branch-like’ morphology was observed. Further increase in the mole fraction of LPS to 20 mol%, the ‘branch-like’ morphology evolved into a ‘cycle-like’ morphology, spontaneously. Thus, the morphology of PUI-LPS can be varied by varying LPS concentration. The observed morphological transformation in PUI-LPS, is believed to be one of the reasons that the incorporation of LPS led to significant changes in the mechanical properties.

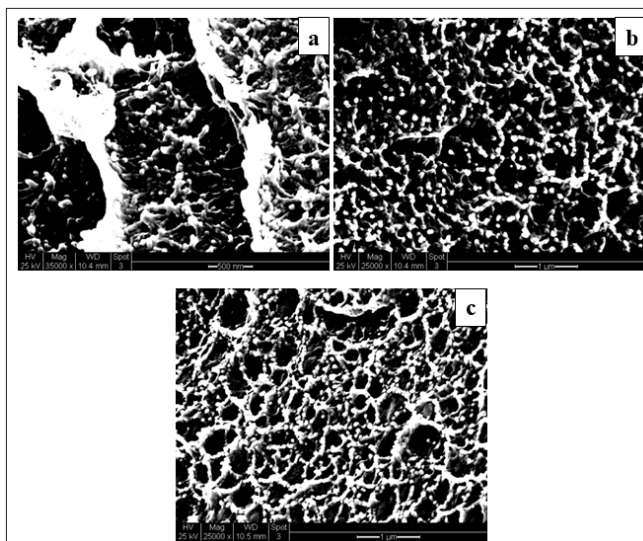


Figure 12: SEM images of cross-section of (a) PUI33 (b) PUI33-10 mol% LPS (c) PUI33-20 mol% LPS

Conclusion

PUI block copolymer and PUI-LPS terpolymer films were successfully synthesized by a three step process. The LPS

composed of mercapto and fluoride side groups was synthesized by using the sol-gel and monomer self-assembly methods. PUI-LPS terpolymer possess well dispersed nanoparticles of LPS in the PUI copolymer matrix, leading to remarkable enhancement in thermomechanical properties. With the incorporation of LPS, T_g decreases slightly while the $\tan \delta$ peak area and rubbery modulus significantly increased, indicating enhancement in the damping ability and dimensional stability. The presence of LPS significantly enhanced the imidization kinetics by producing an increase in the degree of imidization with increasing LPS concentration at low temperature of curing (150°C). The observed decrease in the surface energy with increased LPS concentration, correlates to a remarkable enhancement in adhesion and hydrophobicity. An ultra-low surface energy of 24 mJ/m² was obtained in optimized PUI50-LPS terpolymer containing 20 mol% LPS.

Acknowledgement

The financial support provided by the National Science Foundation NSF-CMMI 0758656 and the Office of Naval Research, ONR, N00014-09-1-0980 are gratefully acknowledged.

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