Quarterly Report

Project: Thermoplastic Elastomers as LOVA Binders

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Publications


Technical Reports Issued

Number 20 "The Modelling of Orientation in Planar Polymer Welding Flows"

Number 21 "Synthesis and Characterization of Block Copolymer"

Number 22 "Synthesis and Characterization of Block Copolymers"
I. Advanced Cry/am TPE

A. Synthesis of Crystalline Segment - poly D/T

Polytrioxane/dioxolane with different $T_m$ ($T_m = 48.39, 73.19, 98.59$ and 139.16°C) have been synthesized by using toluene as the solvent (Fig. 1 - 4). The compositions of P D/T ($T_m = 48.79, 73.19$ and 98.59°C) were measured by $^1$H NMR (CDCl$_3$): trioxene content increased from 0.41 to 0.65. The molecular weights of these poly D/T were determined by Karl-Fisher method (LAH in $O$ as 2000 - 25000. P D/T ($T_m = 139°C$) is insoluble in common solvent, therefore, its composition was determined by solid C NMR: $T/D = 0.748/0.252$.

Different solvents have been used instead of toluene. It was found that CHCl$_3$ is suitable for this reaction, the yield of P D/T ($T_m = 100°C$) increases from 5% (toluene as solvent) to 35%.

B. Fractionation of poly D/T

Poly DT #32 from Olin Company was not homogeneous. Three sampling gave three different DSC traces with different area ratios of low melting to high melting components. A variety of solvent have been tried to fractionate those two different melting ranges, and halogenated solvents are much better than common organic solvents. The soluble fraction from chloroform has two $T_m$ peaks 85, 105°C. Fraction soluble in methylene chloride and dichloroethane showed one $T_m$ at 85°C. Tetrachloroethane soluble materials showed rather wide range of melting behavior. Comparison of the soluble fractions from methylene chloride and dichloroethane at 50°C showed the former...
to possess higher melting fraction than that of the latter fraction. Comparison of the soluble fraction from dichloroethane at 50°C and 64°C showed the latter to be higher melting fraction than the former.

C. Pyrolysis of PDT

Methylene chloride soluble fraction showed that it was very stable. A very minor weight loss was observed around 270°C with significant weight loss beginning at 400°C. In the presence of ethyl naphthalene sulphonate as latent acid. A significant weight loss was observed around the decomposition temperature of ethyl naphthalene sulphonate. For the protonic acid as p-toluene sulfonic acid. The PDT started to decompose by 100°C.

D. Synthesis of Cry/am TPE

PD/T and P4MeDOL were coupled by MDI to form polyurethane (PU). The product is a light yellow elastomer. This reaction can be monitored by IR. The intensity of isocyanate peak (2270 cm⁻¹) decreases and a new peak at 3300 cm⁻¹ (N-H stretch) appears indicating the formation of urethane block. DSC results showed good phase separation behavior, the melting transitions of PU are the same as PD/T, even at very low hard segment (PD/T) composition 10 wt %. This result was also proved by polar microscopy. All the PUs thus made are acid sensitive, TGA results showed that PU started to decompose at 286°C and wt lost was 87% during 420 - 480°C. If toluene sulfonic acid (5 wt %) was added, it started to decompose at 99°C and wt lost was 78% during 99 - 178°C.
II. Advanced Liquid Crystalline TPE

A. Twin LC TPE

Liquid crystalline polymers have been synthesized with PTHF soft spacer for

\[
\text{C}_4\text{H}_9\text{O} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}_4\text{H}_9
\]

Ia \quad n = 8.8 \quad \text{MW} = 1232

Ib \quad n = 13.6 \quad \text{MW} = 1592

Ic \quad n = 28 \quad \text{MW} = 2592

The structure of the polymers were identified by IR of NMR-200. The \(^1\)H NMR results for the polymers are:

\[\delta 1.00 \text{ ppm (CH}_3\text{), 1.61 (butyl H}_\gamma\text{), 1.84 (butyl H}_\beta\text{), 3.44 (THF CH}_2\text{), 4.06 (butyl H}_\alpha\text{), 4.35 (CH}_2\text{ ester), 6.99 (3.5-oxybenzoate), 7.30 (3.5-oxybenzoate), 8.13 (2.6-oxybenzoate).}\]

The molecular weight of the polymers can be calculated by integrated ratios.

Transition temperature of the polymers from DSC) are:

<table>
<thead>
<tr>
<th></th>
<th>(T_m \degree C)</th>
<th>(T_i \degree C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>28</td>
<td>50</td>
</tr>
<tr>
<td>Ib</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>Ic</td>
<td>24</td>
<td>55</td>
</tr>
</tbody>
</table>

The mesophase can be observed on polarizing microscope between \(T_m\) and \(T_i\).
B. Segmented LC TPE

(1) Objective
To prepare a series of polymers with liquid crystalline hard segments and long flexible spacers.

\[ \text{L.C. moiety Flexible spacer} \]

(2) Results and Discussion
In the previous report a series of polyesters were reported that contained two ring azo and azoxy benzene moieties. None of these polymers exhibited liquid crystalline behavior. The inability of these materials to form a mesophase could be due to inefficient phase separation. One way to overcome this would be to increase the length of the mesogen. Two methods are being explored to prepare these polymers. The first calls for the preparation of a functionally endcapped prepolymer. This material can then be polymerized with a number of aromatic dicarboxylic acid chlorides.

The second method enlists chain extension polymerization
techniques. Here short spacers, butanediol (BDO) for example, are used to link together the mesogenic units.

(3) Preparation of Endcapped Prepolymer

The endcapped functional prepolymer was prepared by reacting poly THF 650 with three equivalents of p-benzyloxy benzoylchloride in pyridine.

A number of debenzylation were investigated to reveal the functionalized material. Here only catalytic hydrogenation gave satisfactory results.

Reaction Scheme I

Preparation of functionalized endcapped prepolymer.

\[
\text{HO(\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{OH})}_n\text{H} + \text{O} \quad \text{ClC-} \quad \text{O-CH}_{2}\quad \text{O} \quad \text{Deg} \quad \text{R.T.} \quad \text{3.0 eq.} \\
\text{HO-} \quad \text{C-O(-CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{O})_n\text{-C-} \quad \text{Pd/C 10\%, H}_2 \quad \text{85-95\°C} \\
\text{HO-} \quad \text{C-O(-CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{O})_n\text{-C-} \quad \text{-OH}
\]
This endcapped material has been characterized by $^1$H NMR, IR and thin layer chromatography and is greater than 95% pure. When the L. Kely impurities are monodebenzylated material.

This material will be polymerized with aromatic and aliphatic diacid chloride and investigated for liquid crystalline properties.

(4) Multiple Rings Joined by Short Spacers

Here two polymers have been prepared using azobenzoyl chloride as the hard segment, butane diol as the chain extender and poly THF as the soft segments. These results are in Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Soft Segment</th>
<th>T.P.E.?</th>
<th>L.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poly THF 650</td>
<td>No</td>
<td>?</td>
</tr>
<tr>
<td>2</td>
<td>Poly THF 2000</td>
<td>Yes</td>
<td>?</td>
</tr>
</tbody>
</table>

III. Cationic Copolymerization of 2-Butyl-1,3-Dioxepane with 1,3-Dioxolane

Copolymerization of 2-butyl-1,3-dioxepane (Bu-DOP) (A) with 1,3-dioxolane (DOL) (B) was studied with boron trifluoride etherate ($\text{BF}_3\cdot\text{OCC}_2\text{H}_5$)$_2$ as initiators. It was followed by determining the unreacted monomers by means of gas-chromatography. The time-conversion curves in Fig. 1 and Fig. 2 showed that preferential polymerization of 2-butyl-1,3-dioxepane occurred. In the case of the copolymerization of 2-butyl-1,3-
dioexpane and increased, the polymerization of dioxolane gradually slowed down. At this stage the concentration of unreacted Bu-DOP and DOL monomers were 2.8 - 3.0 and 4.0 - 4.3 mol/l, which is considerably higher than the equilibrium monomers concentration of Bu-DOP and DOL were 1.87 and 1.56 mole/l at -10°C. The 1H-NMR spectrum of one of the copolymer shown in Fig. 3 presents six resonance signals centered at 0.87, 1.29, 1.60, 3.39, 3.56 and 4.42 ppm from TMS, which the composition of the copolymers were obtained from the intensities of the resonance at 3.39, 3.56 and 4.42 ppm. The results are listed in Table 1. A set of copolymerization with varying monomer compositions were made at lower conversion. The experimental results given in Table 1 were used to obtain the composition diagram shown in Fig. 4. The values of the reactivity ratios calculated by the Fineman-Ross were $r_A = 2.13 \pm 0.05$ and $r_B = 0.09 \pm 0.05$ at -10°C.

The isolated copolymers were measured DSC analysis with varying monomer compositions in Fig. 5. The $T_g$ should vary with composition as shown in an expression by Fox equation, which the values ($T_g$) were agreed of these calculated and experimental quantities.

The higher reactivity of 2-butyl-1,3-dioxepane as compared with dioxolane agree with the higher basicity and propagating species.
Fig. 1. Homopolymerization (A) of 2-butyl-1,3-dioxepane (Bu-Dop) and (B) of dioxolane (DOL) with BF$_3$.0(C$_2$H$_5$)$_2$ at -10°C.

[Me]$_A$ = 1.87, 61%
[Me]$_B$ = 1.5-1.6, 67%

[Bu-Dop] = 4.8 mole/l ; [DOL] = 4.9 mole/l ; [BF$_3$.0(C$_2$H$_5$)$_2$] = 3.1 x 10$^{-2}$ mole/l.
Fig. 2. Time-conversion curves for the copolymerization of 2-butyl-1,3-dioxepane (○) with 1,3-dioxolane (●).

\[
\begin{align*}
[\text{Bu-DOP}]_0 & = 4.96\text{ mole/l} ; \\
[\text{DoL}]_0 & = 5.13\text{ mole/l} ; \\
\text{BF}_3 \cdot \text{O} (\text{C}_2\text{H}_5) & = 1.09 \times 10^{-2}\text{ mole/l} ; \\
\text{solvent} & : \text{CH}_2\text{Cl}_2 ; \text{temperature} \ -10^\circ C.
\end{align*}
\]
\[ p(Dol', \text{ Cdp}) = 0.25 \]
Table: Copolymerization of 2-butyl-1,3-dioxepane (Bu-Dop) and dioxolane (DOL)

<table>
<thead>
<tr>
<th>Monomer (mole/l)</th>
<th>DOL Bu-Dop</th>
<th>Bu-Dop</th>
<th>DOL mole fraction</th>
<th>reaction time (hr)</th>
<th>conversion %</th>
<th>DOL in copolymer mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.76</td>
<td>1.28</td>
<td>4.5</td>
<td>0.82</td>
<td>30</td>
<td>5</td>
<td>0.46</td>
</tr>
<tr>
<td>3.53</td>
<td>0.85</td>
<td>4.2</td>
<td>0.81</td>
<td>24</td>
<td>4</td>
<td>0.40</td>
</tr>
<tr>
<td>5.42</td>
<td>2.04</td>
<td>2.7</td>
<td>0.73</td>
<td>15</td>
<td>8</td>
<td>0.35</td>
</tr>
<tr>
<td>3.79</td>
<td>1.90</td>
<td>2.0</td>
<td>0.67</td>
<td>5</td>
<td>8</td>
<td>0.31</td>
</tr>
<tr>
<td>2.83</td>
<td>2.54</td>
<td>1.1</td>
<td>0.53</td>
<td>3</td>
<td>9</td>
<td>0.25</td>
</tr>
<tr>
<td>1.36</td>
<td>2.54</td>
<td>0.54</td>
<td>0.35</td>
<td>3</td>
<td>5</td>
<td>0.15</td>
</tr>
<tr>
<td>0.04</td>
<td>2.54</td>
<td>0.29</td>
<td>0.22</td>
<td>12</td>
<td>7</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Fig. 4. Copolymer composition curve of 2-8u-DOP and DOL at -10°C.
Fig. 5. DSC Curve for copolymerization of 2-butyl-1,3-dioxepane with 1,3-dioxolane. A, Bu-Dop; B, 85:15 Bu-Dop/DoL; C, 75:25 Bu-Dop/DoL; D, 60:40 Bu-Dop/DoL.
Fig. 6. $T_g$ measured by DSC versus composition for copolymer (DOL/BU-Dop)
IV. Design, Analysis, and Simulations

A. Analysis

Analysis of the model concentrates on the high-speed behavior of the vehicle. The predictions of the model are compared to the experimental results for the high-speed behavior. The predictions are based on the linear superposition of the vehicle's mass and the vehicle's inertia. The predictions are compared to the experimental results for the high-speed behavior. The predictions are based on the linear superposition of the vehicle's mass and the vehicle's inertia.
The purpose of the present paper is to discuss the behavior of star clusters and the properties of the interactions in the general case, based on the assumption that the interactions depend on the properties of the medium and the assumptions on the interactions and the parameters, which determine the non-equilibrium parameters of the interactions. The result of the present work is that the parameters are not expected to depend on the interactions, but rather on the environmental conditions and the mass of the star cluster. The equation taken as:

\[ \frac{d}{dt} \begin{pmatrix} x \\ y \\ z \\ v_x \\ v_y \\ v_z \end{pmatrix} = \begin{pmatrix} \dot{x} \\ \dot{y} \\ \dot{z} \\ \dot{v_x} \\ \dot{v_y} \\ \dot{v_z} \end{pmatrix} = \begin{pmatrix} f_1(x, y, z, v_x, v_y, v_z, t) \\ f_2(x, y, z, v_x, v_y, v_z, t) \\ f_3(x, y, z, v_x, v_y, v_z, t) \\ f_4(x, y, z, v_x, v_y, v_z, t) \\ f_5(x, y, z, v_x, v_y, v_z, t) \\ f_6(x, y, z, v_x, v_y, v_z, t) \end{pmatrix} \]

where:
- \( x, y, z \) are the coordinates of the star cluster
- \( v_x, v_y, v_z \) are the velocities of the star cluster
- \( f_1, f_2, f_3, f_4, f_5, f_6 \) are the functions that depend on the parameters of the interactions and the environment.
part as the exacted method. A single solution derived this secret
was also to be confided. Another, but from a fall below the cathode,
and these, as the element.

A. The state of the design with particular to another sentence. And every
and constant, and the numerical element. We all understand the other,
their firmness. This appearance can be a fact, but not in the
of the same area, but in the others, and some further
seen through with the cooled solution. These and other
the same area, and speaking with the country producers
vibrations in electric current in matter.

The current, as described only the steady force
and less in time. It is called a conduction and exists by
the purpose means two terms, and other, for the
they stated, and all have produced.

Where a certain term is a factor, and the time
of the basic, and this description is apparent,
period is the same of the level from the current and more direct.
while the mass some exactly describes a perfectly
of the terms, and where mass is here. The superposition
is the force (time) to achieve more than the tariffs in the heat.
and this, as the money. This becomes a few times,
the mass, which is the outcome, and the more direct the
and which is a different of the solution obtained.
Figure 1. Typical steady shear viscosity curve for a filled polymer melts (solid curve). Dashed lines show the contribution of each term in Eqn. (2).
log complex viscosity [Pa.s]

Viscasil 600000/glass beads
Temp = 30 C
log complex viscomity [Pa.s] vs. log freq rate [rad/sec]

Temp = 60 C

Viscosil 600000/glass beads

Run # 540

Capillary rheometer data
Liner rheometer data
Stress rheometer data
Viscascill/glass beads 50 vol. %
B. Rheology of Triblock Copolymers

Our program to investigate the effects of flow on the properties of triblock copolymers consists of two parts - evaluation of the rheological impact, and determination of the induced morphological changes. The results of the rheological study have been reported earlier, and work has begun on the second phase. In determining the effect of flow on the morphology of these materials, it will also be possible to understand more clearly the flow mechanism involved.

Two principle methods have been used to determine the morphology of a particular styrene-butadiene-styrene triblock copolymer: transmission electron microscopy (TEM), and small-angle x-ray scattering (SAXS). This report will concentrate on the SAXS results.

SAXS data was taken at the National Bureau of Standards in Gaithersburg, MD in order to use their 10m SAXS camera and software. Also the two-dimensional camera available there allows the detection of the entire scattering area, not just sections. This is very useful for measuring the scattering patterns of oriented materials as they will be anisotropic.
The results from the initial study show that as the shear strain is increased on the sample, the primary scattering peak due to the fundamental spacing of the cylinders on a hexagonal lattice becomes stronger. This is due to a more perfect alignment of the cylinders in the flow direction as strain increases. Preliminary quantitative analysis shows that the lattice parameter has a value of 278 Å which with an overall polystyrene volume fraction of .26 corresponds to cylinders of diameter 150 Å. A form factor peak occurring at higher angles is also consistent with a diameter of this magnitude (149 Å). The initial results from TEM show a slightly smaller diameter (133 Å).
V. Prediction of the Mechanical Behavior of Particulate Composites

Introduction

The energy balance type of approach to modelling the debonding behavior of highly filled composites such as propellants described in earlier reports is being more fully developed. This approach equates the change in strain energy of a sample during debonding to the work necessary to create new surfaces on the debonded particles. The predictions appear to be fairly accurate for isotropic composites with spherical filler particles. The experimental phase of the project is progressing. All of the apparatus for the experiments is now functional, and the preparation of samples is commencing. Comparisons of experimental results to model predictions will be forthcoming.

Experimental

A high-pressure gas dilatometer has been constructed and was recently tested for the first time. This instrument concurrently measures stress and volume changes which occur in a sample during uniaxial extension. Superimposed hydrostatic pressures of up to 1000 psi may be used. It
appears to operate properly, and is sensitive to small changes in pressure and load. Atmospheric testing of samples is scheduled to begin immediately. Some problems have been encountered in altering the existing software to work on the lab's new Zenith computer system, but are expected to be solved soon. The instrument is fully operational with the IBM AT software and the data collection will begin with that system.

Preparation of samples is proceeding very successfully. The bulk synthesis of polyurethane from tolylene 2,4-diisocyanate and diols or triols of poly(propylene oxide) to form void-free samples was accomplished after some trouble. Side reactions with water produce carbon dioxide bubbles throughout the samples. The entire reaction must be carried out under vacuum and the cast samples must be immediately transferred to a dessicator in order to produce void-free samples. The optimal isocyanate content for the reaction was determined. Composites of polyurethanes with up to 10 percent by volume glass beads have been made easily in small scale glassware. Larger batches of more highly filled systems have been attempted using the Baker-Perkins high-shear mixer purchased by Dr. Winter with LOVA funds, and appear to yield good results.

Theoretical

The models described in earlier meetings are being further developed. Current work is focusing on determining the proper void volume to add to the sample after debonding
in order to predict reasonable values of dilatation.

Progress is good, and the results will be presented at the September meeting of the Polymer and Materials Science and Engineering division of the American Chemical Society. A paper describing the derivations and the model predictions will soon be submitted for journal publication.
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