EFFECT NANOCLAY ADDITION ON THE COMPATIBILITY AND DIFFUSION PROPERTIES OF COMMERCIAL GASOLINE THROUGH POLYMER MEMBRANES

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Abstract

In this work, we consider the effect of the addition of functionalized clay particles to a poly (tetramethylene oxide) (PTMO) based polyurethane that is a candidate to be used as for flexible storage containment for a variety of military fuels. We have synthesized urethanes with layered silicate inorganic nanoclay concentrations varying from 0% to 10% by weight and evaluated the diffusion of commercial gasoline.

Introduction

Polyurethanes are used as coatings, adhesives, thermal insulation and more recently as polymer binders [1,2]. These thermoplastic materials are typically phase segregated and consist of a combination of hard, rigid, organized segments and soft flexible, rubbery segments. [3,4]. Numerous studies [5-7] have shown that microphase segregation occurs in polyurethanes due to the thermodynamic incompatibility of the hard and soft segments and physical crosslinking among hard segments. Phase segregation leads to a variety of morphologies depending on the content of hard or soft segment in the polymer. Usually, at phase ratios greater than 2:1, the minority phase is dispersed in a matrix of the majority phase, while at near 1:1 phase ratios, lamellae structures are observed [8]. The extent of segregation varies depending on the amount of physical crosslinking that takes place, usually through hydrogen bonding. Hydrogen bonding can occur between the urethane groups of different hard segments, or between the urethane group in a hard segment and the oxygen in a polyester or polyester soft segment [9]. More crosslinking between hard segments leads to a higher degree of phase segregation, while hydrogen bonding between hard and soft segments leads to phase mixing.

The benefits of incorporating nanoclay fillers into polymer systems is a tried and true method for improving many physical and mechanical properties as well as tuning transport properties to individual requirements[8,9]. The unique platelet nanostructure of these inorganic silicate layered clays allow for some interesting properties to develop when blended into polymer membrane matrices due to the ability of the polymer chains to infiltrate the layers of the nanoclays. They offer the ability to separate into individual sheets from their normally layered structure, thus allowing surface functionality to be performed [10]. This complete separation into individual sheets is known as exfoliation and allows a maximum amount of surface area available to interact with host polymer. Usually, this is carried out using an appropriate solvent to disperse the silicate layers. The resultant polymer/clay nanocomposites can be used to control gas permeation as well as water and solvent diffusion. [11,12].

In this paper, we report the effect of the addition of functionalized and defunctionalized nanostructured clays to improve the diffusion of commercial gasoline through clay/urethane membranes. Such polymer membranes allow for coated fabrics to be assembled and be utilized as flexible fuel containment and storage.

Experimental

Materials

Samples of H12MDI/BD/PTMO2000 polyether polyurethane were synthesized using H12MDI (4,4-dicyclohexylmethane diisocyanate) as the hard segment, BD (1,4-butandiol) as the chain extender, and PTMO 2000 (poly(tetramethylene oxide)) (molecular weight 2000) as the soft segment. Details concerning the synthesis and preparation of these samples can be found elsewhere [13, 14]. The nanoclay used was a Montmorillonite clay purchased from Aldrich Chemical that was surface modified using wt 35-45% dimethyl dialkyl amine functionalization (C14 – C18).

Nanoclays and urethane were blended in appropriate proportions with THF to produce a composite slurry and stirred overnight. The solvent was evaporated off and the solid composite was introduced into the mixing head of an Xplore 15cc Micro Compounder, a twin screw extruder. The nanoclay/urethane composite was processed at 100 rpm at 180 °F. Polyurethane composites containing 0%, 2%, 5% and 10%, nanoclay concentrations were processed using this method and extruded into an appropriate mold for testing.

Characterization

FT-IR
Infrared spectra were recorded with a Nicolet Magna 560 ATR-FTIR spectrometer using films placed on a ZnSe (Zinc Selenide) crystal. Spectra were recorded in the mid-infrared region (4,000–400 cm$^{-1}$). Each spectrum was obtained by accumulating 64 scans at a resolution of 4 cm$^{-1}$. Data collection and processing was completed using OMNIC series software.

**Diffusion**

Diffusion experiments were carried out by immersing a 6 mm wide square sample with a thickness of 1 mm into a commercial gasoline (Shell 87 octane). Samples were tested 25°C. The samples were removed at selected time intervals, blotted dried and weighed. If we assume that the diffusion process is Fickian, a plot of the molar percentage weight gain with the square root of time will be linear for the initial portion of the curve before leveling to equilibrium. The fuel sorption for the commercial gasoline was determined from the following equation [15],

$$Q_t = \frac{M_t - M_0}{M_w} \times 100$$

Where $Q_t$ is the percent fuel sorption, $M_t$ is the weight gain at time $t$, $M_0$ is the initial weight of the polymer composite and $M_w$ is the molecular weight of diffusing fuel. In our case, we used the average $M_w$ of commercial fuel components.

The diffusion coefficient can then be calculated from the following equation,

$$D = \left( \frac{h \phi}{4Q_e} \right)^2$$

Where $Q_e$ is the equilibrium sorption, $\phi$ is the slope of the initial line, when $Q_e$ is plotted against $t^{1/2}$, $h$ is the thickness in cm of the composite membrane and $D$ has the dimensions of cm$^2$/s.

**Results and Discussion**

**FT-IR**

Since urethanes are phase segregated polymers, they have hydrogen bonded hard crosslinking segments that can be investigated by Fourier transform infrared spectroscopy. Figure 2 shows the 950 cm$^{-1}$ to 1850 cm$^{-1}$ region for the urethane nanocomposite. These overlaid spectra consist of two critical peaks, the one centered at 1720 cm$^{-1}$ is assigned to the unassociated carbonyl of the urethane linkage and the one centered at 1700 cm$^{-1}$ is attributed to a carbonyl group that is hydrogen bonded to a nearby N-H group. These two IR bands give insight as to the amount of phase mixing occurring within the urethane matrix. The more hydrogen bonding that is present (increase in the 1700 cm$^{-1}$), the more the urethane is phase separated. The IR spectra for the 0% and 10% are virtually identical, no band intensity changes or peak shifts can be observed. This means that the nanoclay is residing completely in the polyether soft segment and not impinging upon the isocyanate hard segments. This allows the crosslink network to remain intact. The fact that there is no change in the intensity of the 1720 cm$^{-1}$ band suggests that the clay particles are not interacting with the non-bonded carboxyls that are residing and dispersed in the polyether chains of the soft segment. The other notable band in this figure is located at 1120 cm$^{-1}$. It is present in the spectrum of the 10% loaded composite and not in the 0% composite, this is due to the FT-IR spectra of the pure nanoclay.

**Diffusion**

The strategy of incorporating fillers of any type into polymer membranes is to deliberately impede the diffusion and/or permeation of solvents or gases through the polymer membrane. This has the effect of creating a more tortuous path for diffusing molecules to encounter as they pass through the membrane. Figure 3 depicts this process for nanoplatelets.

Figure 2. FT-IR spectra compare the 10% nanoclay filled and unfilled nanoclay/urethane composites.

Figure 3. Schematic for a molecular diffusing through a filled polymer composite membrane.

Figure 4 shows the sorption/diffusion results for 0%, 2%, 5% and 10% nanoclay loaded urethanes. For the tested nanocomposites, the solvent weight uptake was found to increase with increasing nanoclay concentration, a direct contradiction to the tortuosity model previously described as well as the results reported by other researchers [16-17]. The addition of nanoclay has a significant accelerating effect on the diffusion process of commercial gasoline into
the nanoclay composite. In addition to the diffusion rate increase, the overall equilibrium sorption/solubility (swelling) has increased.

To test this theory, we needed to defunctionalize the nanoclay surface. This was accomplished by pyrolyzing the nanoclay. The nanoclay was placed in a furnace that was set at 450 °F. This completely cleared the nanoclay surface of the C14-C18 alkyl chains. Figure 5 shows the spectra of the nanoclays before and after pyrolysis. In the spectrum of the functionalized nanoclay (top), IR bands just below 3000 cm\(^{-1}\) can be identified as the C-H stretches of the C14-C18 hydrocarbon chains. Initial attempts to defunctionalize the nanoclay surface was attempted by acid washing the nanoclay in concentrated sulfuric acid. The IR spectra shows no effect of the acid wash as the IR bands at 3000 cm\(^{-1}\) remain present. The bottom two spectra show the nanoclay after pyrolyzing for 1 hour and after pyrolyzing overnight, in both cases, the C-H bands of the alkyl chains have been completely erased, evidence that the clay surface has been cleared of the long alkyl chains.

Figure 4. Sorption isotherm curves for 0, 2% 5% and 10% nanoclay loaded urethanes.

Table 1 gives an estimate of the solubility parameter for the three components. The Hansen solubility parameter is divided into three individual parts, dispersion forces, permanent dipole forces and H bonding forces. The nonpolar components have a much lower solubility parameter, while the more polar components have a higher solubility parameter. Generally, the closer the values are between two components, the more compatible they are to each other [18, 19]. Using this reasoning, the fuel and nanoclay, which are non-polar, are highly compatible with each other, while the nanoclay and fuel are not compatible with polar polyurethane.

Figure 5. FT-IR spectra of nanoclay before and after pyrolysis.

Table1. Hansen Solubility Parameters

<table>
<thead>
<tr>
<th>Component</th>
<th>(\delta_d) (Mpa)(^{1/2})</th>
<th>(\delta_p) (Mpa)(^{1/2})</th>
<th>(\delta_h) (Mpa)(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Functionalized Nanoclay C14-C18</td>
<td>15.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyether PU</td>
<td>18.7</td>
<td>9.9</td>
<td>9.6</td>
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</table>

In Figure 6, the sorption isotherms for the functionalized, defunctionalized and unfilled nanocomposites are presented. The solvent weight uptake was found to decrease with addition of 10% defunctionalized nanoclay. These results are more in line with the expectations that increased filler content should decrease the diffusion coefficient. In addition to the diffusion rate increase, the overall equilibrium sorption/solubility (swelling) has decreased. These
results suggest that the nanoparticle chemistry has a more dramatic effect of solvent permeability than the overall steric effect of the particle. Table 2 tabulates the calculated diffusion coefficients and molar weight uptake for the nanocomposites.

**Table 2. Diffusion coefficients and equilibrium molar weight values**

<table>
<thead>
<tr>
<th>Composite</th>
<th>0%</th>
<th>2%</th>
<th>5%</th>
<th>10%</th>
<th>10% Defunctionalized</th>
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<tbody>
<tr>
<td>Molar % Wt Gain</td>
<td>16.7</td>
<td>17.5</td>
<td>19.2</td>
<td>22.9</td>
<td>12.5</td>
</tr>
<tr>
<td>Thickness (cm)</td>
<td>0.1324</td>
<td>0.1326</td>
<td>0.1332</td>
<td>0.1331</td>
<td>0.1341</td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
<td>1.08E-07</td>
<td>1.79E-07</td>
<td>3.41E-07</td>
<td>5.69E-07</td>
<td>1.03669E-08</td>
</tr>
</tbody>
</table>

**Conclusions**

In this study, we evaluate the effect of incorporating functionalized and defunctionalized nanoclays into a polyether based polyurethane on their structural and transport properties. FT-IR analysis reveals that the carbonyl region is unperturbed by addition of the nanoclay, which suggests that there no interaction with either the H-bonded carbonyls of the isocyanate hard segment or the non-bonded carbonyls residing in the soft polyether phase. The FT-IR results show that a full defunctionalization takes place when the nanoclay is pyrolyzed at 450 °F. This is done intentionally to alter the chemical groups residing on nanoclay surface. When the nanoclay is functionalized with the C14-C18 alkyl groups, an increase in both the diffusion coefficient and the overall solubility is measured. This is a result of the chemical compatibility of nanoclay and fuel. When the surface is altered with polar groups, the trend is reversed and a decrease in the diffusion coefficient and the overall solubility is seen.

**References**