Synthesis and thermal properties of organically modified palygorskite/fluorinated polyurethane nanocomposites

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ABSTRACT: In this article, fluorinated polyurethane (FPU) nanocomposites filled with organic modified palygorskite (Pal) were synthesized and characterized by Fourier transform infrared, X-ray diffraction, thermogravimetric analysis (TGA), and scanning electron microscope individually. The Pal nanorods were modified with 4,4'-methylene (MDI) by chemical bond. TGA results showed that there are almost 27 wt % of 4,4'-methylene grafting or absorbing on Pal nanorods’ surface. Compared with neat FPU, FPU nanocomposites exhibited somewhat increase in the soft segment glass transition temperature and decrease in the hard segment glass transition temperature. It means the compatibility between soft segment and hard segment becomes better than neat FPU. TGA results also showed that the thermal stability of FPU nanocomposites improved with increasing modified Pal loadings. Pal showed good compatibility with the FPU matrix through scanning electron microscope test results. And, the introduction of Pal into FPU matrix will not affect migration of fluoride side chain. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2017, 134, 45460.

KEYWORDS: polyurethane; thermogravimetric analysis; thermoplastics

INTRODUCTION

After the first report of polymer-clay nanocomposites by researchers at the Toyota Central Laboratory, inorganic–organic nanocomposites have attracted considerable academic and commercial research interests because the properties of organic polymer can be greatly improved through modification with the inorganic materials, such as mechanical, electrical, optical, and other functional properties.1,2 Because of the interesting properties and wide applications, organic derivatives of fibrous silicates like palygorskite (Pal) (also known as attapulgite) deserves a new and special chapter. Generally, some silicate minerals themselves are natural nanomaterials, and the performance of the nanocomposites has a lot of ascension though adding a small amount of silicate. When the organic clays are dispersed in a polymer matrix as individual 1 nm thick sheets, resulting nanocomposites always exhibit excellent mechanical properties, thermostability, barrier property, fire retardant, and other material properties, which is much better than neat polymer.3,4 Polymer–clay nanocomposite era was considered to start in 1987. Pal is a member of the family of natural crystalline hydrated magnesium aluminum silicate which has a unique three-dimensional structure and fibrous morphology. In theory, the chemical formula is $\text{Si}_8\text{O}_{20}\text{Mg}_5(\text{Al})(\text{OH})_2(\text{H}_2\text{O})_4\text{H}_2\text{O}$ and the structure of Pal has been studied by Bradley in 1940. The chains of Pal is a 2:1 phyllosilicate structure, which is different with montmorillonite and other layered silicates, and each ribbon is connected to the next by the inversion of $\text{Si}_4\text{O}_4$ tetrahedral along a set of $\text{Si}=$O-$\text{Si}$ bonds.5,6 This structural arrangement makes the formation of channels in Pal’s crystal, and the channels’ size are approximately $3.7 \times 6.0\text{Å}$ and $5.6 \times 11.0\text{ Å}$ wide, respectively.7 These channels may be easily filled with organic molecules and water. At the edges of the octahedral elements, exposed -OH groups are neutralized by protons. Single fibrillary crystal is the smallest structural unit—the size is about 500–2000 nm length and 10–50 nm in diameter. The unique structural characteristics and physicochemical properties provide Pal important role in application compared with other clays. Until now, Pal has been widely used for various commercial applications, such as adsorbents, catalysts, rheological agents, fillers, and so on.8–10

As well know, fluorine is the most negative-electronic element in the periodic table. The high bond energy of $\text{C}=$F (485 kJ/mol), small radius of F (1.32 Å), and low polarizability impart fluorinated polymers incomparable superiority compared with nonfluorinated macromolecules, such as low surface energy, low refractive index, high thermal stability, enhanced chemical resistance, and so on.11,12 To improve neat polyurethane’s (PU’s) properties, fluorinated blocks were introduced into the
molecular chains of PU elastomer in the form of main or side chain. The obtained fluorinated PU (FPU) elastomers not only experts most of the outstanding properties of PU such as high toughness, high strength, and high damping properties, but also act out improved solvent and chemical resistance, a lower surface tension, and a low coefficient of friction which is caused by fluorine. In the existing research, most of commercially available fluorinated polymers usually present a high fluorine content as high as 50–70 wt % which represents an obstacle for their application, such as difficulties for process ability and high costs. In addition to the introduction of fluorine into PU chain, many researchers also tried to modify neat PU with nanofillers, such as Pal, montmorillonoid, carbon nanotube, etc. With the aim of overcoming these application restrictions of FPU, the only way is to keep fluorine’s content at a relative suitable value. And the most commonly and easy way is to add certain nanoparticles to modify FPU to compensate for the lack of fluorite element. For example, 4,4'-methylene bis(phenyl isocyanate) molecules were grafted onto Pal surfaces via chemical bonding (—NHCO—) and the modified Pal was then incorporated into a PU matrix by in situ polymerization as a part of hard segment, where the results showed that the mechanical properties and thermal stability both strengthened. Wang et al. has successfully developed acid activated and silicated coupling agent (KH560 and KH570) modified Pal to reinforce soy polyol-based PU.

Until now, only little research work has been carried out on PU nanocomposites to study the effect of clays on polymer. Especially for FPU, there is still no report. The objective of this article was to explore the structure and loading effect of MDI modified Pal on the properties of FPU nanocomposites based on fluorinated polyether polyol (FPO) which was synthesized by controlled cationic polymerization. We aimed to obtain a new kind of FPU nanocomposites which have a better thermal stability without preventing F migrating to the surface.

**EXPERIMENTAL**

**Materials**

Tetrafluoro propane (TFP) and diphenyl-methane-diisocyanate (MDI) were purchased from Sigma-Aldrich (Shanghai, China). The fluorinated epoxy compound (FO), fluorinated polyether polyol (FPO) was prepared according to the literature. The 1,2-epichlorohydrin (ECH), glycidoxypropyltrimethoxysilane (C3H12O3Si), tetrahydrofuran (THF), sodium hydroxide (NaOH), monomethyl ethylene chloride (CH2-CH2Cl), ethylene glycol (C2H4O2), a boron trifluoride diethyl ether (BF3-EO2), dibutyltinlaurilate, 1,4-butanediol (BDO), sodiumhexametaphosphate (SHMP) were purchased from China Medicine (Shanghai Chemical Reagent Corporation). Pal was supplied by Xuyi Xinyuan Technology Co., Ltd., 600 mesh particle size (Huaian city of Jiangsu Province, China).

**Synthetic Procedures**

**Pretreated and Organic Modified Pal.** The as-received Pal always contained small amounts of SiO2 and other minerals impurities, so the first step is purification. The details were carried out as follows: an amount of 5.0 g of Pal was dispersed in 100 mL water containing 0.2 g of sodium hexametaphosphate. The dispersion was stirred for 4 h and standing for 24 h at room temperature. Aggregated Pal particles and impurities formed sediments. The upper dispersion was centrifuged at 5000 rpm for 10 min and the resulting Pal was dried at 80°C in vacuum. After that, in order to activate Pal’s surface to form more silicon hydroxyl, acid treatment was also needed. Pal nanorods were treated with 1 mol/L hydrochloric acid at room temperature for 3 h. Then after washing it with deionized water to neutral, the acid treated Pal was dried at 100°C for 24 h in vacuum. Finally, dried Pal-OH was dispersed in 300 mL of acetone with mechanical stirring for 30 min. Then, excess MDI was added to the suspension and the mixture was refluxed at 80°C for 1 h. After grafting, the Pal–MDI nanorods were filtered and washed several times with acetone, centrifuged at 4000 rpm to remove ungrafted MDI, and finally dried at 80°C in vacuum for 24 h. The Pal-MDI cake was ground and screened through a 325-mesh sieve (Scheme 1 in Figure 1).

**Preparation of FO and FPO.** FO and FPO was synthesized according to the reported procedure. As one of raw materials to obtain FPO, FO was synthesized by substitution reaction (Scheme 2 in Figure 1), purified by rotary evaporation, and vacuum distillation one after another. After that, the methylene chloride and THF were firstly added into a four-necked round-bottom flask with a stirrer and a thermometer under nitrogen protection. When the temperature of the liquid was at 0°C, FO was dropwise added into the flask containing bulk THF, EG, and BF3OEt2. After 6 h reaction, little distilled water was added to stop the reaction. The resulting product was then washed with distilled water several times to neutrality. Then vacuum dehydration was carried out to purify the product (Scheme 3 in Figure 1).

**Synthesis of FPU Elastomer and FPU/Pal-MDI Nanocomposites**

Polymer nanocomposites FPU/Pal-MDI were synthesized in situ polymerization. The process was as follows: FPO was dehydrated at 100°C for 2 h in vacuum. After cooling to room temperature, stoichiometric FPO and Pal-MDI were placed in a three-necked round-bottom flask under nitrogen protection, heated until 60°C and stirred vigorously for 1 h to make a homogeneous dispersion system. The FPO firstly reacted with Pal-MDI to form OH-terminated fluorinated urethane oligomers. Then, MDI was added to the dispersion and the mixture was stirred for 2.5 h to obtain fluorinated pre-polymer at 80°C under nitrogen atmosphere. Subsequently, mixture started to cool and vacuumize for removal of bubbles about 30 min at the same time. When the temperature dropped to about 50°C, BDO was added to the system with vigorously stirring for 30 s. Finally, the composites were poured into a Teflon mold and cured at 30°C for 20 h to obtain FPU/Pal-MDI nanocomposites. The reaction mechanism was shown in Figure 1 (Scheme 4).

**Characterization**

Gel permeation chromatography (GPC) was carried out on Perkin Elmer GPC30 to determine the average molar mass of FPO. THF was the eluent, polystyrene was the standard sample, and flow rate was 1 mL/min at 35°C. Fourier transform infrared (FTIR) spectra of samples were taken using a Perkin Elmer spectrum 100 spectrometer and the spectra were recorded from
X-ray diffraction (XRD) study was carried out on a Bruker D8 using crystal monochromated Cu-Kα radiation over the range 3° < 2θ < 50° at a scanning rate of 5°/min. Thermogravimetric analysis (TGA) was measured using a Perkin Elmer Pyris 1 TGA with a heating rate of 20°C/min under a nitrogen atmosphere of 50–800°C. Scanning electron microscope (SEM) images of the cryofracture surfaces of the samples were taken with a SPM-9500J3 (SHIMADZU Co., Japan). The freezefractured surfaces of the SEM specimens were obtained in liquid nitrogen. The morphology of Pal nanorods were observed by transmission electron microscopy (Philips EM420). Surface element content was tested on XSAM-800 electron spectrometer (X-ray photoelectron spectroscopy). The spectrometer was equipped with a Mg-Kα achromatic X-ray source (20 kV, 10 mA) and take-off angles of 30° was used with X-ray source. Dynamic mechanical analysis (DMA Q800, TA instruments) was used to test the glass transition temperature (T_g) of neat FPU and FPU nanocomposites. The tests were performed from −30 to 200°C under a tension mode, the heating rate at 2°C/min and a frequency of 1 Hz.

400 to 4000 cm⁻¹ by averaging 64 scans at a resolution of 1 cm⁻¹. The theoretical molecular weight of FPO was dominated by controlling the amount of the initiator EG and the catalyst BF₃·OET₂, which was calculated as follows:

\[ M(\text{FPO}) = \frac{m(\text{FO}) + m(\text{THF})}{n(\text{EG})} \] (1.1)

**RESULTS AND DISCUSSION**

The theoretical molecular weight of FPO was dominated by controlling the amount of the initiator EG and the catalyst BF₃·OET₂, which was calculated as follows:

\[ M(\text{FPO}) = \frac{m(\text{FO}) + m(\text{THF})}{n(\text{EG})} \] (1.1)
In this article, theoretical molecular weight of FPO was designed as 1600. From the GPC test results (Figure 2 and Table I), we can see the actual molecular weight of FPO is 1609.4 and polydispersity indices are approximately 1.25. Molecular weight distribution corresponded to Gaussian distribution.

The FTIR spectrum of different Pal are shown in Figure 3(a). The raw Pal showed two characteristic absorption bands at 3622 and 3551 cm\(^{-1}\) according to Al\(^{3+}\)-OH and (Fe\(^{3+}\), Mg\(^{2+}\))-OH, and two shoulders at 3348–3469 and 3113–3246 cm\(^{-1}\) were attributed to hydrogen bound to oxygen in Si–O–Si and Si–O–Al groups, respectively. But acid treated Pal (Pal-OH) has a relative narrow high wave-number region. Besides, after acid treatment, the absorption band at 882 cm\(^{-1}\) of raw Pal disappeared, the characteristic peak at 977, 1022, 1200 cm\(^{-1}\) still existed and the shoulder around 1000 cm\(^{-1}\) become more wide with a strong intensity. The new shoulder signified that new silanol groups (Si–OH) had formed on the surface of Pal because the Pal’s crystal structure had not been changed. But the spectra of Pal-MDI is very different with raw Pal and Pal-OH, especially the two main regions of –NH absorption and C=O stretching. Hydrogen bonded –NH groups of urethane linkages appeared at 3310 cm\(^{-1}\), while the stretching of free –NH groups appeared at 3444 cm\(^{-1}\). Moreover, in the high wave-number region the broad band caused absence of adsorbed water, indicating that the hydrophilic character of the Pal-MDI strongly decreased. On the other hand, the stretching of –NCO groups appeared at 2268 cm\(^{-1}\) is clearly visible. In other words, –NCO has already existed on the surface of Pal.

### Table I. Molecular Weight of FPO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical (M_n)</th>
<th>Actual (M_n)</th>
<th>Actual (M_w)</th>
<th>Polydispersity indices</th>
</tr>
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<tr>
<td>FPO</td>
<td>1600</td>
<td>1609.4</td>
<td>2013.3</td>
<td>1.25</td>
</tr>
</tbody>
</table>

\[ V(EG) = V(BF_3OEt_2) = m(EG \text{ or } BF_3OEt_2)/\rho \quad (1.2) \]
The bands at 1645, 1511, and 1309 cm$^{-1}$ are also clearly observed and are consistent with polyurea formation, corresponded to $\nu$CO (amide I), $\nu$NH (amide II), and $\nu$C-NH (amide III). All these results indicate that the MDI molecules were successfully grafted onto the Pal surface through chemical bonding.

FTIR spectra of the neat FPU and FPU/Pal-MDI nanocomposites are shown in Figure 3(b). The absorption bands at 3305 cm$^{-1}$ corresponded to the $\nu$NH stretching vibration, while the bands at 2958, 2862 cm$^{-1}$ corresponded to the $\nu$CH$_2$ stretching vibration, 1704 cm$^{-1}$ corresponded to $\nu$NHCOO$^{-}$ stretching vibration, 1107 cm$^{-1}$ corresponded to $\delta$C=O-C=O characteristic absorption. C-F and C-F$_2$ of FPU characteristic absorption appears at 1225, 1205 cm$^{-1}$ and 798, 672 cm$^{-1}$, respectively. The powder XRD patterns of Pal-OH and Pal-MDI are showed in Figure 4(a). The same characteristic peak of Pal-OH and Pal-MDI at $2\theta$ = 8.35, 13.76, 16.32, 19.79, 21.42, and 35.09° correspond to the primary diffraction of (1 1 0), (2 0 0), (1 3 0), (0 4 0), (1 2 1), and (0 6 1) planes of the Pal, respectively. The interlamellar spacing of main peak at $2\theta$ = 8.35° is about 10.4 Å on the basis of Bragg equation. The results clearly showed the consistent six-plane characteristic peaks for both types of Pal and the unchanged interlay space. So, the acid and MDI treatment of Pal (Pal-OH, Pal-MDI) have not significantly influenced Pal’s crystal structure, which is in accord with the previously reported results.

XRD has been an important tool to characterize the structure of clay-polymer nanocomposites (CPN). As shown in Figure 4(b), the neat FPU matrix was always a kind of amorphous polymer with a very strong broad reflection at about $2\theta$ = 20°. But for the FPU/Pal-MDI nanocomposites, there will be a little difference. The new characteristic reflection of Pal at $2\theta$ = 8.2° and the intensity is very low because we just added as more as 2% Pal-MDI into the matrix. But the intensity of the reflection will increase with increasing Pal loading. From the results, we can not only conclude that Pal-MDI has been incorporated into FPU matrix, but also the structure of FPU is not changed.

The TGA curve of different kinds of Pal were shown in Figure 5(a) and it revealed three main weight loss stages of Pal and Pal-OH which was different with Pal-MDI. The first stage around 73°C (6.1% weight loss, 73–131°C) can be assigned to the loss of the free water existing in the Pal powder, and the second stage at 180°C (2.1%, 180–273°C) corresponds to the loss of hygroscopic water and zeolitic water. The third stage (4.5%, 273–600°C) was due to the removal of the hydroxyl group. However, for Pal-MDI, a new weight loss stage appears at 250°C, and it is attributed to the loss of grafted MDI (27%, 250–500°C), which indicated the successful coupling of MDI to Pal surface. It should be noted that Pal tend to be more lipophilic and the thermal stability was greatly enhanced with the grafting of MDI at temperature below 300°C. Figure 5(b) is the TGA and derivative thermogravimetry curves of the neat FPU and FPU nanocomposites containing different Pal-MDI loadings from 0.5 to 2%. As observed in Figure 5(b-1) and Table II, the incorporation of Pal-MDI into FPU matrix improved the initial decomposition temperature (IDT, assumed to the 5% mass loss). The IDT of nanocomposites increased at about 7.1, 5.6, 7.8, 0.1°C individually. Especially, at 0.5% and 1.5% Pal-MDI loadings, the IDT was delayed by 7°C compared with that of the neat PU. But when the loadings is 2%, the IDT...
equals to neat FPU because excess Pal-MDI was hard to disperse uniform in FPU matrix. And with the increase of Pal-MDI content, the residual at 800°C of composite materials increased too, ranging from 4.52 to 11.87% as the Pal-MDI loadings increased from 0 to 2 mass % in FPU matrix. From derivative thermogravimetry curve, Figure 5(b-2), we can clearly see the difference between neat and modified materials. The decomposition process of the neat FPU was divided into two stages corresponding to the degradation of soft and hard segment domains, but FPU/Pal-MDI has three decomposition peaks. And for FPU/Pal-MDI, the peaks after 300°C are attributed to decomposition of tangles of soft segment and hard segment part. It was because that hydroxyl on the surface of Pal made more MDI molecules easy to graft on. In the center of Pal in matrix, the chains wrapped around Pal made decomposition temperature of MDI increase, which was grafted on Pal surface. That was why there was a new decomposition peak between soft and hard segment decomposition peak. Besides, the maximum decomposition temperature (T_max) of FPU/Pal-MDI was higher than that of the neat FPU, indicating uniform dispersion and chemical bonding combination. All these results suggested that the incorporation of Pal-MDI into the FPU matrix remarkably enhanced its thermal stability, the main reason was attributed to uniform dispersed Pal-MDI in FPU matrix (see SEM curves), anisotropic fibrous Pal-MDI could form into barrier to delay the escape of volatile degradation products from CPN.

The morphology of Pal-OH and Pal-MDI was examined with SEM and transmission electron microscopy, respectively. As shown in Figure 6, Pal exhibited a relatively decentralized fibrous shape and the rod crystal has several micrometers in length and approximately 50 nm in diameter (single Pal crystal). The differences between the images of Pal-OH and Pal-MDI is clearly observed. After surface modification with MDI, the Pal fibers were almost coated with MDI and were combined together to form a bundled structure even by sonication dispersion [see Figure 6(b,d)]. These results of morphological observation were consistent with the TGA results, which indicated that the MDI molecules have been grafted on the Pal surface successfully.

The morphology and dispersion of the Pal-MDI in the FPU matrix were examined with SEM. As shown in Figure 7(a), neat

<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT (°C)</th>
<th>First hard segment</th>
<th>Second hard segment</th>
<th>Soft segment</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat FPU</td>
<td>252.26</td>
<td>267.69</td>
<td>-</td>
<td>417.07</td>
<td>4.52</td>
</tr>
<tr>
<td>FPU-0.5%</td>
<td>259.36</td>
<td>268.46</td>
<td>322.91</td>
<td>426.37</td>
<td>9.58</td>
</tr>
<tr>
<td>FPU-1%</td>
<td>257.84</td>
<td>265.43</td>
<td>324.37</td>
<td>426.70</td>
<td>10.50</td>
</tr>
<tr>
<td>FPU-1.5%</td>
<td>252.38</td>
<td>264.55</td>
<td>327.84</td>
<td>426.84</td>
<td>11.18</td>
</tr>
<tr>
<td>FPU-2%</td>
<td>260.05</td>
<td>264.07</td>
<td>323.24</td>
<td>428.72</td>
<td>11.87</td>
</tr>
</tbody>
</table>

Figure 6. SEM images of Pal-OH (a) and Pal-MDI (b); TEM images of Pal-OH (c) and Pal-MDI (d).
FPU exhibits a smooth fracture. But for composites, tiny particles can be seen clearly and size is at the nanometer level, especially for sample FPU-0.5%. Because of Pal’s properties of the intrinsic van der Waals interaction, high specific surface areas, and hydrogen bonding, it always tend to form agglomerates. So when the Pal loadings is 1.5 and 2%, that emerges the existence of some aggregations. Despite this, the Pal-MDI dispersion was still relatively homogeneous in the FPU matrix. Besides, there is also no microvoid structure. As observed in the SEM images, the incorporation of Pal-MDI into PU matrix could improve compatibility with the FPU matrix, which contributed to uniform dispersion of Pal-MDI in the FPU matrix and prevented agglomeration.

As reported before, side fluorine-containing chain of FPU will transfer to surface by mobility of the chain segments. X-ray photoelectron spectroscopy test results (Figure 8 and Table III) revealed that with the mass of Pal-MDI increasing, surface fluorine content have a little decreasing trend. It means that there is a little resistance on movement of side fluorine-containing chain. It may be caused by the increase of crosslinking density. Actually, we regarded the Pal-MDI as another kind of hard segment which is different with MDI itself. That is because MDI just have two \(-\text{NCO}\). But, MDI-modified Pal may possess more than two activating groups, including \(\text{OH}\) and \(\text{NCO}\). In other words, Pal-MDI we added in is possibly another hard segment of different chains. All this will make the crosslinking

![Figure 7. SEM images of neat FPU (a), FPU-0.5 (b), FPU-1 (c), FPU-1.5 (d), FPU-2 (e).](image)

Table III. XPS Results for Neat PU and Nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>F</th>
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<tr>
<td>FPU-0</td>
<td>64.56</td>
<td>24.94</td>
<td>3.31</td>
<td>7.17</td>
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<tr>
<td>FPU-0.5</td>
<td>64.46</td>
<td>25.98</td>
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<tr>
<td>FPU-1</td>
<td>64.06</td>
<td>25.91</td>
<td>3.72</td>
<td>6.32</td>
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<tr>
<td>FPU-1.5</td>
<td>63.64</td>
<td>26.21</td>
<td>3.77</td>
<td>6.39</td>
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<tr>
<td>FPU-2</td>
<td>61.65</td>
<td>28.43</td>
<td>3.03</td>
<td>6.19</td>
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</table>

![Figure 8. XPS curves of neat FPU and nanocomposites.](image) [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 9. DMA curves of neat FPU and nanocomposites.](image) [Color figure can be viewed at wileyonlinelibrary.com]
density increase heavily and this will make soft segment became hard to migrate to surface. As the F element existed in the soft segment of FPU, content of fluorine is reduced.

As we can see from the DMA curve (Figure 9), tan δ of FPU-1.5 is lower than that of FPU-2 and FPU-0.5 is lower than FPU-1 which means four samples have different damping properties. FPU-1 has the highest damping capacity, because mobility property of the material is best (the biggest E” at Tg). Different amount of Pal-MDI loadings in CPN have different dispersion effect. Anisotropic fibrous Pal-MDI formed into barrier to stop molecular chain moving. With Pal-MDI adding into FPU, FPU chains became hard to move from one conformation to another. Molecular chain becomes more rigid and stiff. DMA test results (Table IV) revealed that FPU have two different glass transition temperatures (Tg): soft segment Tg_s and hard segment Tg_h. As shown in Table II, with the increasing of Pal-MDI, the soft segment Tg_s was a little higher than neat FPU. But, for the hard segment, the Tg_h is a little lower. And the ΔTg also became lower. It means that the Pal-MDI increased the compatibility between soft and hard segment. Except this, thermal stability also has a little increase than neat FPU.

**CONCLUSIONS**

In this article, we successfully synthesized FPU/Pal-MDI nanocomposites to study the effect of organic modified Pal on the properties of fluorinated PU. The structural characterization, thermal properties, as well as the morphology of the resulting composites were evaluated by various techniques. The resulting nanocomposites exhibited increases in thermal stability compared with the neat FPU. After modification, Pal showed good compatibility with the FPU matrix through SEM test results. And the introduction of Pal into FPU matrix will not affect migration of fluoride side chain. It is absolutely a new research direction of FPU modification.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (21101107, 51373100, 51173107, and 5140030478), the innovation Project of the Shanghai Municipal Education Commission (no. 15ZZ076), and the Huijiang Foundation of China (B14006).

**REFERENCES**


<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (soft segment) (°C)</th>
<th>Tg (hard segment) (°C)</th>
<th>ΔTg (°C)</th>
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<tbody>
<tr>
<td>FPU-0</td>
<td>15.28</td>
<td>197.46</td>
<td>182.18</td>
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<tr>
<td>FPU-0.5</td>
<td>15.84</td>
<td>172.26</td>
<td>156.42</td>
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<tr>
<td>FPU-1</td>
<td>16.31</td>
<td>174.78</td>
<td>158.47</td>
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<tr>
<td>FPU-1.5</td>
<td>19.44</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>FPU-2</td>
<td>15.41</td>
<td>180.80</td>
<td>165.39</td>
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