

Synthesis and Application of Water-Based Urethane Acrylate Crosslinking Agent Containing Unsaturated Group

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ABSTRACT: In this study, we synthesized 1,1,1-trimethylolpropane (TMP)-based diol which has a pendant anionic group and a reactive double bond in the pendant cyclic ring. Then, a water-based urethane acrylate crosslinking agent (CA) was prepared from isophrone diisocyanate (IPDI), 2-hydroxyethyl acrylate (2-HEA), and a low molecular weight diol bearing pendant carboxylic acid. The CA content was varied in order to investigate the influence of the added content on the mechanical and dynamic mechanical properties. The diol used in this study was TMP-*cis*-1,2,3,6-tetrahydrophthalic anhydride (TPA) which was synthesized from the esterification reaction of TMP with TPA. This diol was liquid at room temperature. As the CA increased, the initial modulus and elongation at break decreased. Also, increase of the rubbery plateau modulus was observed by dynamic mechanical analysis (DMA). This result was believed to result from an increase in the crosslinking density in the mixtures. Shift of the T_{gh} to a higher temperature was also observed by DMA. This is due to the increased hard segments and the phase separation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1216–1223, 2000

Key words: water-based urethane acrylate crosslinking agent; mechanical properties; unsaturated group

INTRODUCTION

A UV-cured system can take advantage of a short reaction time, high energy efficiency, low reaction temperature, low cost, and stiff crosslinked polymer preparation, etc. However, a UV-cured system has limited application because of the toxicity and combustion of the reactive diluents which compose a UV-cured system.^{1,2} Recently, a water-based coating using UV technology has been widely utilized in industry, because it can decrease air pollution and the risk of fire and improve occupational health and safety. Especially, odor, toxicity, a compromise between viscosity control and the effects of the reactive diluent on properties of the cured films, and greater ease of clean-

ing are reasons for the possible use of water as a diluent in a UV-curable system.^{3–8}

Generally, water-based urethane acrylate has been synthesized by the incorporation of hydrophilic groups into the molecular backbone without adding surfactants. Among hydrophilic groups, the ionic group acts as a physical crosslinker due to its forming an aggregation or cohesion by Coulombic force, which has been enhanced by the mechanical properties of the cured film.^{9,10} Many workers have introduced DMPA as potential ionic sites in order to prepare water-based urethane acrylate. However, DMPA needs a hydrophilic organic solvent with a high boiling point for the prepolymer of the poly(urethane acrylate) anionomer, and a DMPA-based urethane acrylate anionomer has the disadvantage of a lower double-bond concentration per one molecular unit.^{11,12}

Other workers have performed such experiments by adding a crosslinking agent (CA) or

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epoxy acrylate (EA) into water-based urethane acrylate to improve the mechanical property of the final cured film.⁸ But the formation of a stable CA droplet or epoxy droplet was prevented by the big difference in the interfacial tension between CA or EA and the water continuous phase. So, as the CA or EA content increased, the stability of the emulsion decreased due to the low hydrophilicity of CA or EA. Therefore, there is a need for reducing the interfacial tension in order to improve the stability.⁸

In this study, we carried out three objects: First, we synthesized 1,1,1-trimethylolpropane (TMP)-based diol which has a pendant anionic group and a reactive double bond in the pendant cyclic ring. Second, we prepared a water-borne urethane acrylate CA from isophrone diisocyanate (IPDI), 2-hydroxyethyl acrylate (2-HEA), and TMP-based diol as an ionic site. Finally, we studied the mechanical and thermal properties of the cured films after they were mixed with the water-based urethane acrylate CA and an urethane acrylate anionomer.

EXPERIMENTAL

Materials

cis-1,2,3,6-Tetrahydrophthalic anhydride (TPA; Aldrich Chemical Co., Milwaukee, WI, USA) was purified from acid by extraction with CHCl_3 and filtered. This material was recrystallized from CHCl_3 . TMP (Aldrich) was dried at 60°C for 5 h in a vacuum oven. IPDI (Aldrich), triethylamine (TEA; Junsei Chemical Co., Japan), dibutyltin dilaurate (DBTDL; Nine Chemica Co., South Korea), and 2-HEA (Aldrich) were used as received. Benzophenone (Janssen Chemica Co., Belgium) was used as a photoinitiator. *N*-Methylpyrrolidone (NMP, Junsei) was used as a viscosity reducer solvent in the course of the reaction. Tetrahydrofuran (THF) was dried over 4 Å molecular sieves for 24 h before use. The poly(urethane acrylate) anionomer (PUDA; Prof. Kyung Do Suh, Hanyang University, Seoul, South Korea) was used as received.

Synthesis of TMP-based Diol (TMP-TPA)

The synthesis of TMP-TPA was carried out in a four-necked glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. TMP was poured into the glass reactor after nitrogen gas was inlet for 10 min to

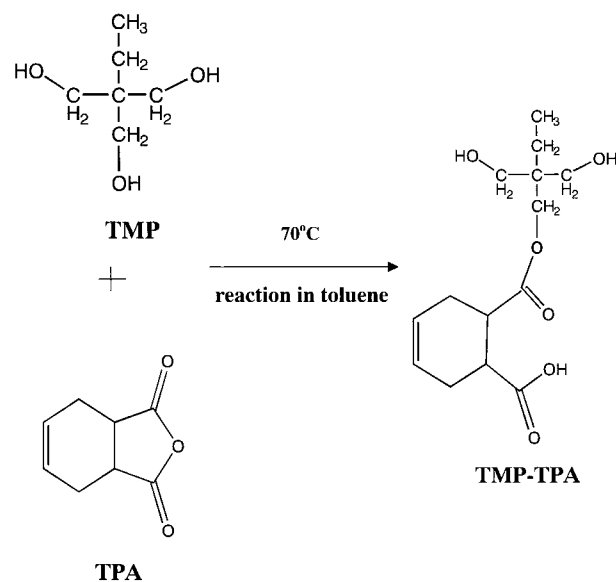


Figure 1 The molecular structures for the diol-bearing pendant carboxylic acid group and an unsaturated double bond.

eliminate the residual moisture and the temperature was increased to 70°C. TPA and H_2SO_4 , as a acid catalyst, were dissolved in THF and dropped slowly into the reactor at 70°C. The reaction temperature was maintained for 12 h so that 1 mol of TMP reacted with 1 mol of TPA. The reaction time was determined as the time required to reach a theoretical acid value. Finally, an ester product was obtained via esterification, which was liquid at room temperature.¹¹ Figure 1 shows the molecular structure for the diol bearing pendant carboxylic acid employed in the work.

Synthesis of TMP-based Urethane Acrylate CA (TCA)

TCA was synthesized by a stepwise procedure. A schematic presentation for the reaction procedure and the molecular structure is shown in Figure 2. Since TMP-based diol (TMP-TPA) was liquid at room temperature and was miscible with the other reactants, a NCO-terminated prepolymer was prepared in the absence of a solvent.

In the first step, TMP-based diol was charged into the glass reactor after nitrogen gas was inlet for 10 min to remove the residual moisture. IPDI and DBTDL (1 wt %) was dropped slowly into the reactor at room temperature. The reaction temperature was increased to 70°C so that 2 mol of IPDI reacted with 1 mol of TMP-TPA and this temperature was kept for 2 h so that the NCO-terminated prepolymer was obtained. The reac-

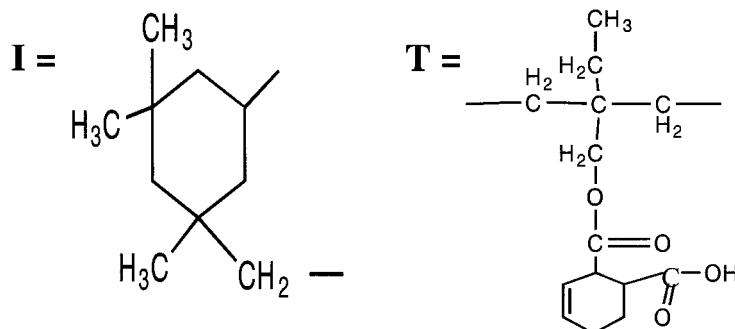
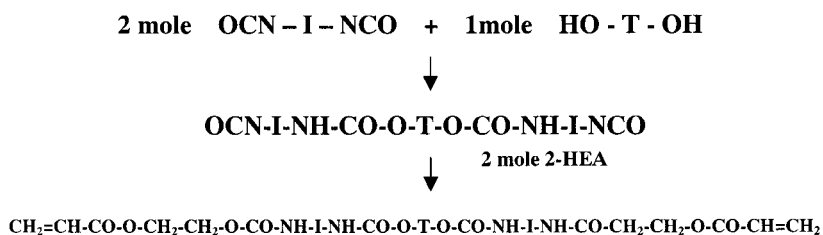


Figure 2 Reaction procedure and molecular structure of TCA.

tion end point was determined using FTIR and GPC. In the second step, 2 mol of 2-HEA was reacted with the NCO groups at 45°C for 12 h, capping both molecular ends with vinyl groups. The end point of the reaction was determined by the disappearance of the NCO stretching peak (2270 cm^{-1}) through FTIR spectroscopy and then the neutralization of the carboxylic acid was carried out at 45°C for 30 min with TEA. The molar concentration of TEA was the same as that of the carboxylic acid of the prepolymer. TCA was dispersed by adding deionized water under constant stirring at 200 rpm. The total solid content in water was 20 wt %. The water-dispersion process was carried out for 2 h at 45°C and, finally, TCA containing a pendant anionic group and a double bond in the pendant cyclic ring was prepared. The double bond in the pendant cyclic ring was cured through UV irradiation. Besides, the pendant anionic group was used to decrease the interfacial tension between the CA and the water continuous phase.

Preparation of PUDA and TCA Blend Film

A PUDA and TCA blend was prepared by varying the amount of TCA. TCA was placed in a 20-mL beaker together with the PUDA and 3 wt % of benzophenone. This mixture was stirred with a magnetic bar at 50°C to obtain a homogenized

mixture. The solution or emulsion prepared was poured into a Teflon sheet, of which the inner dimension was $10 \times 10 \times 0.6 \text{ cm}$ and dried at room temperature for 24 h and then completely dried in an oven at 60°C for 24 h. The dried films were cured with a UV lamp (1.5 kW) for 2 min and postcured at 100°C for 3 h. The films obtained were about 0.3–0.4 mm thick. The TCA content introduced for the preparation of the PUDA and TCA blend film is given in Table I. The TCA contents introduced are weight percent units. The number of the sample means the amount of TCA added. The amount of PUDA in the sample is omitted.

Table I TCA Contents Used for Preparation of PUDA and TCA Blend Film

Sample	PUDA Content (wt %)	TCA Content (wt %)
TCA0	100	0
TCA2	98	2
TCA5	95	5
TCA7	93	7
TCA10	90	10
TCA15	85	15
TCA100	0	100

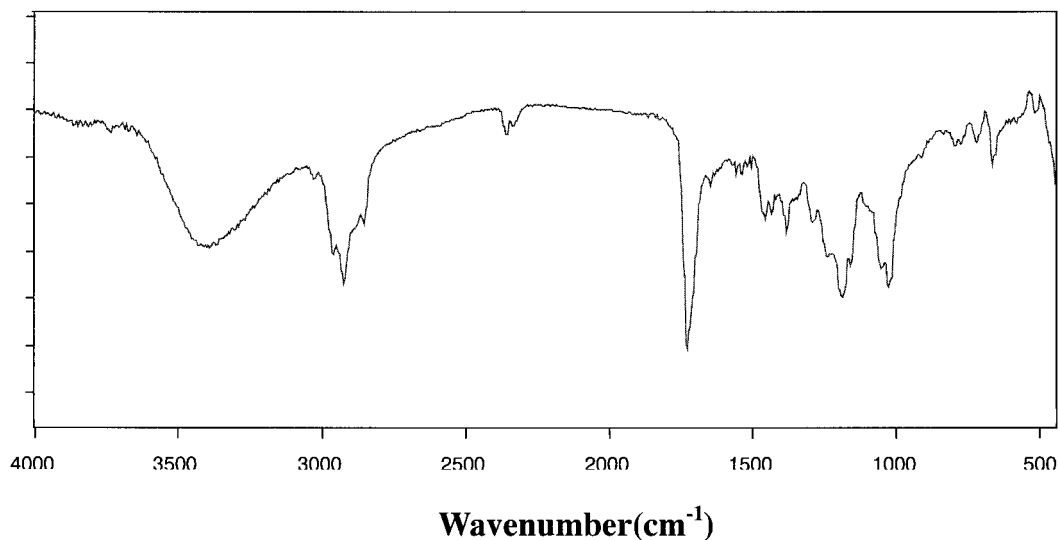


Figure 3 IR spectra of TMP-based diol.

Measurements

The TMP-TPA characterization analysis was measured at 35°C using a gel permeation chromatography (GPC) system with a differential reflective detector (Waters 410) and a KF-G (Shodex) free column. The flow rate of the carrier solvent, THF, was 1.0 mL/min. Low polydispersity polystyrene was employed as a standard to draw a calibration curve. The conversions were determined by measuring the gel fraction of various cured samples after extracting the unreacted materials in MEK for 24 h. The gel fraction of the cured samples was determined from the difference in weight before and after the extraction experiment as follows: gel fraction (%) = $W/W_0 \times 100$, where W_0 and W are the sample weight before and after extraction, respectively. FTIR spectra were recorded at a 4-cm^{-1} resolution on an FTS-7 (Bio-Rad) spectrometer. The tensile properties of the UV-cured films were measured at room temperature using a universal testing machine (United Co., Model STM-10E) with a crosshead speed of 50 mL/min. An average of at least five measurements was taken. The dumb-bell-type specimen was 10 mm wide at two ends, 0.3–0.4 mm thick, and 3 mm wide at the neck. The dynamic mechanical properties of the UV-cured films were obtained at 1 Hz using a DMA2980 (TA instrument) with a heating rate of 2°C/min over a temperature range of –100 to 100°C. The sample chamber was kept dry by a stream of moisture-free nitrogen.

RESULTS AND DISCUSSION

Figure 2 shows the molecular structure of TCA. It has three unsaturated double bonds which can crosslink each other at both ends and a pendant cyclic ring and a pendant ionic group to hydrate in the molecular backbone. These ionic groups are expected to exert influence on the final coating properties by ionic aggregation.^{9,10} In addition, the stability of the water continuous phase was decreased in the case of the typical acrylate CA.⁸ On the other hand, the TCA containing the ionic

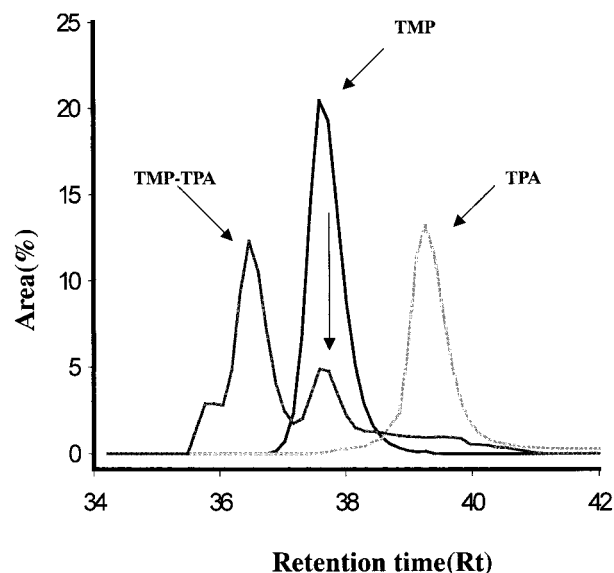


Figure 4 GPC chromatogram of TMP-based diol.

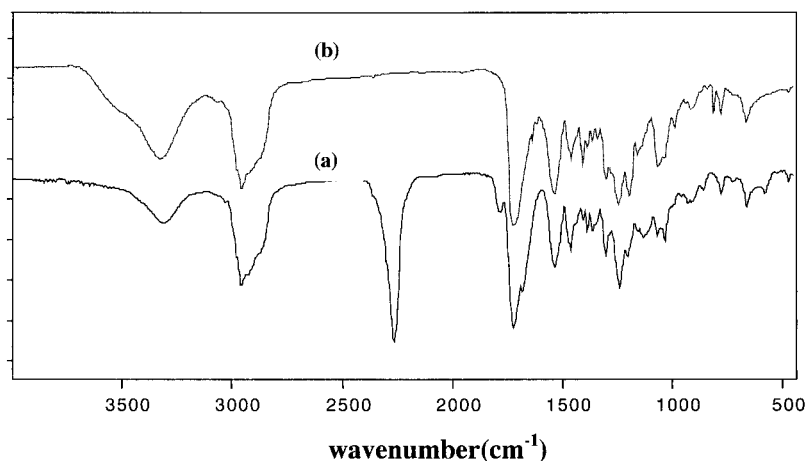


Figure 5 IR spectra of (a) before and (b) after reaction between NCO-terminated prepolymer and 2-HEA.

group could increase the stability of the water continuous phase due to its hydrophilic properties.

Identification of Reactions

Figure 3 shows IR spectra of the TMP-based diol synthesized. Usually, the characteristic peak of the TMP based at 1730 cm^{-1} , corresponding to the C=O carbonyl stretching peak, is used to identify the synthesis of TMP-based diol.^{10,13} The C=O characteristic peak at 1730 cm^{-1} confirmed the apparent appearance after the synthesis ended. This indicated that TMP-based diol was synthesized via esterification. A GPC chromatogram of TMP-based diol is shown in Figure 4. The GPC chromatogram shows the TMP-based diol, unreacted TMP, and a by-product with one OH

functionality. But because the OH value of this material was close to the theoretical OH value (2-functionality), this material was used to make TCA without purification. The molecular structure of the TMP-based diol synthesized is shown in Figure 1.

IR spectra taken (a) before and (b) after the reaction between the NCO-terminated prepolymer and 2-HEA and plotted to show the spectroscopic changes resulting from the reaction are shown in Figure 5. The disappearance of the NCO stretching band at 2270 cm^{-1} indicated the complete reaction of the NCO-terminated prepolymer and 2-HEA and the existence of the vinyl C—H deformation peak, the C=C stretching peak, and the cyclic C=C stretching peak at 810, 1635, and 1620 cm^{-1} , respectively, and also indicated that

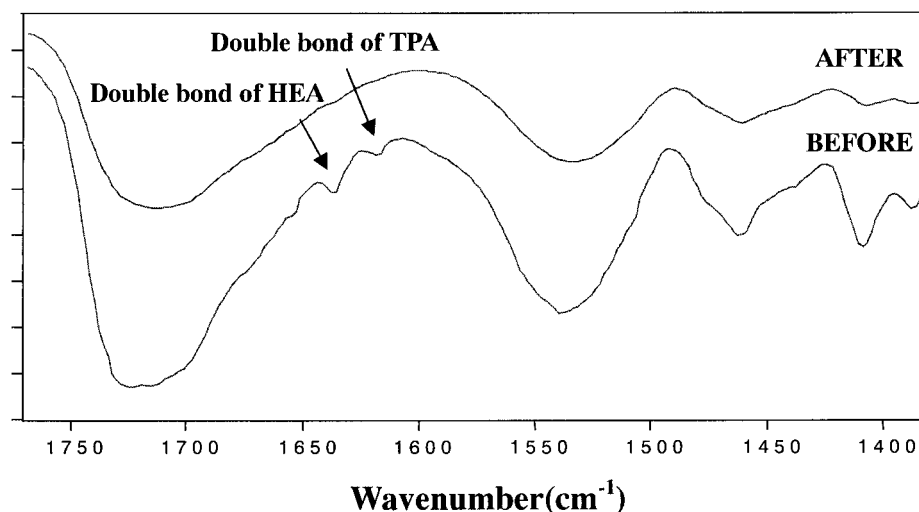


Figure 6 IR spectra of TCA before and after curing.

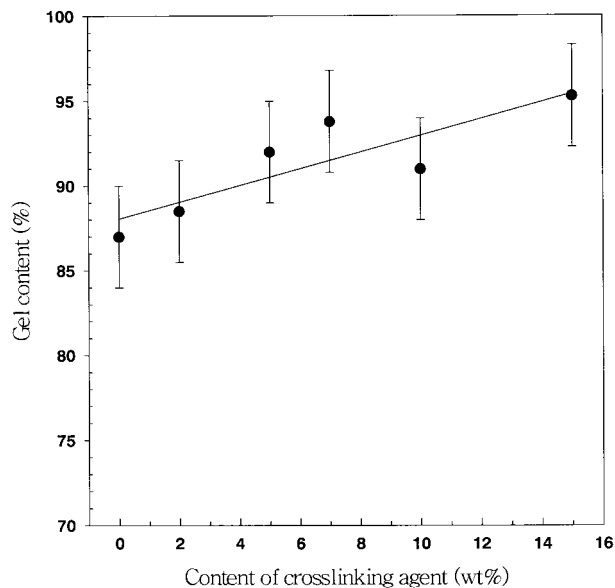


Figure 7 Gel fraction change with the added amount of TCA.

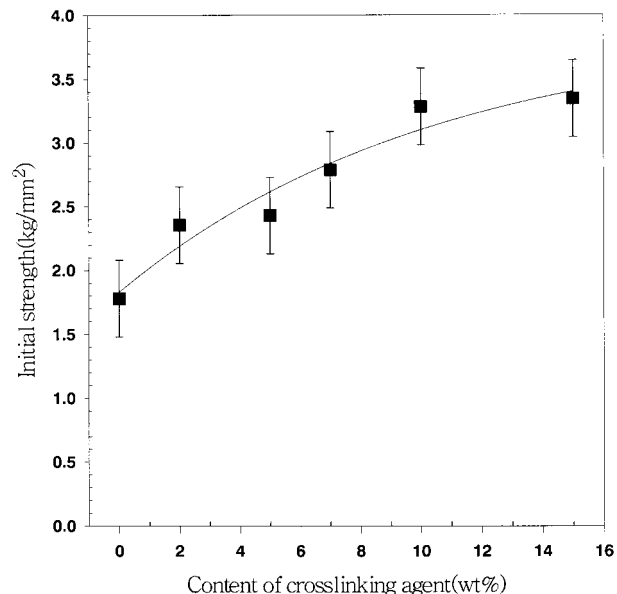


Figure 8 Change of initial modulus with different content of TCA.

they are not cured by the temperature in the course of the reaction.

Figure 6 shows IR spectra taken before and after 2 min of UV irradiation. Generally, the absorbance bands of acrylate at 1635 and 810 cm^{-1} , corresponding to the C=C stretching peak and the vinyl C—H deformation peak, are used to

identify the curing of acrylate.¹⁰ In this study, the characteristic C=C absorbance band of urethane acrylate at 1635 cm^{-1} was used to determine the vinyl polymerization reaction. The C=C absorbance band at 1635 cm^{-1} disappeared completely after curing. Besides, the characteristic C=C absorbance band of TPA at 1620 cm^{-1} was used to

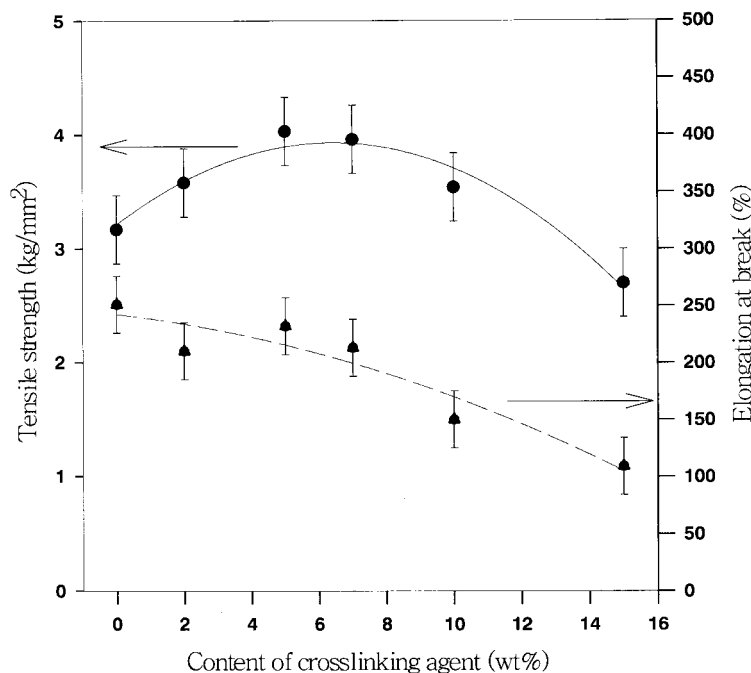


Figure 9 Change of (●-) tensile strength and (▲-) elongation at break with different contents of TCA.

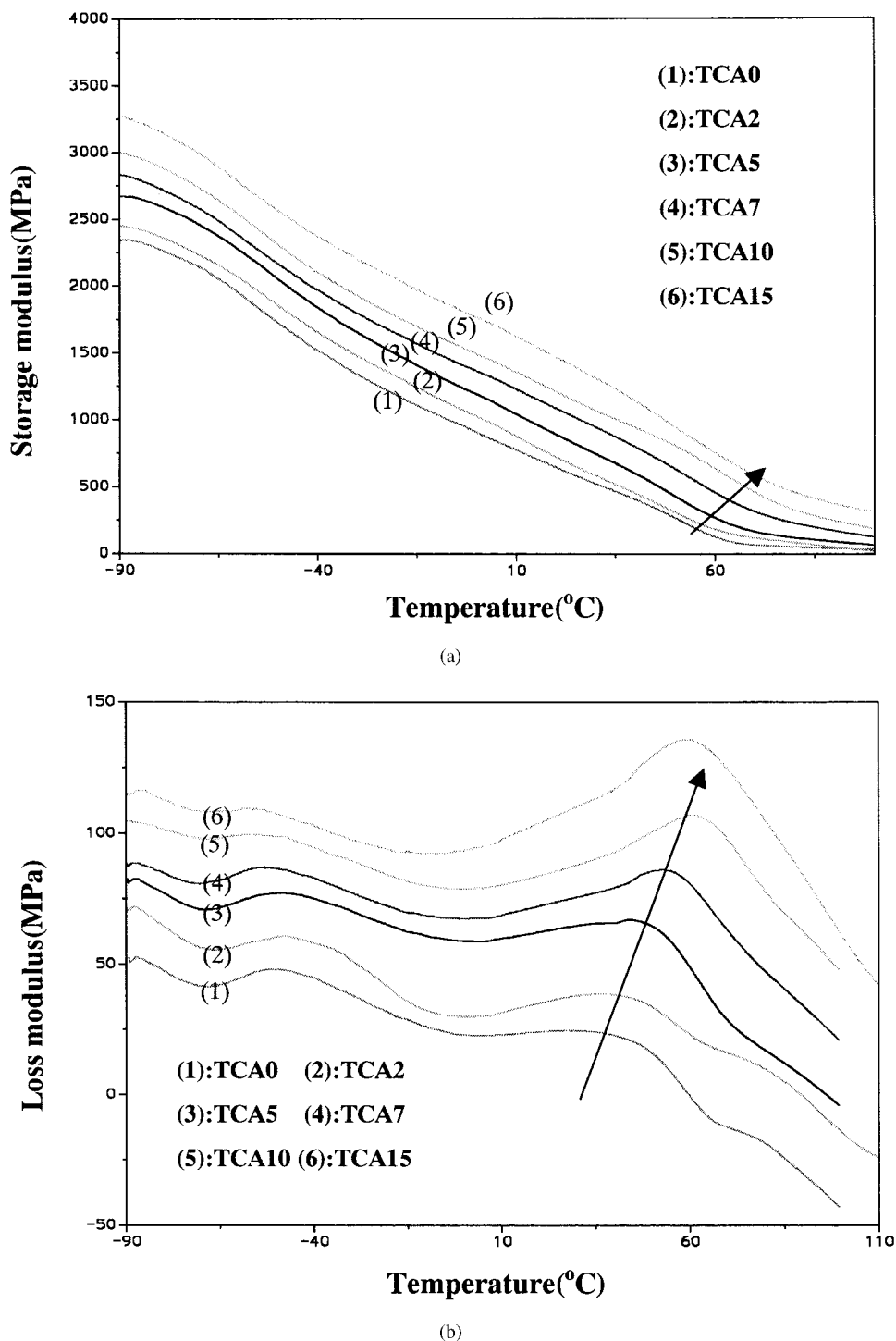


Figure 10 DMA for different TCA content: dependence of the storage modulus (E') on (a) the temperature and (b) the loss modulus (E'') on the temperature.

confirm the curing of TPA in this study. The disappearance of the $\text{C}=\text{C}$ band at 1620 cm^{-1} indicated that the double bond in the cyclic ring was reacted completely.

Figure 7 shows the change in the gel fraction with the added amount of TCA. The gel fraction increased with increasing CA. The samples were found to have greater than a 91% gel fraction.

This is because the crosslinking density in the mixtures increased by adding TCA into PUDA.

Mechanical Properties of PUDA and TCA Blend Films

The initial modulus, tensile strength, and elongation at break with different contents of TCA are shown in Figures 8 and 9. The initial modulus increased and the elongation at break decreased as the content of TCA increased. This result was in good agreement with the result of another study.¹⁴ This result suggests that there is a synergistic effect on the coating properties by means of the aggregation of ionic groups into the mixtures and increase of the crosslinking density.⁹ As the TCA is added to 7 wt %, there is an increase in the tensile strength, but there is a decrease in the tensile strength with a greater increasing content. This means that the crosslinking density and the aggregation of the ionic groups through Coulombic forces and hydrogen bonds increased dramatically, resulting in hardening of the UV-cured films.^{9,14,15} The explanation for this result was found through dynamic mechanical analysis (DMA).

The effect of the TCA level on the dynamic mechanical properties is shown in Figure 10. As the TCA content increased, the storage modulus increased and the rubbery plateau region was exhibited at a higher temperature [Fig. 10(a)], and the T_{gh} peak shifted to the higher temperature. However, the T_{gs} peak shifted to a little lower temperature with decrease of the magnitude. We considered the above tendency in term of the crosslinking density. The increase of the crosslinking density could be confirmed by the increased rubbery plateau modulus [Fig. 10(a)]. The increased crosslinking density is responsible for the dynamic mechanical property variations with the TCA content, as known from the increase of the rubbery modulus.^{14,16,17} The broadened temperature difference between T_{gs} and T_{gh} results from the shift of T_{gh} toward the higher temperature, and this would not mean greater phase separation. Once the soft segment–hard segment phase separation increases, a big difference of T_{gs} and T_{gh} is expected. Therefore, the shift of T_{gh} to the higher temperature is due mainly to the increased hard-segment physical crosslinking within the hard-segment domains.¹⁴

CONCLUSIONS

The TMP-based diol employed in this study was liquid at room temperature and was miscible with

the other reactants, which allowed the preparation of a prepolymer in the absence of a solvent. As well, the C=C in the pendant cyclic ring of TMP-based diol was confirmed to be cured through UV irradiation.

When the PUDA and TCA blend films were prepared with the content of TCA, their coating properties were much influenced by the double-bond concentration introduced with the TCA content. In the DMA measurement, the increased magnitude of the T_{gh} , corresponding to the glass transition temperature of the hard segment, was apparently obtained with the TCA content and is due mainly to the increased crosslinking density, as evidenced from the increased rubbery plateau modulus [Fig. 10(a)]. The increased crosslinking density influenced the mechanical properties of the UV-cured films, resulting in an increased gel fraction.

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