Microstructure and Properties of 3,3’4,4’-Biphenyltetracarboxylic Dianhydride (BPDA)-p-Phenylene Diamine (PDA) Polyimide/Poly(vinylsilsesquioxane) Hybrid Nanocomposite Films

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ABSTRACT: Hybrid nanocomposite films of poly(vinylsilsesquioxane) (PVSSQ) and polyimide (PI) (PI/PVSSQ) were prepared via sol-gel process from triethoxyvinylsilane (VSSQ) and thermal imidization from 3,3’4,4’-biphenyltetracarboxylic dianhydride (BPDA)-p-phenylene diamine (PDA) polyamic acid (BPDA-PDA PAA). We investigated the microstructure; interfacial interaction; and optical, thermal, dielectric, and mechanical properties of the hybrid films. The phase morphologies and degree of surface roughness were evaluated by scanning electron microscope (SEM) and atomic force microscope (AFM), respectively. It was found that the surface topography was influenced by the composition of PVSSQ. Hydrogen bonding interactions between polyimide (PI) matrix and PVSSQ domains were proved with FT-IR spectroscopy. The transparency of the hybrid films was found to be dependent on the PVSSQ content. Incorporating of the PVSSQ in the hybrid composites increased the glass transition temperature of PI. Dielectric constants of the hybrid films were in the range of 2.37–3.59. Properties of the PI films were also significantly enhanced by adding 5–30 wt % of PVSSQ. For comparison, we also prepared the hybrid composites of PI and mixtures of VSSQ and tetraethoxysilane (TEOS) and the PI/silica hybrid composite containing 30 wt % of silica obtained from TEOS. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 5189–5199, 2004

Keywords: dielectric constant; polyimide; hybrid; nanocomposites; silsesquioxane

INTRODUCTION

In recent years, increasing attention has been paid to preparing organic/inorganic hybrid composite hybrid materials that comprise desirable organic and inorganic characteristics. These materials not only have synergistic properties, but can also be tailored to specific applications. Molecular design of the organic and inorganic segments has produced new hybrid composite materials with distinguished physical and chemical properties via the sol-gel process. The sol-gel processes are affected by many controllable synthetic parameters such as structure and concentration of reactants, solvent, and catalysis, as well as reaction temperature and the rate of removal of byproducts and solvents. For these hybrids, polyimides (PIs) have been used as the high performance polymer matrix materials due to their outstanding thermal stability, mechanical proper-
ties, and electrical properties.\textsuperscript{2–6} In addition, silica has also been investigated as an inorganic component in hybrid composites for many diverse applications.\textsuperscript{7–21} More recently, polysilsesquioxane (PSSQ) has attracted extensive research interest among the materials scientists and integration engineers because of its unique thermal and mechanical properties, as well as its low dielectric constant and low moisture absorption. In this sense, silsesquioxane (SSQ) materials with an organic group have already been proposed as replacement for silicon dioxide.\textsuperscript{22} A novel PSSQ material can easily be hybridized with organic moieties to form molecular composites through hydrogen bonding or covalent bonding for various important applications.\textsuperscript{22–32} Accordingly, the formation of inorganic/organic hybrid nanocomposite materials utilizing SSQs as the link between the inorganic and organic components has been one very active area of research in recent years.\textsuperscript{33–39}

It is evident that the organic moieties in PSSQ play an important role in determining the microstructure and properties of the hybrids of PI and PSSQ. The organic part of PSSQ can provide a bond with the PI matrix that has led to the homogeneously dispersed morphologies of resulting hybrids, and ultimately effect on the overall properties of final hybrid composites.\textsuperscript{7,12,26–33} The provided bond between the organic and inorganic phase can prevent phase separation between two phases and plays a vital role in controlling the phase behavior of resultant hybrids for desired properties. Importantly, forming nanocomposites from PSSQ materials with PI may be an effective way to reduce the dielectric constant of PI without degrading its thermomechanical properties.\textsuperscript{26}

In this paper, we investigated the microstructure, interfacial interaction, thermal and mechanical properties, dielectric constants, and optical behavior of the PI/poly(vinylsilsesquioxane) (PVSSQ) hybrid. For comparison we also prepared the hybrid composites of PI and mixtures of vinylsilsesquioxane (VSSQ) and tetraethoxysilane (TEOS) and PI/silica hybrid containing 30 wt % of silica obtained from TEOS.

Experimental Procedures

Materials

3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), \textit{p}-phenylenediamine (PDA), TEOS, triethoxysilane (i.e., VSSQ), and anhydrous dimethylacetamide (DMAc) were used as received from Aldrich, Milwaukee, WI.

Preparation of Poly(amic acid) (PAA), Binary and Ternary Hybrid Composite Films

Schemes 1 and 2 illustrate the synthetic procedures for preparing the BPDA-PDA PAA, binary and ternary hybrid composite films as well as the chemical structures of BPDA-PDA. The BPDA-PDA PAA solution was prepared with equimolar ratio of BPDA 12 mM) and PDA (12 mM) in DMAc under nitrogen atmosphere. The reaction was continued for 24 h to make a homogeneous mixture. The premixing solution of VSSQ and/or TEOS in a stoichiometric amount of deionized water was added dropwise into the reaction mixture with stirring to avoid local inhomogeneities. Detailed preparation recipes employed here are listed in Table 1. Then the reaction was allowed to proceed overnight to form a homogeneous solution, followed by spin-coating the resulting silica sol/PAA precursor hybrid solution onto a glass substrate. The PAA/VSSQ or TEOS as cast films were soft-baked and thermally imidized. The solid content of the solution was 13.5 wt %. The imidization process was carried out at 60 °C for 2 h, 80 °C for 2 h, 200 °C for 1 h, and 300 °C for 1 h in nitrogen atmosphere to obtain hybrid films. The heating rate was 2 °C/min. PI/VSSQ/TEOS hybrid films as well as PI/silica hybrid of 30 wt % of silica obtained from TEOS were also prepared by similar procedures as those of PI/PVSSQ hybrids. Sample codes are summarized in Table 1.
Measurements and Characterization

Fourier Transform Infrared (FTIR) analyses of hybrids were performed with a React IR (React IR™ 1000, Applied System, ASi). Scanning electron microscope (SEM; Hitachi S-4200) and atomic force microscope (AFM; Nanoscope III®, Digital Instruments Co.) were used to investigate the phase behavior of the hybrid films. Prior to SEM measurements, the fractured surfaces from liquid nitrogen were gold coated. For AFM mea-

Table 1. Preparation of BPDA-PDA PI/PVSSQ Binary and PI/VSSQ/TEOS Ternary Hybrid Composite Films

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>PAAa (gm)</th>
<th>VSSQ (gm)</th>
<th>TEOS (gm)</th>
<th>PVSSQ or Silicabw (wt %)</th>
<th>Film Statec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary hybrid films</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI</td>
<td>12.67</td>
<td>-</td>
<td></td>
<td></td>
<td>T</td>
</tr>
<tr>
<td>PI/VSSQ5</td>
<td>12.67</td>
<td>0.64</td>
<td></td>
<td>5</td>
<td>T</td>
</tr>
<tr>
<td>PI/VSSQ10</td>
<td>12.67</td>
<td>1.27</td>
<td></td>
<td>10</td>
<td>T</td>
</tr>
<tr>
<td>PI/VSSQ20</td>
<td>12.67</td>
<td>2.53</td>
<td></td>
<td>20</td>
<td>T</td>
</tr>
<tr>
<td>PI/VSSQ30</td>
<td>12.67</td>
<td>3.80</td>
<td></td>
<td>30</td>
<td>O</td>
</tr>
<tr>
<td>PI/TEOS30</td>
<td>12.67</td>
<td>-</td>
<td>3.80</td>
<td>30</td>
<td>O</td>
</tr>
<tr>
<td>Ternary hybrid films</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI/VS50/TE50</td>
<td>12.67</td>
<td>1.90</td>
<td>1.90</td>
<td>30</td>
<td>O</td>
</tr>
<tr>
<td>PI/VS75/TE25</td>
<td>12.67</td>
<td>2.85</td>
<td>0.95</td>
<td>30</td>
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a Polyamic acid.
b VSSQ or TEOS content (weight %) in hybrid composite films was calculated by assuming that sol-gel reaction was completed.
c T: Transparent; O: Opaque.
measurements, the cantilever used in the present study was V-shaped, mounted at the end of a quadrangular pyramid Si₃N₄ microtip (Olympus). The spring constant of the cantilever was 0.022 Nm⁻¹. In the AFM measurement, a feedback loop kept the vertical position of the tip constant by moving the sample surface up and down with the piezoelectric scanner in the topography mode. AFM images were taken with 2 μm × 2 μm scan area from 1 cm × 1 cm hybrid films. Thermogravimetric analyzer (Perkin-Elmer TGA-7) was used to investigate the thermal stability of PI and hybrid films. The heating rate was 20 °C/min in nitrogen atmosphere. The transparency of the hybrid films was measured with UV-Visible-Near IR spectrophotometer (CARY 5E, Varian Co) at 638 nm. The thickness of the films was about 100 nm. Mechanical properties were measured using a UTM machine (Tenius Oisen 1000, Digital Indicator Green PL 9700W). The gauge length was 50 mm and crosshead speed was 2 mm/min. Three samples were averaged. Wide angle X-ray diffraction (WAXD) measurement was conducted at room temperature in reflection mode using Rigaku diffractometer (Model Rigaku Miniflex). The CuKα radiation (λ = 1.54 Å) source was operated at 50 kV and 40 mA. The 2θ scan data were collected at 0.01° intervals over ranges of 5°–45° and scan speed was 0.5°(2θ)/min. Dynamic mechanical properties were measured using a dynamic mechanical thermal analyzer (DMTA) (Rheometrics Dynamic Analyzer RDA II, Resource Series) with heating rate of 5 °C/min at 1 Hz. The dielectric constant was obtained at 1 MHz with the Impedance-Gain Phase Analyzer (HP4194A) using the formula K = C/d/ε₀, where C is the observed capacitance, d the film thickness, A the gold area, and ε₀ the free permittivity. The thickness of the films was 0.14 ± 0.01 μm.

RESULTS AND DISCUSSION

The appearances of the PI/PVSSQ and PI/silica binary hybrids (from TEOS) and the PI/VSSQ/TEOS ternary hybrid films are reported in Table 1. A hybrid film was transparent when VSSQ content was ≤ 20 wt % in the composites. All hybrids were flexible except the PI/TEOS30 hybrid. The transparency of the PI/PVSSQ hybrid films, as shown in Figure 1, decreased with increasing the amount of VSSQ. The hybrid films with PVSSQ ≤ 20 wt % showed high transparencies, but the transparency significantly decreased when the content was 30 wt % of PVSSQ. This phenomenon can be explained in terms of the increasing of the PVSSQ domain sizes with increasing VSSQ content, resulting in high scattering.

Figure 2(A) shows the FT-IR spectra of PI and hybrid films. Typical characteristic peaks are assigned as follows: 1779 cm⁻¹ (C=O symmetric stretching), 1711 cm⁻¹ (C=O symmetric stretching), 1368 cm⁻¹ (C-N stretching), 737 cm⁻¹ (imide ring deformation), 1497 cm⁻¹ and 829 cm⁻¹ (νC₆H₄). The band at 1173 cm⁻¹ is attributed to the νC₆H₄ or νC₅H₃. The imide peak was observed at 1711 cm⁻¹ for imidized films, which indicates the successful imidization of the prepared hybrid materials. The bands at 1623 and 1422 cm⁻¹ correspond to the Si-CH₂ group. The Si-OH band is overlapped at around 881 cm⁻¹ with the band of νC₆H₄. The broad band near 1082 cm⁻¹, caused by the presence of the Si-O-Si bond, is indicative of the network formation in the hybrid composites. Overall, the narrowing of the Si-O-Si band for the PI/PVSSQ hybrids indicates that the silica environment for the PVSSQ containing hybrids is more homogeneous in comparison to that for the PI/TEOS30 hybrid. The peak intensities at 1623 and 1422 cm⁻¹ correspond to the Si-CH = CH₂ group.

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Specific interaction between PI and PVSSQ was investigated using FTIR spectra and is illustrated in Figure 2(B). In Figure 2(B), the peaks around 1711 and 1779 cm\(^{-1}\) for pure PI were shifted for the hybrid films, and the peak shifts were found to be larger in the order of PI/VSSQ10 < PI/VSSQ20 < PI/VSSQ30 hybrids. The peak shift suggests the presence of stronger hydrogen bonding interactions between the C=O group of PI and the silanol of VSSQ in the binary PI/PVSSQ hybrid systems. The fact that there is no remarkable wavenumber shifting for the PI/TEOS30 hybrid indicates the absence of interaction between PI and silica domains, as we already reported.\(^{26}\) Previously, such hydrogen bonding interactions between the organic and inorganic phases have also been reported.\(^{42}\)

XRD patterns of the pure PI, binary, and ternary hybrid composite films are shown in Figure 3. The main diffraction peaks for pure PI are centered at \(2\theta = 13.75^\circ\), 16.57\(^{\circ}\), 18.20\(^{\circ}\), 21.56\(^{\circ}\), 25.14\(^{\circ}\), and 28.03\(^{\circ}\) corresponding to \(d\)-spaces of 6.43, 5.35, 4.87, 4.12, 3.54, and 3.18 \(\AA\), respectively, indicating the crystalline structure as well as the intermolecular regularity. Based on the previous X-ray diffraction measurements,\(^{43-46}\) three main peaks can be indexed as (110), (200), and (210), which suggests the in-plane orientation of the PI molecules. Unfortunately, however, the peaks at around \(2\theta = 13.75^\circ\) and 16.57\(^{\circ}\) (peaks marked with asterisks in Figs. 3a and 3b) are not to be assigned at this moment. The crystalline structure is affected after hybridizing with VSSQ or TEOS in the PI film.

It is interesting to note that the introduction of VSSQ disrupts the PI regularity to a lesser extent than the TEOS does. The disappearing trend in the XRD peaks becomes clearer as the VSSQ content increases for the PI/PVSSQ hybrids or as the TEOS content increases for the PI/VSSQ/TEOS ternary hybrids. According to Economy and his coworkers,\(^{47}\) the hybrid prepared with different amounts of PVSSQ showed almost the same \(d\)-spacings, suggesting the independence of \(d\)-spacing from the SSQ crosslinking segment. The decreasing intensity of the broad peak with the increase in the crosslinking of PVSSQ content in the binary and ternary composites, however, hints that the rigid rod nature of the PI segment is diminished by the presence of PVSSQ in the hybrids.\(^{47}\)

Figure 4 shows the fractured surface morphologies of binary and ternary hybrid composite films by SEM. There are not noticeable domains of PVSSQ particles for PI/VSSQ5 and PI/VSSQ10 hybrids. Careful inspection of Figures 4a and 4b indicates that the PVSSQ domains in the hybrid materials are smaller than 17 nm, suggesting the formation of nanocomposites. The PI/VSSQ20 and PI/VSSQ30 hybrids produced homogeneously dis-
persed domain phase in the range of several tens of nm to max. 260 nm. Figures 4d and 4e indicate that the phase compatibility of PI with PVSSQ is better than that with silica obtained from TEOS. The micrograph in Figure 4e reveals that silica domains are almost smooth and debonded from the surrounding PI matrix, suggesting weak interfacial adhesion between two phases. Partial replacement of TEOS with VSSQ in Figures 4f and 4g also indicates that silica particle sizes are decreased as the ratio of TEOS to VSSQ is decreased from 50/50 to 25/75, proving better interfacial interaction in the PI/PVSSQ hybrid in comparison to that of the PI/silica hybrid (from TEOS) system. The enhanced phase compatibility may be achieved due to hydrogen bonding between the C/H group of PI and the silanol of PVSSQ as evidenced in Figure 2(B). The interac-

**Figure 3.** (a) XRD patterns of pure PI and PI/PVSSQ binary hybrid composite films; (b) XRD patterns of pure PI and PI/VSSQ/TEOS ternary hybrid composite films.

**Figure 4.** Fractured surface morphology of hybrid composite films: (a) PI/VSSQ5, (b) PI/VSSQ10, (c) PI/VSSQ20, (d) PI/VSSQ30, (e) PI/TEOS30, (f) PI/VSSQ50/TE50, and (g) PI/VSSQ75/TE25.
tion may also include some intercrosslinking between the PI and silica network due to the presence of vinyl groups.7,26,30

In general, the topographic features obtained with AFM for hybrid composite films were found to depend on the inorganic/organic phase behavior and can affect the values of average roughness (Ra) and mean squared roughness (Rq).49,50 The Ra is the main height as calculated over the entire measured length or area, while the Rq describes the finish of optical surfaces, taken over the evaluation length/area. Ra and Rq values depend on the surface textures, since the surface roughness can be defined as the irregularities of the surface texture. However, in the case of present systems, the values of Ra and Rq in Figure 5 for the PI/VSSQ30 hybrid are lower compared to the PI/TEOS30 hybrid, suggesting that the degree of surface roughness of the PI/VSSQ30 hybrid is higher compared to the PI/TEOS30 hybrid. These results also suggest that the domain sizes of the PVSSQ in the PI/VSSQ30 hybrid are smaller in comparison to the PI/TEOS30 hybrid. Usually, high roughness values indicate a high degree of phase separation between organic and inorganic phases in hybrids.49,50 In the case of the PI/TEOS30 hybrid, the incompatibility between TEOS and PI under the studied conditions probably allows the growth of larger particles and leads to higher Rq, whereas the compatibility via hydrogen bonding between PI and PVSSQ limits the growth of the PVSSQ segment, resulting in

Figure 5. AFM images of hybrid composites: (a) PI/VSSQ30, and (b) PI/TEOS30, where D indicates dimensions.
lesser domains, and ultimately leads to lower Rq. The SEM and AFM morphologies directly show better phase compatibility between the PI and PVSSQ systems compared to that between PI and silica obtained from TEOS.

Figure 6 illustrates the TGA curves of PI and hybrid composite films. There is no weight loss below 100 °C, indicating the complete removal of water and solvents. The higher amounts of residues at 900 °C for the hybrids in comparison to the PI film suggest successful incorporation of the PVSSQ or silica moiety into the PI matrix. Figure 7 shows the tan δ behavior of PI and its hybrid films, where the temperature at which the peak shows a maximum is taken as Tg of the systems. In general, the Tg of hybrids increased with increasing amount of the VSSQ or TEOS by 2–10 °C, although the hybrid containing 5 wt % of PVSSQ did not show any significant increase in Tg due to the lower amount of PVSSQ. The Tg shifts from 293 °C for the pure PI, to 297.58 °C for PI/VSSQ10, to 298.34 °C for PI/VSSQ20, to 303.68 °C for PI/VSSQ30, to 299.27 °C for PI/TEOS, and to 303.60 °C for PI/TEOS/TEOS75 hybrid composite. The tan δ peak shifts to higher temperatures with increasing VSSQ or TEOS content reflect the reduced segmental mobility of the PI chains, due to the incorporation of interaction introduced by the fairly dispersed PVSSQ or silica (from TEOS) domains with the matrix PI as well as (possibly in part) the increasing degree of crosslinking with increasing the amount of the VSSQ. The magnitude of tan δ peaks for all hybrids also decreases and broadens with increasing VSSQ/TEOS content, indicating an increase in heterogeneity of molecular motions of the PI chains. It is also shown that the partial replacement of TEOS with VSSQ results in substantial increase in the tan δ peak. This observation is in accordance with that of earlier reports.

The dielectric constants of the prepared PI and PI/PVSSQ hybrid composite films with different PVSSQ contents are shown in Figure 8. Figure 8 shows that the introduction of PVSSQ into the PI matrix leads to decrease in dielectric constants up to 20 wt % of PVSSQ, but thereafter there is no further change when PVSSQ content reaches to 30 wt %. It should be noted that the dielectric constant was decreased from 3.59 for pure PI to 2.37 for the PI/PVSSQ hybrids. It is reasonable to consider that the dielectric constants of the cured PI/PVSSQ hybrid films are affected by the increased free volume and also probably by the hydrophobic of the vinyl groups of PVSSQ domains in the final hybrid structure, based on the literature. The trend in Figure 8, therefore, can be explained in terms of the increasing free volume, increased domain sizes of PVSSQ, and hydrophobicity of the final cured material. On increasing the PVSSQ content, more PVSSQ domains may cause more nodes in the three dimensional networks that bond the PI block together. The
BPDA-PDA PI is rigid rod like polymer. A bigger PVSSQ domain may increase slightly the separation between the PI interblocks and increase in free volume. Hence, introducing more PVSSQ in the hybrid film reduces the dielectric constant. SSQ-like materials generally possess cage-like or ladder-like structures and have interpore and intrapore voids in the final materials. Low dielectric constants of SSQ-like materials may be related to the high free volumes due to such molecular structures, as explained above. In this way, dielectric constants of poly(phenylsilsesquioxane) and poly(methylsilsesquioxane) were reported as low as ~ 2.7. Similarly, the dielectric constant of poly(methyl-co-trifluoropropyl)-silsesquioxane was reported as 2.2. The dielectric constant of SSQ-like materials becomes much lower when they are used as the matrices in hybrid materials for organic polymers (known as porogens) as the dispersed domain to produce nanopores upon thermal decomposition. It should be noted, however, that the dielectric properties of the SSQ-like materials are strongly dependent on the processing conditions used as well as the nature of organic groups in the structures (especially for the bridged PSSQ). That is why even the same SSQ material gives different dielectric constants depending on the employed processing environment. Different structure of SSQ may directly impact on the dielectric constant values. For example, if the SSQ-like materials possess cage-like structures, then free volumes are increased, giving low dielectric constant values. If the chances of moisture attack in the final materials are increased, however, the dielectric constants ultimately will be increased.

For the hybrids of VSSQ with BPDA-4,4’-oxydianiline (ODA) PI, it was found that VSSQ decreases dielectric constants up to a certain composition, but the dielectric constants are increased again with further increasing contents of VSSQ.

Figure 9 shows the results of tensile tests, as expressed in tensile strength and elongation at break. As is well known, the strength should be reduced if there are no bonding sites between the organic polymer phase and the inorganic phase. The mechanical properties of the composites are generally dependent on the bonding between the two phases, the inorganic surface area of the filler, and the arrangement between the fillers. The improvement in the mechanical properties can be explained by aid of the result of the introduction of fine silica particles into a polymer matrix and better adhesion as well as strong hydrogen bonding between PI and the organic part of PVSSQ. This indicates that the flexible organic phase of PVSSQ plays a significant role in the interfacial adhesion between PI and the PVSSQ. The results in Figure 9 indicate that chemical interactions between the polymer phase and the PVSSQ are very important.

When the PVSSQ content was > 10 wt %, reduction in tensile strength was observed, which is indicative of larger domains of the PVSSQ due to
poor interfacial adhesion. Similarly, the elongation at break is decreased when the content of PVSSQ is > 10 wt %, though the values are still higher compared to the pure PI matrix.12,26

The mechanical properties in Figure 9 can be explained on the basis of observed morphologies in Figure 4 that the reduction in mechanical properties for the PI/TEOS30 hybrid is due to the weak interaction as well as the debonding phase between two phases. Moreover, the individual smooth particles can act as stress concentration defects rather than as effective reinforcing fillers. Importantly, the partial replacement of TEOS with VSSQ results in compatibilized ternary hybrids, which was already proved in Figure 3. As the composition of VSSQ relative to TEOS is increased in the hybrids, the introduction of PVSSQ brings an increase in tensile strength. The result is related to the development of fine morphology for the ternary hybrids, due to presence of the VSSQ in ternary composites. It is clearly seen in Figure 4 (f–g) that the addition of VSSQ to the binary PI/TEOS30 hybrid in Figure 4 (f–g) produces better morphology than without VSSQ. Probably, after introduction of VSSQ into binary systems brought better interfacial adhesion through hydrogen bonding, that may help the formation of cocontinuous phase morphologies, which may improve the efficiency of stress transfer mechanisms between the two phases.

**CONCLUSION**

In this work, BPDA-PDA PI/PVSSQ binary and PI/VSSQ/TEOS ternary hybrids were prepared. The prepared hybrid composite films were optically clear when the PVSSQ contents are equal to or less than 20 wt %. Properties of BPDA-PDA PI films were remarkably enhanced by hybridizing 5–30 wt % of PVSSQ. The interfacial interaction between PI and PVSSQ was higher than that in the PI/silica (from TEOS) hybrid. The SEM and AFM images indicate that the homogeneity of resulting films was dominated by the presence of PVSSQ. The interaction of the organic and inorganic phase with SSQ materials has a significant effect on the phase morphology of resultant hybrid composites, which can dictate the properties. The homogeneously fine dispersed morphology for the PI/PVSSQ hybrids resulted in improved mechanical properties. The prepared hybrids have low dielectric constant and optical transparence, which could have potential applications for optoelectronics devices.

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**REFERENCES AND NOTES**

27. Tsai, M.; Whang, W. Polymer 2001, 42, 4197.