Studies on Isothermal Curing and Kinetics of Degradation of Acrylate/Diisocyanate System

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Received: 24 January 1998; accepted 11 August 1999

ABSTRACT

The cure of a two component system such as: acrylate copolymer resin with blocked 2,4-toluene diisocyanate cross-linker, which react to form polyurethane network, has been investigated using a dynamic mechanical technique, torsional braid analysis (TBA). The mixture is cured, with and without catalyst, at various temperatures. The apparent activation energy, evaluated from Arrhenius plot of logarithm of gelation time vs. \(\ln T (K)\), for the uncatalyzed reaction is found to be greater than that of the catalyzed reaction. Furthermore, the activation energy of the system is found to decrease with increasing concentration of catalyst (dibutyltin dilaurate). The results indicate that gelation time decreases when dibutyltin dilaurate is added into the system. Degradation of polyurethane (PU) networks formed by the cross-linking reaction has, also, been studied by thermogravimetry (TGA) and activation energy of degradation of PU has been determined.

Key Words: curing, diisocyanate, isocyanate, polyurethane, TGA, torsional braid analysis

INTRODUCTION

The curing of thermosetting materials involves the formation of infinite networks of polymer chains by chemical reaction between the reactive groups in the system. PU networks are of great practical and theoretical importance due to simple built-up of structure from hydroxyl and isocyanate, and have been used extensively to study the relationship between structure and mechanical behaviour [1–3]. Composition and structure of polyurethane can be varied within wide limits and consequently there is no definite property pattern. Copolymer of methyl methacrylate, ethyl acrylate, and monomer containing reactive groups are widely used as thermosetting resin in enamel applications.

Formation of PU by polyaddition of diisocyanate and diols has been widely reported in the literature. Blocked isocyanates are suitable building blocks for light stable two component urethane coatings [4]. Isocyanate group is blocked by the formation of weak bond between isocyanate and compound containing

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active hydrogen. At elevated temperatures, the isocyanate and blocking agents are regenerated. Wicks [5, 6] has described a number of blocking agents in his review on blocked isocyanate. A wide variety of alcohols such as isopropanol [7], 2-ethylhexanol [8, 11], n-butanol [12, 13], have been used as blocking agents. The kinetics of urethane formation by the reaction between isocyanates and alcohols have been extensively studied [14, 17].

Cure monitoring of polymer and thermosetting resin is very important because it provides a technique for the control over cross-linking process and has become essential part of composite process technology. There are various methods to study the curing reaction of polymers. The chemical method involves the analysis of degree of conversion of reactive groups by methods such as chemical analysis, IR spectroscopy and calorimetry. The physical approach involves the measurement of changes in physical properties such as density, refractive index, viscosity, mechanical and electrical properties. Among various methods of curing, dynamic mechanical technique such as TBA [18-21], has drawn considerable importance to cure the system which takes few hours to cure.

In present work we investigate the isothermal curing of acrylate copolymer/diisocyanate by TBA, and thermal degradation of PU networks by means of thermogravimetry (TGA) [22-24].

**EXPERIMENTAL**

**Synthesis**

**Preparation of Acrylate Copolymer Resin (1)**

Styrene (0.2 mol), dimethylaminoethyl methacrylate, MNA, (0.2 mol), 2-hydroxypropyl methacrylate, HPMA, (0.2 mol), butylacrylate, BA, (0.6 mol), were radically copolymerized with AIBN initiator [25]. The average molecular weight, measured from GPC spectra with the monodispersed polystyrene standard, was $M_w = 2880$.

**Preparation of Cross-linker 2 (Trimethylpropane-toluene-2,4-diisocyanate-2-ethylhexanol Resin)**

A non-ionic cross-linker 2 was prepared [26] by slowly adding 74.9 g (0.576 mol) of 2-ethylhexanol (2EH) to 100 g (0.576 mol) toluene-2,4-diisocyanate (TDI) over a period of about 1 h, while mixing under the blanket of dry nitrogen gas and temperature kept below 10 °C. The batch was heated to 40 °C and held for 2 h. Then 25.7 g (0.192 mol) trimethylolpropylene (TMP) was added slowly over a period of 1 h while the reaction temperature was raised to 60 °C, and the reaction was permitted to continue for about 1 h at this temperature to consume all isocyanate groups. The resultant product was non-ionic TMP-TDI-2EH cross-linker 2. The concentration of unblocked isocyanate group was less than 1%.

**Torsional Braid Analysis (TBA)**

Acrylate copolymer 1 (4 g) and cross-linker 2 (1 g), were combined at room temperature and acetone was used to reduce the viscosity of the mixture. This mixture was used to prepare specimens for torsional braid analyses. The polymer-braid composite specimens were prepared by impregnation of multifilament glass fibre braid with mixture and dried at room temperature for 12 h.

The specimens were then mounted in a fully automated TBA apparatus which were being maintained at predetermined constant temperature. The TBA isothermal spectra were then obtained at temperatures 440, 450, 460, 470 and 485 K.

The remainder of mixture was divided into two parts i.e., mixtures A and B. Dibutyltin dilaurate, of 1% and 2% were, respectively, added to the mixtures A and B. The specimens were prepared by impregnating multifilament glass fibre braids with reactive mixture A and was mounted in the TBA apparatus and curing data were recorded as above. The same procedure was adopted to cure the mixture B.

**Thermogravimetric Analysis**

The samples were prepared by making an emulsion of 4 g acrylate copolymer 1 with 1 g cross-linker 2. Acetic acid was used as neutralization agent and ethyl glycol mono-n-butyl ether and deionized water were utilized as the emulsion solvents. The mixture was removed from emulsion by electrodeposition and vacuum dried. A series of samples were taken and
each sample was heated with temperature programmed heating rate using Dupont 1090 TGA apparatus. Samples were heated from 30 to 450 °C with heating rates of 5, 10, 15, and 20 °C/min in N\textsubscript{2} atmosphere. The specimen weight loss was recorded as a function of temperature. From the resultant thermal curves, the temperatures for constant decomposition level were determined. The software supplied with apparatus provided the activation energy and pre-exponential factor for the whole reaction system.

RESULTS AND DISCUSSION

Scheme of Cure
Blocked TDI was employed to provide cross-linking sites. Usually, the temperature below 120 °C is required to preserve the capped isocyanate group to avoid gelation [27]. When blocked TDI is heated at elevated temperature, isocyanate and blocking agents are regenerated. The regenerated isocyanate can react with the terminal hydroxyl groups (−C\textsubscript{2}H\textsubscript{4}OH) pendant on the copolymer backbone, with the formation of urethane linkage between the interpolymer (reaction schemes I–III).

Isothermal Curing of Acrylate Copolymer/Diisocyanate by TBA
The details of TBA technique and data reduction have been given elsewhere [28, 29]. Isothermal TBA experiments were carried out at 440, 450, 460, 470, and 485 K. Mechanical parameters were, relative rigidity (1/P\textsuperscript{2}, where P is period in seconds of damp waves) and logarithmic decrement (−ln A\textsubscript{i}/A\textsubscript{1}, where A\textsubscript{i} is the peak amplitude of i th oscillation). Relative rigidity and logarithm decrement are plotted against the cure time at different temperatures in Figures 1–3.

The curves are smooth at the beginning and at the end of reaction. The gelation times, t\textsubscript{gel}, were obtained from the relative rigidity versus cure time curves, by extrapolating the smooth portions of the curves and finding the point of intersection. The gelation times for each of isothermal experiments are tabulated in Table 1, which show that the time of occurrence of gelation decreases with increasing

![Figure 1. Plot of cure time vs. relative rigidity and logarithmic decrement for uncatalyzed system.](image)

![Figure 2. Plot of cure time vs. relative rigidity and logarithmic decrement for system catalyzed by 1% organism catalyst.](image)
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Resin 1

\[
\begin{align*}
\text{Scheme I} \\
\text{Cross-linker 2}
\end{align*}
\]

Where \( R \) is:

\[
-\text{N-C-O-CH}_2-\text{CH-}(\text{CH}_2)_3-\text{CH}_3
\]

Scheme II
process, it is possible to correlate the logarithm of gelation time $t_{gel}$ and the reciprocal of absolute temperature by using Arrhenius relationship [30]:

$$\ln t_{gel} = \frac{E_a}{RT} + A$$

where, $E_a$ is the activation energy, $R$ is the molar gas constant, $T$ is the absolute temperature and $A$ is the kinetic Arrhenius factor. The plot of logarithm of gelation time $t_{gel}$ vs. $1/T (K^{-1})$ is displayed in Figure 4. The slope of straight lines is directly related to activation energy. The graphs are nearly linear, yielding activation energies 67.0, 56.1 and 50.1 kJ/mol for uncatalyzed, catalyzed by 1% and 2%
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Figure 3. Plot of cure time vs. relative rigidity and logarithmic decrement for system catalyzed by 2% organism catalyst.

dibutyltin dilaurate, respectively.

Table 1 shows that activation energy of reactive system decreases as the amount of organotin catalyst increases and the reactive system becomes more efficient. A possible explanation is that the complex of type:

\[
\begin{array}{c}
\text{H} \\
\text{R-O-Sn}
\end{array}
\]

is formed, which is more reactive towards isocyanate molecule [31].

Thermogravimetry

TG Curve Characteristics

The thermal properties of mixture of acrylate copolymer and diisocyanate (PU networks) were investigated by TGA. The TGA curve of thermal deblocking of diisocyanate and degradation of PU networks is shown in Figure 5, with the heating rate of 15 °C/min in N₂ atmosphere.

The temperature at which weight loss occurs indicates the beginning of deblocking reaction of blocked isocyanate [32]. From Figure 5 it can be seen that the TG curve reveals no significant weight loss below 180 °C and above 180 °C the weight loss occurs in two stages. In the first stage a low level of evolution occurs at about 180–240 °C. The deblocking of blocked isocyanate group begins at about
180 °C and is complete at 240 °C, with the 5% weight loss. The weight loss detected in this region is due to evolution of 2-EH and TMP from the reaction mixture and beginning of cross-linking reaction. This reaction is complete at about 240 °C and further increase in temperature causes degradation of PU networks. This is indicated by the sharp decrease in the weight loss in the second stage, which starts at 240 °C and continues to 450 °C. The second stage corresponds to degradation of PU networks.

Determination of Kinetics Parameters

The TG results of weight loss, at various heating rates in N₂ atmosphere, are plotted against the temperature in Figures 5 and 6.

Supposing that thermal degradation of polymers follows the model of random initiation and degradation, then the rate of degradation dC/dt can be:

\[ \frac{dC}{dt} = 2k(C^{1/2} - C) \]  

where C and k are the percent conversion and reaction rate constant, respectively. For the dynamic degradation, dC/dt may be written as:

\[ \frac{dC}{dT} = \frac{dC}{dt} \times \frac{dT}{dt} \]

\[ \log[\log(1 - C^{1/2})] = \log(\frac{AE}{2.3R\beta}) - 2.315 - 0.457E/RT \]

where B, E, R and A represent heating rate (dT/dt), activation energy, molar gas constant and pre-exponential factor, respectively. According to TGA curves at different heating rates, the heating rates are plotted against reciprocal of absolute temperature for indicated percent weight loss and results are shown in Figure 7.
Table 2. Properties of acrylate copolymer/diisocyanate coating film.

<table>
<thead>
<tr>
<th>Adhesion test</th>
<th>Impact resistance</th>
<th>Hardness</th>
<th>Water resistance test (boiling water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Grade</td>
<td>50 kg cm</td>
<td>3–4 H</td>
<td>No effect for 30 min</td>
</tr>
</tbody>
</table>

The plot of heating rates against the reciprocal of absolute temperatures give parallel straight lines i.e., Ozawa [34] plot. According to Ozawa plot the overall activation energy and pre-exponential factor, for the thermal degradation of PU networks, are 76.7 kJ/mol and 1.48 x 10^6 min^-1, respectively.

The properties of acrylate copolymer/diisocyanate coating film are tabulated in Table 2.

CONCLUSION

The apparent activation energy for the cure of a two component system, acrylate copolymer resin with blocked 2,4-toluene diisocyanate cross-linker, for uncatalyzed reaction is found to be greater than that of catalyzed reaction. The mixture is cured, with and without catalyst, at various temperatures.

Furthermore, the activation energy of the system is found to decrease with increasing concentration of catalyst (dibutyltin dilaurate). The temperature 170 °C is the good curing temperature with the cure time of 20–30 min. The activation energy of degradation of PU networks formed by the cross-linking reaction is reasonably higher, so the coating material may be durable. The properties of coating film, especially, the hardness (abrasion resistance) are improved.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation of China and Special Research Foundation of Doctoral Education of Chinese Universities for their grants in support of this work.

REFERENCES


