

Effects of Calcium Ion on Polyester-Type Polyurethane Emulsion and Properties of Polyurethane Film

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Received 18 October 2002; accepted 17 June 2003

ABSTRACT: Polyurethane (PU) emulsions were prepared from polytetramethylene adipate diol, toluene diisocyanate, dimethanol propionic acid, and so forth. The effects of calcium ion on the stability of PU emulsion as well as on the water-resistance property, tensile strength, and tensile yield of PU film were discussed. The results show that calcium ion can quickly damage the stability of PU emulsion. Mean-

while, calcium ion can distinctly counteract the unfavorable effects water has on the tensile properties of PU film. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1285–1288, 2004

Key words: calcium ion; polyurethane emulsion; films; water resistance; tensile property

INTRODUCTION

Polyurethane (PU) emulsions dispersed in water have been widely used in many fields^{1–5} such as fabric coating, leather finishing, adhesives, and coatings, because of its good stability and excellent property after filming. Polyester-type PUs have better intensity, rigidity, heat resistance, and oxidization resistance than those of the polyether type. To obtain high quality backing material of calcium carbonate type wall-protective agent and bright leather coating, we investigated the synthesis techniques of the PU emulsion system of toluene diisocyanate (TDI)–polytetramethylene adipate diol (PTAd)–dimethylol propionic acid (DMPA) and the effects of calcium on the wall environment in the PU emulsion and the film behaviors. We also discovered a new way to improve the water resistance of waterborne PU emulsion products.

EXPERIMENTAL

Materials

The following products were used in the experiments: toluene diisocyanate [TDI, analytical reagent (A.R.) grade; Wanhua Jiangbei Chemicals, China]; polytetramethylene adipate diol (PTAd, $M_n = 2000$, commercial product; Xiantao PU Manufactory, China); acetone (A.R. grade; Hubei University Factory, China); triethylamine (TEA, A.R. grade; Chinese Pharmaceutical Shanghai Reagent Station); anhydrous calcium chloride

(CaCl₂, A.R. grade; Zhengjiang Chemicals, China); and deionized water (H₂O; laboratory-made).

PU emulsion synthesis

PTAd was charged into a 250-mL three-neck flask and heated to melt, followed by adding TDI and heating to 80°C. The mixture was stirred for 1.5 h, then cooled, after which DMPA and small amounts of acetone were added. The reaction was carried out at 65°C for 2.5 h, then cooled and neutralized with TEA for 15 min, and finally emulsified with deionized water. A light orange and semitransparent PU emulsion was obtained.

Preparation of PU films

PU emulsion films were poured into a glass mold, air-dried at room temperature, then dried in an oven for 24 h at 60°C.

Water-resistance behavior determination of pu films

PU films were divided into 10 pieces with the same dimensions (diameter 80 mm, thickness 0.8 mm) and the same weight (W_0). Five pieces were dipped into water (film 1); the other five were dipped into calcium chloride solution for 1 day (not including the days for dipping into water) and then dipped into water (film 2). The films were removed from the water and surface water was quickly absorbed using blotter paper every 3 days, after which films were weighed (W). The average water absorption was calculated according to the following formula:

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TABLE I
Data of IR and %Ca

Sample	IR (cm ⁻¹)	%Ca
1	3338, 2956, 1732, 1599, 1537, 1462, 1368, 1224, 1171, 1065	0
2	3339, 2956, 1728, 1599, 1537, 1460, 1359, 1224, 1175, 1066	0.087
3	3338, 2956, 1723, 1599, 1537, 1462, 1366, —, 1184, 1067	0.960

$$\text{Water absorption} = \frac{W - W_0}{W_0}$$

Mechanical behavior measurement of PU films

PU films were clipped according to GB 528-824. Some were dipped into water (sample 1); others were dipped into calcium chloride solution for 1 day (not including the days for dipping into water) and then dipped into water (sample 2). Every 3 days five samples were removed from the water and dried. Tensile strength and elongation at break of the PU films were measured using an AG-A electronic puller at the extension rate of 500 mm/min at 25°C and an average was obtained.

Calcium ion content measurement

PU films were burned in a muffle at 650°C and then dissolved in nitric acid, followed by diluting to a certain concentration with distilled water. Calcium ion content was determined by ICP-AES (United States).

Infrared spectroscopy

IR studies were carried out on a Perkin-Elmer Spectrum One IR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

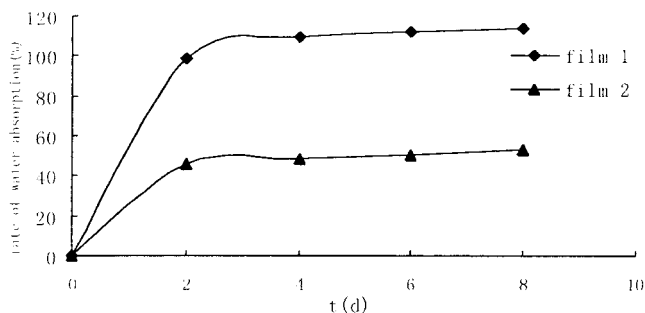


Figure 1 Effect of days in water on water-absorption rate.

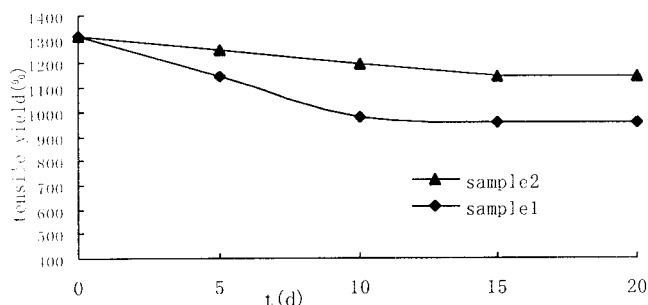


Figure 2 Effect of days in water on break elongation.

Differential thermal analysis

Differential thermal analysis was performed on a Perkin-Elmer DSC apparatus at a heating rate of 20°C/min in nitrogen atmosphere.

RESULTS AND DISCUSSION

IR data on PU films and calcium ion content

Table I shows the data of IR and calcium ion content.

With increasing calcium ion content in the sample, the absorption peak assigned to the C=O group decreased from 1732 to 1723 cm⁻¹ (by 1728 cm⁻¹) and the absorption peak assigned to -COO⁻ increased from 1171 to 1184 cm⁻¹ (by 1175 cm⁻¹), which indicates that the calcium ion combined with -COO⁻ in the material after PU films were treated with CaCl₂ solution.

Effect of calcium ion on PU emulsion stability

The general preparation of PU emulsion is to introduce the hydrophilic group to the molecular chain and emulsify with deionized water. In this study, stable PU emulsion was obtained by introducing -COO⁻NH₄⁺ as the hydrophilic group and emulsifying. After dropping small amounts of CaCl₂ solution into the emulsion, its stability was damaged and

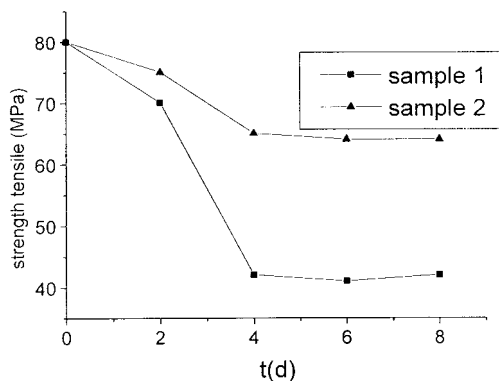


Figure 3 Effect of days in water on tensile strength.

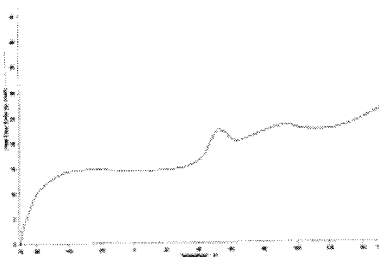


Figure 4 DSC thermogram of PU film.

formed an indiscernible micelle. The same phenomena were observed in investigations with soluble salt of zinc, copper, and barium. However, there was no obvious change in studies with the soluble salt of sodium and potassium. It was thought that Ca^{2+} substituted NH_4^+ to combine with COO^- and the obtained salt could not dissolve in the water. The micelle was repeatedly washed with distilled water and dried, and was designated Sample 3. We determined its calcium ion content at a value of 0.91%, which substantially agrees with the theoretical value of 0.96%.

Effect of calcium ion on the water resistance of PU films

From the appearance of PU films, the surface of Sample 1 turned white in 1 day and there was no obvious change on Sample 2, which was semitransparent. Figure 1 shows the relationship between water absorption and days dipping in water. It was found that water absorption of film 2 was obviously less than that of film 1, which indicates that the combination of Ca^{2+} and PU films could distinctly reduce water absorption and intensify its water resistance. As a rule, to obtain a stable PU emulsion we must import some hydrophilic group to the PU molecular chain so that it can self-emulsify; however, the hydrophilic group was not damaged after the emulsion was cast into films. When

PU films were dipped directly into water, the existence of hydrophilic group promoted water delivery in PU films; thus PU films had a large water absorption capacity and poor water resistance. PU films were dipped into CaCl_2 solution for 1 day and the exterior high-hydrophilic $\text{COO}^- \text{NH}_4^+$ transformed into low-hydrophilic $(\text{COO}^-)_2 \text{Ca}^{2+}$, which could prevent further delivery of water to a certain extent and thus decrease water absorption.

Effect of calcium ion on elongation at break and tensile strength

Figure 2 shows the relationship between elongation at break and days in water. It was found that the elongation at break of Sample 1 is not greater than that of Sample 2. Figure 3 shows the relationship between tensile strength and days in water. We also found that the tensile strength of Sample 1 is not greater than that of Sample 2.

It is thought that water changed the structure of PU films, causing the hydrophilic COO^- to turn out from the interior to the exterior. This action damaged the close frame of PU films and thus they became loose. As a result elongation at break decreased accordingly. For Sample 2, the superficial COO^- chelated Ca^{2+} . On one hand, it enhanced the intensity of PU films; on the other hand, it effectively prevented water molecular permeation deep into the films. PU films were thus only slightly affected by water, with little loss of mechanical properties.

Differential thermal analysis and the structure of PU films

Figures 4, 5, and 6, respectively, show the differential thermal analyses of PU films treated with different methods. The untreated films (Fig. 4) had a strong absorption peak at 56–57°C, although the peak disap-

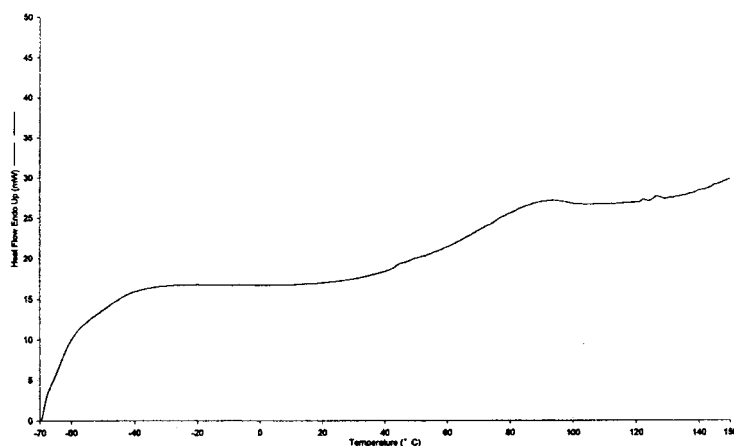


Figure 5 DSC thermogram of PU film (in water).

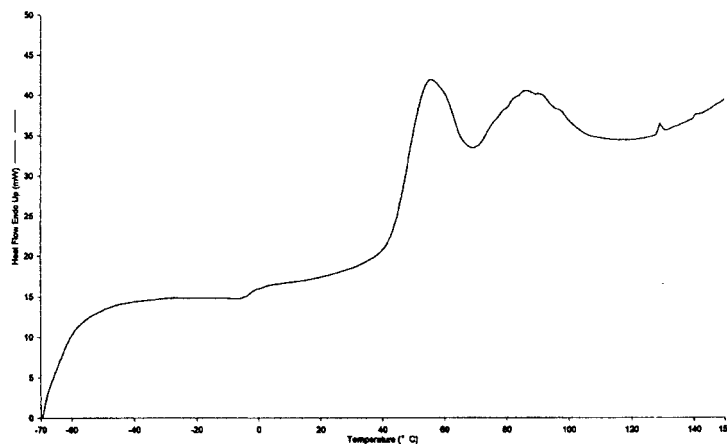


Figure 6 DSC thermogram of PU film (CaCl_2).

peared completely in the films dipped into water (Fig. 5) and still existed to a marked extent in the films dipped into CaCl_2 solution first and then water. These phenomena indicated that the process of dipping into water changed the structure of PU films and CaCl_2 solution could restrain this action.

CONCLUSIONS

It was determined that Ca^{2+} could quickly damage the stability of PU emulsion; the chelation of Ca^{2+} and

$-\text{COO}^-$ was obviously able to reduce the unfavorable effects water has on the films.

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