Synthesis and Properties of $\gamma$(Co- 60) Cured Acrylated Urethane Coating

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Received 5 May 1999; accepted 25 December 1999

ABSTRACT

In this paper, synthesis method of acrylated urethane based on polyethylene glycol and toluene di-isocyanate as a mixture of two isomers (2,4 and 2,6) has been investigated by application of IR spectra and GPC technique. In this method, reaction schemes were controlled by surveying the $-\text{NCO}-$ and $-\text{OH}$ absorption peak elimination and $-\text{NH}-$ absorption peak formation in IR spectra during the reaction. The mixture of the two isomers leads acrylated urethane resins to contain three oligomers (II, III and IV) in the final product. The study of physical and mechanical properties of $\gamma$-cured resin showed that hardness and impact resistance vary with increase in dose; meanwhile these quantities indicate a little variation after 60 kGy. This could be due to increasing of cross-link density. Also, addition of reactive monomers to the resin showed that increase in double bonds density in the resin system at a given dose, caused an increase in hardness and a decrease in impact resistance. By addition of a rutile type titanium dioxide as pigment, the hardness of film increases, but the variation of hardness-dose curve in both unpigmented and pigmented film is the same.

Key Words: acrylated urethane, gamma-cured resin, hardness, reactive diluent, pigmented coating

INTRODUCTION

Through the years, radiation sources have become an accepted means of curing organic coatings [1-5]. This curing method has several advantages with respect to conventional thermal cure [6-8]:

- Solvent elimination: This factor eliminates the environmental pollution and decreases the cost of product due to lack of solvent, these systems are therefore called “full percent” reactive coating systems.
- Low temperature curing: Temperature sensitive substrates such as thin vinyls and magnetic media can be coated and cured without suffering any heat distortion.
- Rapid cure: Radiation curable coatings are suitable for high-speed productions, as it is found in a web line. Therefore, using suitable radiation sources with
enough intensity can decrease the curing time.

– Energy saving: Required energy for radiation curing is smaller than the other conventional curing systems. Radiation curable coatings require approximately 10–50% of the energy needed to cure conventional coatings.

– Enhanced product durability: Cured coatings with these techniques have excellent solvent, abrasion and stain resistance.

– Small room space requirements: Curing units are safe and compact.

For the above reasons, the use of ionizing radiation for curing has shown rapid growth [1, 6, 8]. Principally, radiation curing is used for optical fibers coating, wood and plastic coating, wire coating such as signal wire and magnetic wire, rubber printing plate and magnetic media [7, 9].

Due to the high response shown by acrylates with radiation systems [10], acrylated resins are used for increasing the curing rate. Activities of functional groups with radiation follow the order [10, 11]:

\[
\text{acrylate} > \text{methacrylate} > \text{vinyl} > \text{allyl}
\]

Reactive monomers (diluents) are mainly used for viscosity reduction of resins. There are several one-, two- and multi-functional reactive diluents. The functional groups accountability of reactive monomers demonstrates the above sequence with electromagnetic sources [10].

Radiation curing coatings can be carried out by wide range of electromagnetic energies such as α, β, γ, X-rays, EB, UV and IR [10,12,13].

γ-Ray has high energy due to its short wavelength (10^-4–10^-2 nm), but its equipment is more expensive than UV system. In spite of that, the use of gamma ray is important because of the following reasons:

– Cured film does not need any photoinitiator and photosensitizer.

– Energy saving is smaller than the UV.

– Pigmented coatings or paints can easily cure with γ-ray.

– Weathering properties of γ-ray film is better than UV-cured film.

– Cured film properties such as solvent and abrasion resistance are better than UV-cured film.

γ-Ray has high penetration depth with respect to UV and EB.

Oraby and Walsh investigated the effect of molecular weight of acrylated polyester urethane oligomer, reactive monomers and chain transfer agent on mechanical properties of EB-cured film [14, 15]. They showed that by increasing the molecular weight of the oligomer from 1000 to 4000 resulted in a decrease in the stress-at-break and young modulus, while elongation increased. Also, it was found that the addition of a 2% to 3% of chain transfer agent caused an increase in both extensibility and breaking strength. Zue-Teh and Liang-Chang studied the effect of the structure and molecular weight of oligomers on the curing rate and curing dose of different acrylated polyether urethane, which were cured by EB [16].

During initial period of irradiation, curing proceeds very rapidly and in a certain value of dose gel percent tends to level off. Zue-Teh and Liang-Chang defined this corresponding dose as the critical curing dose (CCD) and determined it by gel percent content of different oligomers. Using gel percent content, IR spectrophotometer and ESR showed curing speed and final gel percent decrease as the molecular weight increases, whereas, the CCD increases with the increase of molecular weight. On the other hand, although the degree of cure of irradiated material tends to a constant level, there still remains a large amount of double bonds in the gel phase. Czajlik et al. studied surface property of various EB-cured coatings [2]. It was found that the pendulum hardness of the cured films depends on (i) double bond concentration in the oligomer, (ii) type of monomer and (iii) curing dose. In the mentioned works, EB is used as a high energy source for curing the resins. Recently, some researchers have used γ-ray as a high energy source for bulk polymerization of vinyl monomers such as acrylics [17, 18].

In this paper, synthesis method of acrylated urethane resin based on polyethylene glycol (PEG) and toluene di-isocyanate (TDI) as a mixture of two isomers (2, 4 and 2, 6 isomers) was investigated. Then synthesized resin was cured as a coating substance by means of γ-ray and the role of curing dose and
reactive monomer on physical and mechanical properties of the cured resin were studied. It was found that major part of the physical and mechanical properties was obtained after the CCD.

EXPERIMENTAL

Materials
PEG (M_w=400 g/mol) and 2-hydroxyethyl methacrylate (2-HEMA) from Merck and 2,4 and 2,6 mixture of TDI were used for synthesis of the acrylated urethane. In this reaction, tin octoate and anhydrous THF were used as catalyst and solvent, respectively. Also, ethylene glycol dimethacrylate (EGDMA) and rutile type TiO_2 were applied as viscosity reducer and pigment, respectively.

Purification
TDI and 2-HEMA were distilled under vacuum. PEG was vacuum dried at 80 °C for 10 h to eliminate the moisture. THF was distilled before use.

Resin Synthesis
There are many reports about the synthesis method in the literature [19–21]. This reaction was carried out in two steps under a nitrogen atmosphere.

First Step
An amount of 70 mL anhydrous THF, 0.2 g catalyst and 52.2 g (0.3 mol) TDI were poured in a half-liter four necked reaction vessel equipped with a magnetic stirrer, thermometer, dropping funnel, inlet and outlet tubes for dry nitrogen. Then, the reaction vessel was placed in the water bath for temperature control. In this step, reaction temperature was fixed at 25 °C. Then, 39 g (0.3 mol) 2-HEMA was gradually added to the reaction vessel containing the end product of the first step through the dropping funnel. Reaction temperature was 45 °C, and the reaction proceeded until complete elimination of –NCO absorption peak and conversion of –OH absorption peak to –NH– at IR spectrum. Reaction time for this step was 120 min. At the end of the reaction, THF was removed by vacuum distillation. Finally, a yellow viscous liquid was obtained which could be dissolved in some solvents such as THF.

Second Step
An amount of 60 g (0.15 mol) PEG was gradually added to the reaction vessel containing the end product of the first step through the dropping funnel. Reaction temperature was 45 °C, and the reaction proceeded until complete elimination of –NCO absorption peak and conversion of –OH absorption peak to –NH– at IR spectrum. Reaction time for this step was 120 min. At the end of the reaction, THF was removed by vacuum distillation. Finally, a yellow viscous liquid was obtained which could be dissolved in some solvents such as THF.

IR Study for Characterization of Products
Absorption peak variation of hydroxyl (–OH), amide (–NH–) and isocyanate (–NCO–) groups during the reaction, which appear at 3430, 3330 and 2265 cm⁻¹, respectively, were recorded by the employment of Bruker IFS 45 model FT-IR spectrophotometer. The samples were coated as viscous thin film on KBr.

Determination of Molecular Weight of Products
Molecular weight and molecular weight distribution of products and PEG in THF as a solvent were determined using a Waters type 150-C GPC system. The calibration curve was obtained by using monodisperse polystyrene (standard M_n=800, 1000 and 2000).

Coating Preparation
Synthesized resins were coated on to glass and metal substrates with 60 and 30 μ thickness, respectively by using a film applicator. They were, then, irradiated by a Co-60 γ source (Gamma cell-220 manufactured by Atomic Energy of Canada Ltd.) at doses up to 100 kGy. Dose rate was 1.64 Gy/s. A thin Mylar film was used on the coating to eliminate oxygen effect during irradiation.

Coating Properties
The gels of irradiated samples which had been polymerized, were extracted by THF at 60 °C for 60 h. Then, samples were dried under vacuum at 60 °C and were weighed to give the gel percent. The gel percent was calculated through the following relation:

\[
\text{gel(\%)} = \frac{\text{weight of polymer after extraction}}{\text{weight of original cured polymer}} \times 100
\]
Hardness and Impact Resistance
A Konig type model Ericksen hardness tester and DIN-304 model Ericksen impact tester were used for determination of hardness and impact resistance of coatings, respectively. The hardness and impact tests were carried out on to glass and metal substrates, respectively.

RESULTS AND DISCUSSION

Acrylated Urethane Reactions
The experiments have shown that in toluene diisocyanate, group in the ortho position is less active than para position due to spatial hindrance of methyl group in the ortho position. Reaction of 1 mole 2-HEMA and 1 mole 2,4TDI mainly occurs on para position at 25 °C [22].

There are two ortho –NCO functional groups in 2,6-isomer. 2,4 TDI has one –NCO functional group in ortho and the other one in the para position. Because of using the mixture of both isomers, the reactions are expected the follow according to Scheme I (these results are based on GPC curve and IR spectra which will be explained later).

IR Spectra of TDI, 2-HEMA and intermediate product of first step (I) have been compared in Figure 1. In this figure, –OH absorption peak of 2-HEMA at 3450 cm⁻¹ completely has been converted to –NH– absorption peak at 3330 cm⁻¹.

The hydroxyl functional group of 2-HEMA has completely reacted with –NCO functional group of TDI. But, in this step –NCO absorption peak at 2265 cm⁻¹ still exits in the spectrum. This is due to
remaining of —NCO functional group in the final mixture of first step. In the second step (Scheme II),

Second step:

\[
\begin{align*}
\text{(PEG)} & \quad \text{(I)} \\
\text{HO—[—CH}_2\text{—CH}_2\text{—O—}_n\text{—H} + CH_2=COO(CH}_2\text{)}_2—\text{OOCHN—Ph—NCO} & \\
\text{2,6-TDI)} & \\
\text{CH}_3 & \\
\text{CH}_2=COO(CH}_2\text{)}_2—\text{OOCHN—Ph—NHO}—\text{—(CH}_2\text{)}_2—\text{O—}_n—\text{OOCHN—Ph—} & \\
\text{—NHO}OCO(CH}_2\text{)}_2—\text{OOC—C=CH}_2 & \quad \text{(II)}
\end{align*}
\]

and

\[
\begin{align*}
\text{CH}_2=\text{C(CH}_3\text{)—COO(CH}_2\text{)}_2—\text{OOCHN—Ph—NHO} —\text{—CH}_2\text{—CH}_2—\text{O—}_n—\text{OCN—H—Ph—} & \\
\text{—CO—[—CH}_2\text{—CH}_2—\text{O—}_n—\text{OCN—H—Ph—NHO} —\text{—(CH}_3\text{)C—CH}_2 & \quad \text{(IV)}
\end{align*}
\]

m: degree of polymerization

\text{Scheme II}
Synthesis and Properties of γ-Cured Acrylated Urethane Coating

Table 1. GPC molecular weight results for final product (peaks 1, 2 and 3 in Figure 3) and PEG as a reference.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Calculated molecular weight (g/mol)</th>
<th>Experimental $M_w$ (g/mol)</th>
<th>Experimental $M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>1450</td>
<td>1.104</td>
</tr>
<tr>
<td>2</td>
<td>1008</td>
<td>810</td>
<td>1.04</td>
</tr>
<tr>
<td>3</td>
<td>434</td>
<td>410</td>
<td>1.016</td>
</tr>
<tr>
<td>PEG</td>
<td>400</td>
<td>430</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Physical and Mechanical Properties of γ-Cured Film

The dependence of gel percent of cured film to irradiated dose is demonstrated in Figure 4. It is clear that gel percent increases rapidly with dose during the initial period of irradiation. Almost after 6 kGy, the content of gel percent is approximately constant. This dose can be defined as CCD, based on Zue-Teh definition [16].

There is no decrease in gel percent of cured film when irradiation continues up to 100 kGy. This indicates the good resistance of obtained resin to ionizing radiation, which is due to the presence of aromatic groups in the resin molecule [16].

By increasing the curing dose, the cross-link density of coated film increases. As reflected in hardness increase (Figure 5) and impact resistance decrease (Figure 6) until 60 kGy irradiation dose. After that dose, properties would indicate only little changes.

Figure 2. IR Spectra for intermediate product (3), PEG (4) and final product (5).

Figure 3. GPC curve for final product.

Figure 4. Gel percent vs. radiation dose for pure resin.
Reactive diluent stays in the cured system and affect the film properties, as it is seen in Figure 7. By increasing EGDMA percent (up to 30%), the double bond density increases in resin base. So, after irradiation of coating at 40 kGy dose, the density of cross-link in cured coating increases and cause an increase in hardness and a decrease in impact resistance. It must be noticed that concentration of diluent should not exceed its optimum level, where it causes the cured film to become brittle.

Effect of Pigment
Effect of rutile type titanium dioxide (TiO$_2$) as white pigment on γ-curing of coating has been shown in Figure 9. Rutile type TiO$_2$ is relatively inactive photochemically and has a stabilizing effect on photodegradation [23]. So, by addition of TiO$_2$, the slope of hardness-dose curve does not vary with respect to unpigmented one, but its hardness increases in comparison to unpigmented sample.
CONCLUSION

Preparation of acrylated urethane was studied by IR and GPC techniques. In this reaction –NCO absorption peak at 2265 cm\(^{-1}\) and –OH absorption peak at 3400 cm\(^{-1}\), are completely converted to –NH– absorption peak at 3330 cm\(^{-1}\). The GPC results showed that three types of acrylic terminated oligomer (II, III, IV) exist when we use TDI as a mixture of 2,4 and 2,6 isomers.

Also, increasing of irradiation dosage makes hardness to increase and impact resistance to decrease due to increasing of cross-link density. The major part of these properties occurs after CCD. Meanwhile, after 60 kGy irradiation dose the degree of hardness and impact properties indicate little changes. Addition of EGDMA as a reactive diluent to the resin increases hardness and decreases impact resistance with respect to pure resin at specified dosage. In addition, rutile type TiO\(_2\) as pigment does not have any degradable effect on \(\gamma\)-cured coating and pigmented resin has high hardness with respect to unpigmented one.

ACKNOWLEDGEMENTS

This work was supported by the Atomic Energy Organization of Iran. The authors would like to thank Dr. M. Sohrabpour, Director and N. Sheikh, Supervisor of Polymer Division of Gamma Irradiation Center of Iran, for their interest and attention to this work.

REFERENCES