

Low-Temperature Curing of Water-Dispersible Cationic Diisocyanates for Cathodic Electrodeposition Coatings

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Received 26 March 2007; accepted 5 November 2007

DOI 10.1002/app.27627

Published online 13 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Water-dispersible cationically modified diisocyanates T1b and T1d blocked by *n*-butanol (BAO) and 3,5-dimethylpyrazole (DMP) for cathode electrodeposition (CED) coating curing were synthesized by introducing cationic triethanolamine (TEOA) into isophorone diisocyanate (IPDI). The crosslinkers T1b and T1d were characterized with FTIR, gel permeation chromatography, dynamic light scattering for size distribution, differential scanning calorimeter, and thermogravimetry techniques. The emulsion for CED coating made of T1b or T1d and cationic acrylic copolymer showed a high stability with narrow particle diameter distribution because of the ionization of the crosslinker. TG and DSC indicated that the deblocking and

crosslinking temperatures of T1d and T1d containing CED film were always lower than the corresponding temperatures of the T1b and T1b containing CED film. With 0.5 wt % of catalyst dibutyltin dilaurate (DBTL) in T1d-CED emulsion and cured at 140°C for 40 min, 90% of the gel content in the T1d-CED film was realized. Hence, T1d can meet the requirement of low-temperature curing for the CED coating. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 4036–4042, 2008

Key words: low-temperature curing; blocked cationic diisocyanate; cathodic electrodeposition coating; emulsion stability; gel content

INTRODUCTION

Isocyanates have been intensively utilized in a lot of fields as the curing reagent to crosslink polymer chains, such as soft and hard elastomers, foams, adhesives, coatings, and so on. The reaction between an isocyanate and a molecule containing active hydrogen atoms, like alcohols or amines, is fast and forms the carbamate ($-\text{HN}-\text{CO}-\text{O}-$).¹ Because the activity of this reaction is very high and isocyanates are usually toxic, utilization and storage of isocyanates with other reactants in one-package products as used in coating become difficult. The way to solve this problem is to block the isocyanate with small molecules containing active hydrogen atoms.² Blocked isocyanates can be used as the curing reagent for various coatings.^{3–5} In electrodeposition coatings, especially in the cathode electrodeposition (CED) coatings, the largest amount of curing reagent is blocked diisocyanates.⁶ There are more than 400 references, most are patents, released between 1980 and mid-2000 concerning this topic.^{1,6–8}

The popularly used diisocyanates are toluene 2,4-diisocyanate (TDI), 4,4'-methylene biphenyl isocyanate (MDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate (IPDI). The reaction activity for IPDI with water is lower than TDI, thus, the reaction of IPDI with blocking reagents is easy to be controlled. In addition, the use of IPDI is in favor to avoid the coated film becoming yellow under heat or sunlight radiation, for IPDI has no phenyl groups. Common blocking reagents are phenols, oximes, alcohols, ϵ -caprolactam, 3,5-dimethylpyrazole (DMP), diethyl malonate, and amines. A number of patents and articles have suggested that the heterocyclic compounds, such as triazoles, imidazolines, and imidazoles, would be more suitable blocking reagents for isocyanates.^{9–13}

The blocked isocyanates will be deblocked through removing the blocking group by heating for curing other molecules. The factors that influence the deblocking temperature and rate of the blocked isocyanates include structure of the isocyanate, blocking reagents,^{14–16} solvents,¹⁷ catalysts,¹⁸ and so on. For the CED coating, the curing reagent is required to be stable in water, compatible with the coating resin, and curable at low temperature, because high-curing temperature will damage the workpieces, which contain rubber or plastic parts. There have been many studies on low-temperature curing CED coatings, which can be cured at 120–150°C.¹⁹ The low-temperature curing CED coating

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Contract grant sponsor: The NSF of China; contract grant number: 20534020.

Contract grant sponsor: The NSF of Guangdong Province; contract grant numbers: 015036, 2005B10301010.

ED-6 from PPG, for an example, can be cured at 150°C.

Introduction of cationic groups into the blocked diisocyanates is expected to improve their water dispersion and electrophoretic abilities, which will lead to a more homogeneously cured CED coating film. To authors' knowledge, there is no report concerning blocked cationically modified diisocyanates for the CED coatings up to now. In this work, we used triethanolamine (TEOA), DMP, *n*-butanol to block IPDI to prepare two blocked cationic diisocyanates, and then investigated their curing property with a synthesized cationic acrylic copolymer after CED coating.

EXPERIMENTAL

Materials

All the reagents used in this work were the analysis grade chemicals made in China. 2-Butanone, methyl methacrylate (MMA), butyl acrylate (BA), *N,N*-dimethyl aminoethyl methacrylate (DMAEMA), and 2-hydroxyethyl methacrylate (HEMA) were dried with anhydrous magnesium sulfate and distilled before use. TEOA was dried under vacuum. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized before use. Other chemicals were used as received without further purification.

Synthesis of cationic acrylic copolymer DH-M10B50

A 250-mL four-necked flask equipped with mechanical stirrer, argon inlet, and condenser was charged with solvent *n*-butyl acetate (BAC, 150 g) and initiator AIBN (1.35 g). And then, monomers MMA (10 g, 0.1 mol), BA (50 g, 0.39 mol), HEMA (20 g, 0.15 mol), DMAEMA (20 g, 0.13 mol), and AIBN (0.45 g) in BAC were added to the flask during 2 h, and the mixture were heated to 85°C. AIBN (0.2 g) was supplemented and the mixture was continually stirred for another 2 h until the conversion was higher than 95%.^{20,21} The raw product was dissolved in tetrahydrofuran (THF) and precipitated in petroleum ether twice. The cationic acrylic copolymer DH-M10B50 was obtained after drying under vacuum at 60°C.

Synthesis of blocked cationic IPDI-based crosslinkers

The blocked cationic isophoron diisocyanate (IPDI, Degussa-Huels Pacific, Frankfurt, Germany) was synthesized according to the formulation given in Table I. IPDI was added to a 250-mL three-necked flask equipped with mechanical stirrer under argon atmosphere. To this three-necked flask, TEOA and 2-

TABLE I
Formulation for Blocked Cationic IPDI, T1b, and T1d

Reagent	T1b	T1d
IPDI (g, mol)	22.23, 0.1	22.23, 0.1
TEOA (g, mol)	6.42, 0.06	6.42, 0.06
BO (g, mol)	7.41, 0.1	—
DMP (g, mol)	—	9.6, 0.1
Butanone (g)	90	90

butanone were added during 1 h at 30°C. The reactants were heated to 65°C for 2 h until calculated —NCO content was reached, and then *n*-butanol (BO) and 2-butanone were added into the flask over 1 h. The reaction was continued until the —NCO groups were blocked completely (about 2 h). The product was precipitated into petroleum ether and dissolved in THF. By repeating this process twice and drying under vacuum at 30°C, the cationic *n*-butanol-blocked IPDI (T1b) was obtained.

The synthesis of DMP-blocked IPDI (T1d) was the same as described earlier for the T1b, except that the reaction temperature was 70°C.

CED coating

The emulsion for CED coating was prepared according to the formulations in Table II by uniformly mixing the components for 1 h at 50°C and acidifying with acetic acid to pH = 5.5. Deionized water was added into the mixture and stirred at high speed (20,000 rpm) for 30 min to form the emulsion thoroughly. All the emulsions had the same solid content.

CED coating was carried out on a 30 mm × 40 mm of stainless steel plate (304, Cr18Ni9) at room temperature for 3 min using 100 V DC supplied by a DC source of WJT-20001D. The anode to cathode distance was 2 cm and the area ratio of the anode to workpiece (cathode) was 1 : 1.

Characterization

Crosslinking degree of the CED film

Crosslinking degree of the CED film was described with the gel content. The wet film (uncured) as deposited through CED was scraped off from the substrate, dissolved in THF, and coated on an aluminum foil. The wet film on aluminum foil was cured at specified temperature for 40 min. Degree of crosslinking (gel content) D was estimated as $D = (W_2/W_1) \times 100\%$ from the film weights before and after acetone refluxing extraction for 24 h in a Soxhlet extractor, where W_1 is the film weight before extraction and W_2 is the film weight after extraction.

—NCO content

The —NCO content in the reactants was determined using the standard dibutylamine reverse titration.²²

TABLE II
Formulation of CED Coating Emulsions

Component	E1	E2	E3	E4
DH-M10B50 (g)	20	20	32	–
TId (g)	12	–	–	–
TIb (g)	–	12	–	32
EGBE (g)	8	8	8	8
THF (g)	17	17	17	17
Acetic acid (g)	2.25	2.25	2.25	2.25
Water-borne silicone oil (g)	1	1	1	1
Deionized water (g)	168	168	168	168
Amine value (mg/g KOH)	29.48	31.75	44.5	19.0

Here, quantitative TEOA was added, which was determined by the content of tertiary amino groups in a given sample. This method can avoid the deviation in the final $-\text{NCO}$ value caused by the reaction between hydrochloric acid and tertiary amino groups.

Instrumental analysis

FTIR spectra of the cationic acrylic copolymer and the blocked cationic diisocyanates coated on KBr flakes were recorded with a Bruker Vector33 FTIR spectrometer at room temperature.

Molecular weight (M_w and M_n) and polydispersity of the cationic acrylic copolymer were measured with a Waters gel permeation chromatography (GPC) using a series of Styragel[®] columns (HR3, HR4, HR6) at 35°C. THF was used as the elution solvent at 1.0 mL/min with narrow distributed polystyrene standards.

A differential scanning calorimeter (DSC) of Netzch DSC 204C was used to investigate the thermal properties of the blocked cationic diisocyanates and the CED film at heating rate of 10°C/min under nitrogen purge of 20 mL/min. The wet CED film was dried in vacuum at 30°C for 24 h before measurement.

Thermogravimetric (TG) analysis was carried out with a Netzch TG209 thermogravimetric analyzer from 30 to 600°C at heating rate of 10°C/min in nitrogen atmosphere at flow rate of 20 mL/min.

Particle size distribution of the CED emulsions was observed with a Malvern Nano-ZS90 zeta sizer. Emulsions were diluted to 1/100 before measurement.

Conductivity of the CED emulsion was measured with a Shanghai Leici DDS-11A conductivity meter at room temperature.

RESULTS AND DISCUSSION

Cationic copolymer DH-M10B50

The composition of DH-M10B50 was optimized during previous experiments to achieve suitable T_g , water dispersion, and electrodeposition ability for

the CED coating. The FTIR spectrum of the cationic acrylic copolymer DH-M10B50 is shown in Figure 1. The strong absorption at 1728 cm^{-1} belongs to the C=O stretching of ester, and that at about 2965 cm^{-1} belongs to the C–H stretching of CH_2 and CH_3 . The absorption at 1459 cm^{-1} belongs to the scissor vibration of CH_2 . The wide absorption band ranging 1168–1239 cm^{-1} belongs to the $-\text{C}-\text{O}-\text{C}-$ groups of the esters because of the existence of several ester groups in MMA, DMAEMA, HEMA, BA. The absorption corresponding to the $-\text{OH}$ of HEMA segments appears at about 3500 cm^{-1} .

The desired molecular weight for the CED resin is around 6000–15,000 as required by homogeneously crosslinking and emulsion viscosity.^{23,24} Here, the molecular weight of the copolymer was controlled within 10,000–15,000 by the amount of initiator. For the cationic acrylic copolymer DH-M10B50, M_n was 14,000 and polydispersity index (PDI) M_w/M_n was about 1.5 as determined by GPC when the initiator was 2 wt % relative to the monomers.

Blocked cationic isocyanates TIb and TId

Scheme 1 outlines the synthesis reactions of blocked cationic isocyanates TIb and TId. First, TEOA reacted with IPDI to make its $-\text{NCO}$ groups semi-blocked. Then, the semi-blocked isocyanate reacted with another blocking agent *n*-butanol or DMP to produce the cationic blocked-isocyanate TIb or TId. The FTIR spectra of TIb and TId are shown in Figure 2. There is no characteristic absorption of $-\text{NCO}$ groups at around 2250–2270 cm^{-1} , indicating complete block of the $-\text{NCO}$ groups. The strong absorptions are assigned as 2956 cm^{-1} for C–H stretching, 3325 cm^{-1} for N–H stretching, 1701–1713 cm^{-1} for

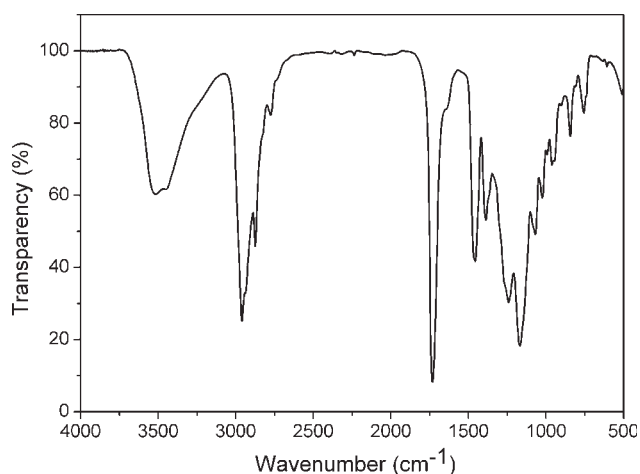
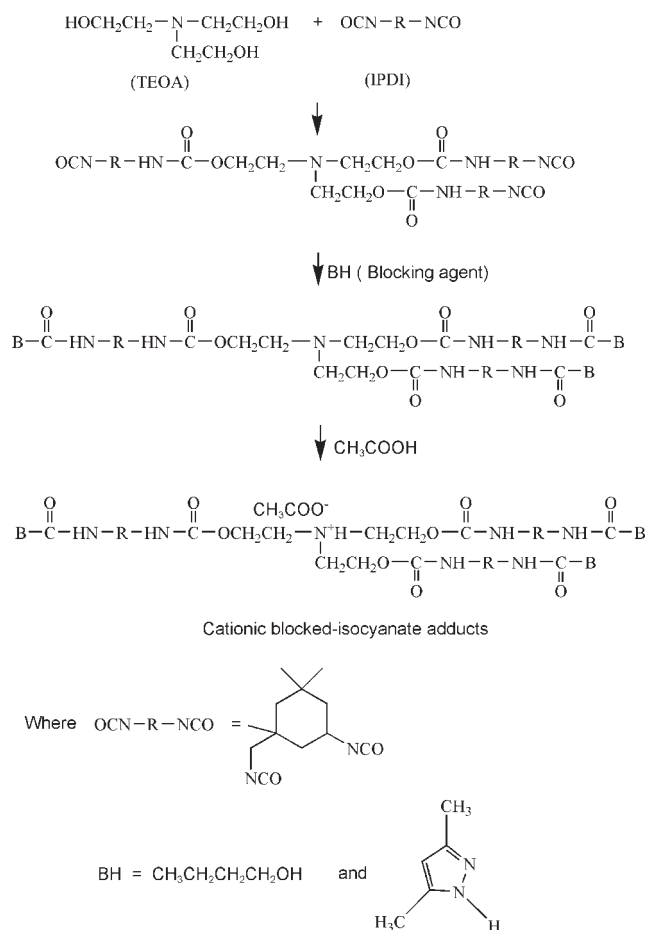


Figure 1 FTIR spectrum of cationic acrylic copolymer DH-M10B50.



Scheme 1 Synthesis of blocked cationic isocyanates T1b and T1d.

amide C=O stretching, 1518–1533 cm^{-1} for N–H bending, and 1126–1138 cm^{-1} for C–N bonds.

Figure 3 depicts the TG curves of the blocked cationic isocyanates T1b and T1d. Because of their complex chemical structure, there are two weight-loss steps for T1d and three weight-loss steps for T1b, respectively. The temperature at which the weight-loss begins is 83°C for T1d and 107°C for T1b, suggesting the possibility of low-temperature curing.

Particle size distribution and stability of CED emulsions

The particle size distribution of the CED emulsions E1, E2, E3, and E4 is shown in Figure 4. The mean particle diameter d of E1, E2, E3, and E4 is 154, 164, 168, and 574 nm, respectively; the PDI of E1, E2, E3, and E4 is 0.108, 0.174, 0.034, and 0.518, respectively. The appearance of E1 and E2 was translucent, E3 was transparent, and E4 was opaque milky.

The PDI of the emulsion decreases in the order of $E4 > E2 \approx E1 > E3$. The amine value (the amount of acid required to neutralize 1 g of copolymer and crosslinker, see the last row in Table II) of E3 is the

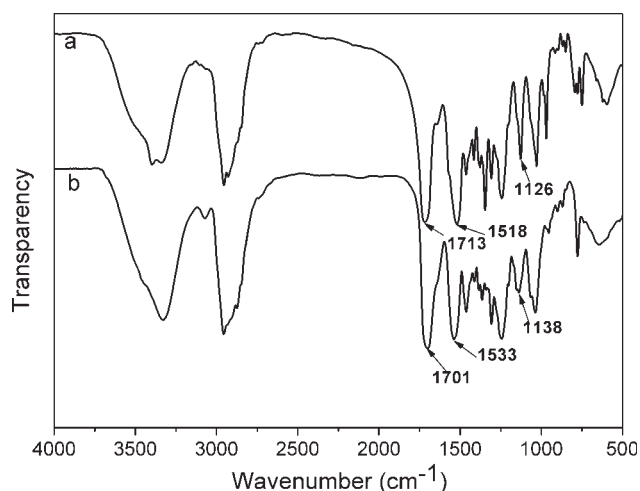


Figure 2 FTIR spectra of cationic DMP-blocked isocyanate T1d (a) and *n*-butanol-blocked isocyanate T1b (b).

highest among these four emulsions, endowing it the narrowest size distribution and better stability in aqueous environment. The amine value of E4 is the lowest among these four emulsions, leading to the biggest d and PDI values for E4. The essential reason for this behavior is surface charge density of the colloid particles in the emulsion. For the emulsion with high-amine value, the particles consisting of the cationic acrylic copolymer and blocked cationic isocyanate carry more charges on the surface, which stabilize the colloid particles with small size and narrow distribution.

The present cationic crosslinkers have enough charges to assure themselves dispersed in water to form an emulsion without the cationic acrylic copolymer (E4 in Table II). This fact was also tested with Table II). The average particle size of the emulsion consisting of the nonionic *n*-butanol-blocked isocyanate and DH-M10B50 was 830 nm

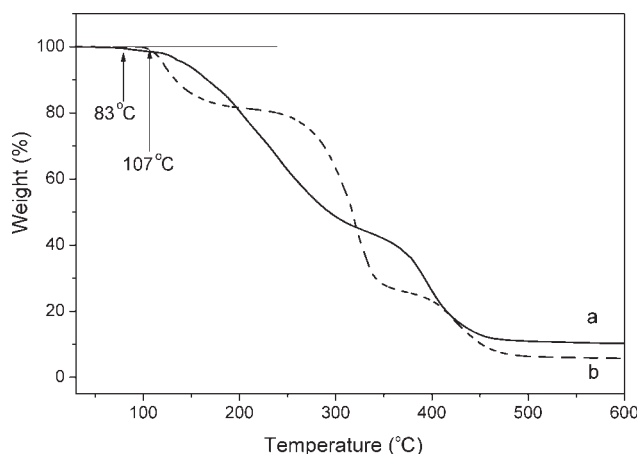


Figure 3 TG curves of cationic DMP-blocked isocyanate T1d (a) and *n*-butanol-blocked isocyanate T1b (b).

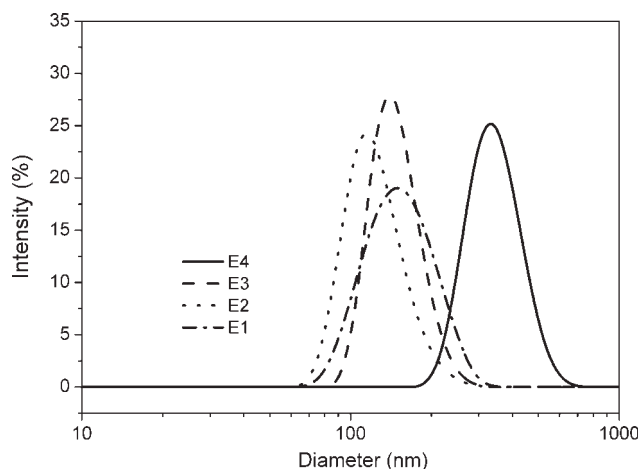


Figure 4 Particle size distribution of emulsions E1, E2, E3, and E4.

and PDI was 1.0, the emulsion appeared opaque milky. This indicates that the stability of the CED emulsion can be improved by ionization of the cross-linker.

The conductance of the CED emulsions E1, E2, E3, and E4 was 943, 973, 1247, and 526 $\mu\text{S}/\text{cm}$, respectively; which also reflects the surface charge density of the colloid particles. This manifests that the cationic modification of blocked-isocyanates contributes more positive charges to maintain the CED emulsion stable.

Deblocking temperature

Thermal properties of the blocked cationic isocyanates TId and TIb and the CED films were investigated with TG and DSC. TG curves of TIb and TId in Figure 3 reveal that the start decomposition temperature of TIb and TId is 107 and 83°C, respectively. It has been reported that DMP-blocked-TDI and DMP-blocked-MDI undergo decomposition at 75 and 105°C, respectively.²⁵ There are three steps in decomposition of TIb, which may correspond to the weight loss of *n*-butanol (19 wt %), IPDI (55 wt %), and TEOA (15 wt %). In contrast, there are only two steps in decomposition of TId, for DMP has higher decomposition temperature and may decompose with IPDI together.

An endothermic peak appears at DSC curves of the first run for the TIb- or TId-CED films (Figs. 5 and 6), which can be attributed to the deblocking of the blocked cationic isocyanates. The deblocking temperature for the TId-CED film is in the range of 92–121°C, lower than that for the TIb-CED film in the range 117–175°C. The same trend was observed from the TG curves for the TIb and TId (Fig. 3). The second run of DSC curves demonstrates almost the same T_g at about 74°C for the TIb-CED and TId-CED films. Disappearance of the endothermic peak in the

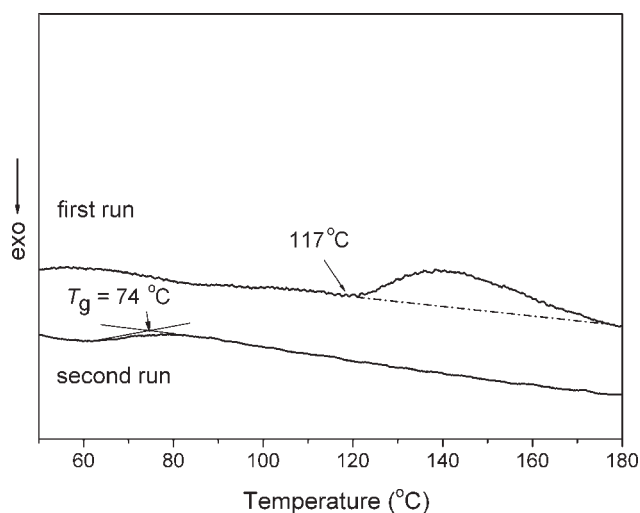


Figure 5 DSC curve of TIb-CED film.

second run confirms that the deblocking reaction has been completed during the first heating process.

The curing reaction of the cationic acrylic copolymer with the blocked cationic isocyanate is a complex process including deblocking and crosslinking reactions as being heated. According to Liang and coworkers,^{26,27} it took about 30 min for the deblocking and crosslinking reactions to proceed completely. The heating-up time during the DSC measurement was not long enough for accomplishment of the crosslinking reaction in the CED film because of fast heating rate (10°C/min), thus, no exothermic peak was observed from the DSC curve.

On the other hand, the effect of catalyst dibutyltin dilaurate (DBTL) on the deblocking temperature was investigated. DSC curves on the first run of the TId-CED films with different amounts of DBTL are illustrated in Figure 7. The deblocking temperature of the TId-CED film is significantly shifted toward lower

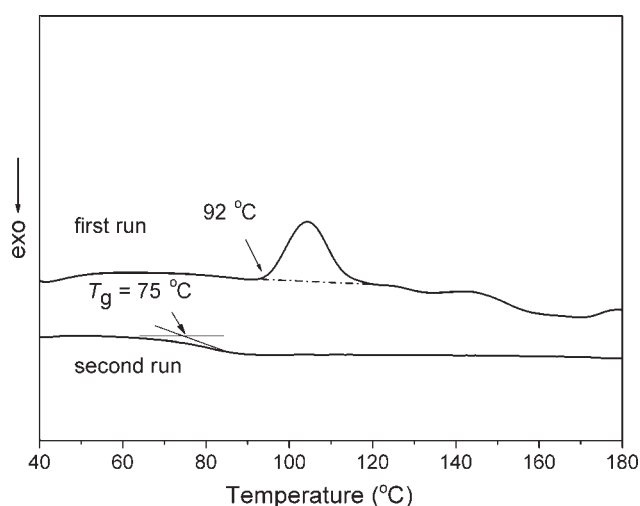


Figure 6 DSC curve of TId-CED film.

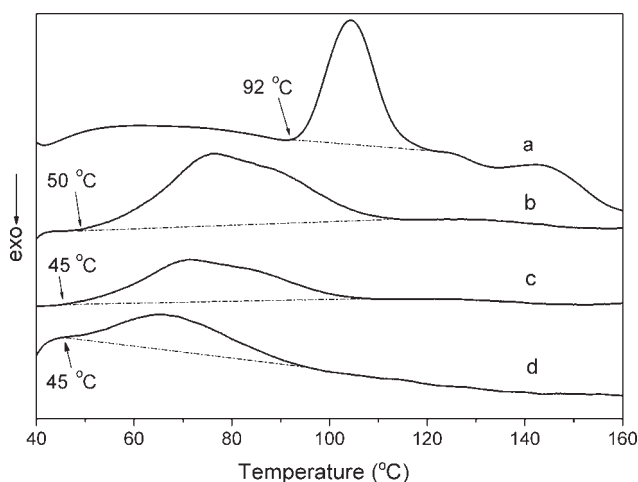


Figure 7 DSC curves on the first run for the TId-CED film with different amounts of catalyst DBTL: (a) 0 wt %; (b) 0.5 wt %; (c) 0.7 wt %; (d) 1.0 wt %.

temperature with increasing DBTL. This change in deblocking temperature, however, becomes smaller when amount of DBTL is beyond 0.5 wt %.

Degree of crosslinking of cured CED film

The degree of crosslinking of the Tlb- and TId-CED films was expressed by the gel content shown in Figure 8. The crosslinking reaction begins at 140 and 90°C for the Tlb-CED and TId-CED films, respectively, as indicated by a remarkable increase in the gel content. The gel content increases with increasing curing temperature. If the gel content of the cured CED film is required to be 90%, the curing temperature for the Tlb-CED film and TId-CED film should be 180 and 140°C, respectively. These results suggest that TId is more suitable for the purpose of low-temperature curing.

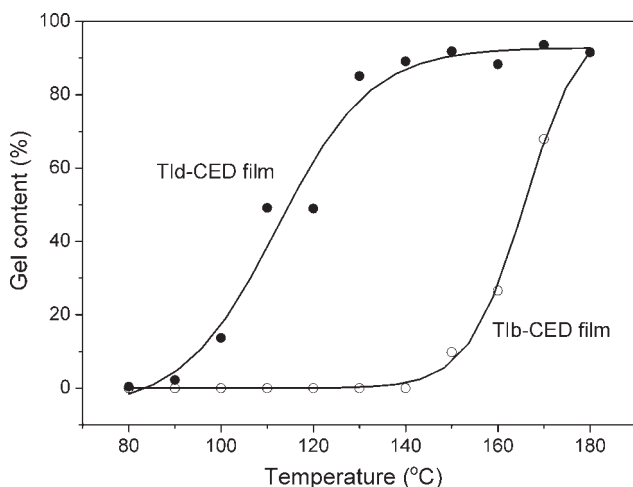


Figure 8 Gel content of Tlb-CED film and TId-CED film as a function of curing temperature.

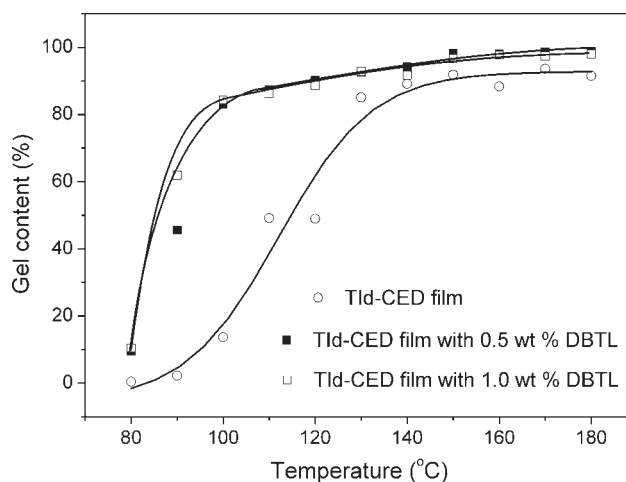


Figure 9 Gel content of TId-CED film as a function of curing temperature at indicated catalyst DBTL concentration.

Figure 9 shows the effect of catalyst DBTL amount on the gel content of the TId-CED film. The gel content of the TId-CED film increases with the increase in DBTL, leading to low-temperature curing, because the addition of DBTL reduces the activation energy of the curing reaction. But the gel content has no notable increase when DBTL is beyond 0.5 wt %. Figure 10 illustrates the effect of curing time on the gel content of the TId-CED film when 1.0 wt % of DBTL was used and the curing temperature was 150°C. The result indicates that it takes about 30–40 min to reach the high gel content (>90%).

CONCLUSION

Water dispersible blocked cationic isocyanates Tlb, TId, and cationic acrylic copolymer DH-M10B50 were successfully synthesized and characterized. The

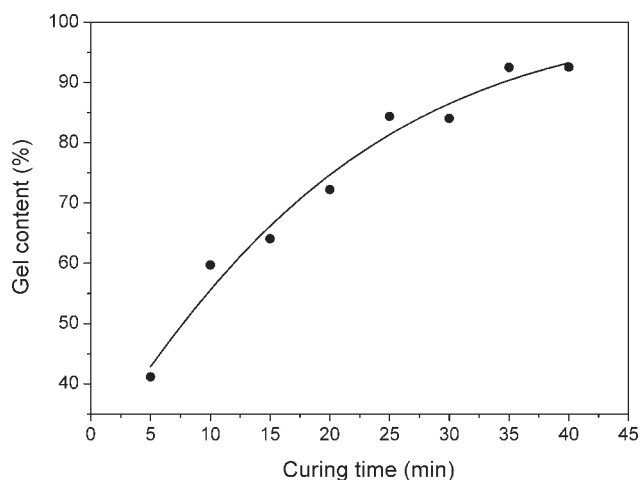


Figure 10 Gel content of TId-CED film as a function of curing time with 1.0 wt % of DBTL cured at 150°C.

CED emulsions consisting of either T1b or T1d and the cationic acrylic copolymer showed a high stability resulted from ionization of the crosslinkers T1b and T1d. The blocked-isocyanates and the CED film possessed low deblocking and curing temperatures, those of the T1d and T1d-CED film were always lower than the corresponding temperatures of the T1b and T1d-CED film. Under the optimum condition, i.e., catalyst DBTL of 0.5 wt %, curing time of 40 min, and curing temperature of 140°C, the T1d-CED film reached the high gel content of 90%. Therefore, T1d will meet the requirement of low-temperature curing for the CED coating.

The authors thank Mr. Yan Zhu of SCUT for his help in the experiments.

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