**MICROWAVE PROCESSING OF WATERBORNE POLYURETHANE COATINGS ON GLASS**

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**ABSTRACT**
Microwave processing of polyurethane (PU) coatings on glass substrates was studied. A kinetic study was done on the selected PU species using IR to monitor the intensity of NCO in the system. Caustic resistance and scratch resistance of the microwave cured PU coatings were evaluated. Results show that microwave processing could substantially accelerate the reaction kinetics and improve caustic and scratch resistance of the PU coatings. The effectiveness of microwave processing depends on the material system. A 2-component waterborne PU system, Bayer RR6895, showed significant susceptibility to microwave processing. The reaction kinetics of this system was accelerated by an order of magnitude in the microwave process. At 443K, the time required to complete the PU reaction was reduced from 56 min to 5 min for microwave versus continual heating. The microwave acceleration in this case include drying, unlocking of the chemically-blocked isocyanates (NCO), polymerization reaction and diffusion processes (7×), and the diffusion of the reactants in the substantially cross-linked high-viscosity state to finally complete the reaction (23×). The caustic resistance of the microwave samples increased from 11 h to 508 h in the 2% NaOH solution at 358K. The scratch resistance of the microwave samples showed up to 67% higher scratch resistance than the reference. This indicates that the hardness, density, moisture stability, chemical resistance, and adhesion of the PU coating to the glass substrate all have been effectively improved by microwave processing. We speculate that the enhanced properties of the microwave processed coatings is due to more complete elimination of water reaction products, especially at the glass/PU interface.

**KEYWORDS**: Microwave, processing, polyurethane, coating, film, caustic resistance, kinetics

**INTRODUCTION**
Polyurethanes are a number of important organic materials with ever increasing applications due to their excellent adhesion to most materials, excellent scratch resistance, excellent chemical stability, and optical clarity. Because of environmental concerns, the waterborne polyurethanes are more and more popular compared to the solvent-borne polyurethanes. A PU coating can effectively improve mechanical performance and chemical stability of the coated substrate and help protect the coated articles; hence, coatings are a common PU application.

There are many PU systems. Some are single component, while others are two- or multi-component. Most PU systems cure during thermal treatment. The isocyanate group, NCO, is the most important functional group in PU materials. NCO groups can readily react with polyols. The isocyanate groups can be chemically blocked by compounds such as caprolactam, butanone oxime, phenol, or dimethylpyrazole. At room temperature, the blocked polyisocyanates do not react with polyols at any appreciable rate. At elevated temperatures, the blocked polyisocyanate liberates the blocking agent, which may leave the film, and the polyisocyanate reacts with the polyol.

Microwave activation of polymerization reactions at 2.45 GHz first came into use in the early 1970's. Substantial investigations have been done since then. Some significant improvement in properties of the microwave cured polyurethanes are reported. The objective of this study is to evaluate the effects of microwave processing on the reaction kinetics, chemical stability, and mechanical property of polyurethane coatings on commercial glass substrates.
EXPERIMENTAL

Materials and sample preparation

Bayer RR6895: a 2-component PU with chemically blocked NCO, recommended conventional curing condition: 443K/30 min in air after drying. Component 1 contains Bayhydur VP LS 2240 (crosslinking agent, 35% solid, water-dispersed blocked aliphatic polyisocyanate resin based on dicyclohexylmethane diisocyanate, H12MDI, dissolved in water/MPA/xylene, 56:4.5:4.5) and the Bayhydrol VP LS 2239 (water-thinnable hydroxyl-bearing polyurethane dispersion). Component 2 includes dipropylene glycol and two silanes. The NCO/OH ratio in the dispersion was 1.04:1. The solid content on application was about 34%. The polyurethane reaction in Component 1 of this system is as the following:

\[
\begin{align*}
\text{R} & \quad \text{N} & \quad \text{C} & \quad \text{BL} & \quad + & \quad \text{R'} & \quad \text{OH} & \quad \xrightarrow{\Delta} & \quad \text{R} & \quad \text{N} & \quad \text{C} & \quad \text{OR'} & \quad + & \quad \text{H-BL}
\end{align*}
\]

“2240” “2239” polyurethane blocking agent

Component 2 includes dipropylene glycol and 2 silanes (0.2% each) as adhesion promoters: Silquest® A-189 Silane (Gamma-mercaptopropyltrimethoxysilane, CAS: 56938-96-6, Crompton, Middlebury, CT 06749, USA)

\[
\begin{align*}
\text{OCH}_3 \\
\text{HSCH}_2\text{CH}_2\text{CH}_2\text{-Si-OCH}_3, \\
\text{OCH}_3
\end{align*}
\]

Dynasylan® AMEO (3-Aminopropyltriethoxysilane, CAS: 919-30-2, Degussa Corp., Parsipany, NJ): 

\[
\begin{align*}
\text{H}_2\text{N-(CH}_2)_3\text{-Si(OCH}_3\text{H}_3)_3
\end{align*}
\]

The two components were mixed together at room temperature before application. PU coatings were made by spin coating of the PU onto a 12.7 mm × 25.4 mm × 1 mm soda-lime silicate glass slides. The samples were then cured by microwave processing for 1-7 min. in a thermally insulated package (made of FiberFrax Duraboard 3000) that was microwave preheated to about 443K.

The microwave source used in this study was a 1250 W, 2.45 GHz microwave oven (Panasonic, Model NN-S935BF). In order to assist the samples to heat up uniformly in the microwave cavity, a thermally insulated shroud was made with SiC as the microwave susceptor. A Teflon sample holder with slots, located in the center of the insulated casket, was used to hold the PU-coated silica slides. In order to get uniform heating, several thin rods containing SiC as microwave susceptors were vertically arranged in the insulation. Temperature was measured with a Raytek MT6 Mini Temp Infrared Thermometer (Raytek Corporation, Santa Cruz, CA). Duplicate samples were cured thermally in a conventional oven set at 443K. The average thickness of the cured PU coating was about 10 μm.

Kinetic study

FT-IR spectra were performed on the sample during the drying/curing process to trace the change in the characteristic band at 2270 cm\(^{-1}\) (NCO) to monitor the reaction between NCO and ROH- groups to form polyurethane. The integrated area of the NCO band on the FT-IR curve is used to determine the extent of reaction.

Caustic resistance study

The caustic resistance of the PU coatings was evaluated under accelerated conditions by soaking the cured samples in a 2% NaOH solution set at 358±2K in an oil bath. The samples were
checked periodically until the coating failed.

**Scratch resistance study**

The cured samples were mechanically evaluated on a simple comparative scratch tester as shown in Fig. 1. The sample to be tested was set horizontally under a tungsten tip. The sample was moved in one direction under the pressure of the weight at the tungsten tip. The weight was adjusted until the sample was scratched by the tip; this weight was recorded as the scratch resistance of the sample. The higher the weight, the better the scratch resistance.

![Fig. 1. Schematic showing the setup for scratch resistance testing of the coating samples: 1. Balance weight, 2. Support, 3. Weight, 4. Level, 5. Tungsten tip, 6. Sample holder, and 7. Sample](image)

**RESULTS AND DISCUSSION**

**Reaction kinetics**

Fig. 2 shows the FT-IR intensity of the band corresponding to NCO. In the conventional processing, the curing process can be divided into 4 stages: unlocking of NCO (1), reaction (2), intermediate (3), and final (4).

![Fig. 2. FT-IR intensity of NCO as a function of time showing the reaction kinetics of PU RR6895 cured by microwave processing and conventional processing, respectively, at 443K](image)

Table 1 compares the slopes of IR intensity of the NCO band in microwave and conventional curing. It is seen that in the NCO unlocking and the reaction stages, the rate of microwave processing was 7 times that of the conventional. In the final stage, in which the polymerization was almost complete, the rate in the microwave process was about 23 time that of the conventional. This
implies that microwave processing substantially enhanced the cross-linking reaction and/or out-diffusion of the reaction products in the high viscosity state. The total time for completion of the reaction in the microwave processing was only 1/7 of the conventional processing.

Table 1. Comparison of the slopes of the kinetics curves in Fig. 1 in different stages

<table>
<thead>
<tr>
<th>Stage</th>
<th>Microwave</th>
<th>Conventional</th>
<th>Ratio (MW/Conv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. unlocking</td>
<td>1919</td>
<td>270</td>
<td>7.1</td>
</tr>
<tr>
<td>2. reaction</td>
<td>1110</td>
<td>152</td>
<td>7.3</td>
</tr>
<tr>
<td>3. intermediate</td>
<td>No show</td>
<td>64.61</td>
<td>--</td>
</tr>
<tr>
<td>4. final</td>
<td>216</td>
<td>9.23</td>
<td>23.4</td>
</tr>
<tr>
<td>Total time</td>
<td>8 min</td>
<td>56 min</td>
<td>1/7</td>
</tr>
</tbody>
</table>

Caustic resistance
The conventional samples cured at 443K for 30 min survived the caustic test for 11 h. The microwave samples cured for 7 min at the same temperature survived 508 h, 45 times longer than the conventional sample. When the samples were conventionally cured at 463-483K and turned slightly yellowish, the caustic resistance was up to 308 h. Even compared to this extreme heating, the samples cured by microwave processing were still 67% more resistant to caustic attack. Since caustic resistance of the PU coating depends on density, chemical stability, and interfacial adhesion to the substrate, microwave processing must have enhanced the sample properties in all these aspects.

Scratch resistance
The conventional samples cured at 443K for 30 min resisted 50-70g loads without exhibiting a visible scratch. The microwave samples cured for 5 min showed a comparable scratch resistance. When cured for 7-8 min, the microwave samples were almost 2x more scratch resistant (100g).

CONCLUSIONS
Microwave processing of polyurethane coatings on glass was studied with a commercial waterborne polyurethane. Caustic resistance and scratch resistance of the microwave processed samples were tested and compared with the conventionally cured samples. The reaction kinetics of the PU in this study was accelerated by 7-23 times depending on the specific stage of the process. The final stage showed the most significant microwave enhancement. In addition to the accelerated kinetics, the caustic resistance and the scratch resistance of the microwave processed PU samples were significantly improved. The results imply that to this specific PU system, microwave processing effectively improved the properties related to caustic and scratch resistance such as density, hardness, moisture stability, chemical stability, and adhesion of the PU coating to the substrate.

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REFERENCES