Curing Behavior of Anionic Poly(urethane urea) Dispersions Crosslinked with Partially Methylated Melamine Formaldehyde

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ABSTRACT: A rigid-body pendulum rheometer was used to observe the isothermal cure behavior of an anionic poly(urethane urea) dispersion crosslinked with different amounts of partially methylated melamine formaldehyde (PMMF). In this experiment, the anionic poly(urethane urea) dispersion had a large number of >N—H crosslinking or branching sites in urethane and urea groups per molecule, which allowed a large amount of PMMF to couple with the elastic polyurethane (PU) backbone. The test results showed that the cure response of the PU dispersion crosslinked with PMMF was a function of the concentration of PMMF and indicated that 30 phr PMMF could be the optimum amount of the crosslinking agent and that 120°C was the optimum temperature for the curing process. In addition, PMMF self-condensation could take place during the curing process. The self-condensation of PMMF also was monitored by a thermogravimetric method. Moreover, the dynamic mechanical properties of PMMF-crosslinked PU films were affected by the concentration of PMMF. From the curing behavior and dynamic mechanical analysis test results, it was reasonable to assume that highly PMMF branched PUs with partial crosslinking structures could be formed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 849–856, 2007

Key words: crosslinking; dispersions; polyurethanes; thermogravimetric analysis (TGA); viscoelastic properties

INTRODUCTION

Waterborne polyurethane (PU) dispersions that contain low amounts of volatile organic compounds and are nonflammable have been developed and are widely used in coatings and adhesives.[1] A waterborne PU dispersion is a colloid system in which a discontinuous PU phase is dispersed in a continuous aqueous phase.[2] Our previous study[3] on the preparation and characterization of tetramethyl-*m*-xylylene diisocyanate (*m*-TMXDI) based poly(urethane urea) dispersions containing various amounts of 2,2-bis(hydroxyl methyl) propionic acid (DMPA) showed that the average particle size of the poly(urethane urea) dispersions decreased with an increase in the DMPA content, and this led to an increase in the viscosity. However, aqueous PU dispersions are deficient in chemical resistance in comparison with crosslinked two-pack solvent-based PUs because most waterborne PUs are linear thermoplastic polymers that are resoluble in solvents. To improve the properties,

such as the solvent and chemical resistance, many different strategies have been pursued in the crosslinking of aqueous PU dispersions. Aqueous PU dispersions can be crosslinked at room temperature and elevated temperatures. Polyaziridines and carbodiimides are available for low-temperature crosslinking through the carboxylic acid groups.[4–6] For high-temperature crosslinking, methylated melamine formaldehyde resins are the most versatile crosslinking agents for many polymer systems, which may include PU dispersions.[7–9] Crosslinking can be accomplished through the reaction of a melamine formaldehyde resin with the hydroxyl- and/or carboxyl-functional groups of the polymer. Hexamethoxymethyl melamine (HMMM) is often used.[10–12] The water solubility of HMMM is quite limited; hence, it is used primarily in solvent-based or aqueous dispersion coating systems.

Partially methylated melamine formaldehydes (PMMFs) are complex mixtures of melamines with different degrees of hydroxymethylation and methoxymethylation.[13] Despite the extensive industrial applications of melamine resins, the characterization of these resins has been a difficult task because of their complex compositions. Methylated melamine formaldehyde resins, commonly known as
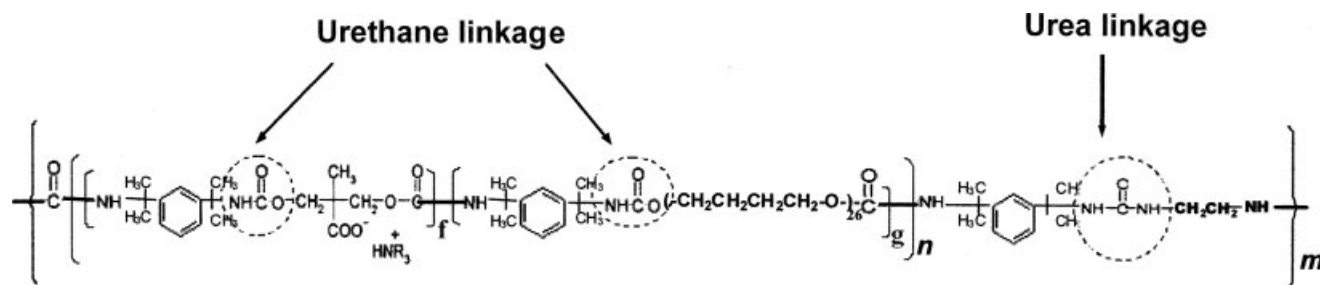
Figure 1 Chemical structure of anionic poly(urethane urea) dispersions.

melamine resins, are widely used in various industries as binder components and crosslinkers. Melamine resins are synthesized through the reaction of the primary amino groups of melamine with formaldehyde to form hydroxymethyl groups and the conversion of these hydroxymethyls to methoxymethyl groups by condensation with methanol. The degrees of hydroxymethylation and methoxymethylation are varied according to the intended end-use applications. The structures of melamine resins are traditionally expressed by the general formula $MF_{(x)}Me_{(y)}$,[14] where M represents the melamine ring, F represents the formaldehyde units on the three primary amino groups, and Me represents the end-capping methyl group. Most commercial products use this general formula to indicate the degree of hydroxymethylation (x) and the degree of methyl end capping (y). The different groups that are found in melamine formaldehyde resins are methylol ($-CH_2OH$), alkoxymethyl ($-CH_2OR$), imino ($>N-H$), and acetal ($-CH_2OCH_2OR$) end groups, which have a high tendency toward self-condensation.[15] The basic reactions of the functional groups were discussed by Blank and Hensley.[16] In self-condensation, functional groups on the melamine formaldehyde molecules react with one another, causing undesirable properties. It has been shown that alkoxy groups do not self-condense to any appreciable extent even under strong acid catalysis.[17]

In this study, PU dispersions based on m-TMXDI were crosslinked with different amounts of PMMF at a constant temperature. The curing behavior was observed with a rigid-body pendulum rheometer, and the effect of the PMMF content on the dynamic mechanical properties was examined.

EXPERIMENTAL

Materials

Tetramethyl-m-xylylene diisocyanate (m-TMXDI; extra pure grade) was obtained from Tokyo Kasei Kogyo Co. (Tokyo, Japan). DMPA was obtained from Lancaster Synthesis Co. (Windham, NH). Poly

(tetramethylene) ether glycol (number-average molecular weight = 2000) was obtained from Scientific Polymer Products, Inc. (Ontario, NY). Triethylamine, 1,2-ethylenediamine, and N-methyl-1,2-pyrrolidone were obtained from Tedia Co. (Fairfield, OH).

Preparation of the anionic poly(urethane urea) dispersions

As reported in our previous article,[3] m-TMXDI-based anionic poly(urethane urea) dispersions were prepared by a prepolymer mixing process. The chemical structure is presented as Figure 1. The colloidal properties were as follows: the nonvolatile content was 38 ± 1 wt %, the viscosity was 120 ± 10 cps at 25°C, the pH was 8.3 ± 0.1, and the particle size was 400 ± 100 nm. PMMF (Cymel-385) was obtained from Cytec, Inc. (West Paterson, NJ). The structural formula of PMMF can be expressed as $MF_{(4)}Me_{(2)}$, where M represents the melamine ring, F represents the formaldehyde units on the three primary amino groups, and Me represents the end-capping methyl group. Figure 2 shows the representative chemical structure of PMMF.

Samples prepared for the rigid-body pendulum rheometer

The samples were prepared through the mixing of an anionic poly(urethane urea) dispersion with 0, 5, 10, 20, 30, or 40 phr PMMF.
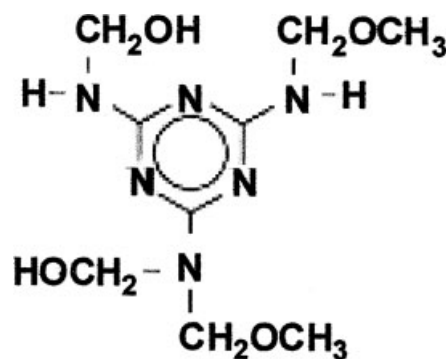

Figure 2 Chemical structure of PMMF.

Film preparation for dynamic mechanic analysis

The films were prepared through the casting of aqueous poly(urethane urea) dispersions mixed with PMMF onto silicone-coated surfaces, which were allowed to dry at room temperature for 2 days and were cured at 120 or 150°C for 30 min.

Rigid-body pendulum rheometer measurements

The curing process measurements were taken with a rigid-body pendulum rheometer (model α-100, Tohoku Electronic Industrial Co., Sendai, Japan). A frame-type pendulum (FRB-100) with a knife edge (RBE-130) was chosen, and the setup inertia was 500 g cm.

Principle of the rigid-body pendulum rheometer[18,19]

It is possible to use a instrument with a free-damping pendulum system to observe drying or curing behavior that is in compliance with the specifications of ISO 1522. To measure the curing process, a rigid-body pendulum equipped with a knife edge was provided. The test piece was fixed through coating or setting on a plate and placed on a heating mount. The pendulum was set so that the edge, or the fulcrum of the swing, came vertically in contact with the coated surface, as shown in Figure 3.

When an external force was applied by a magnetic adsorption force to the pendulum, the pendulum started to vibrate freely. Both sides of the edge of the pendulum yielded the strain of compression and elongation of the coated test pieces. As a result, the viscoelastic property of the test pieces created a swinging period of the pendulum and swing damping action. Through the measurement of the time variation of this period of oscillation of the pendulum, the curing behavior of the test
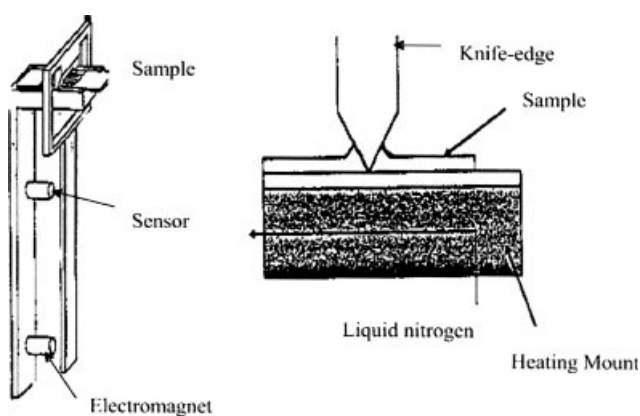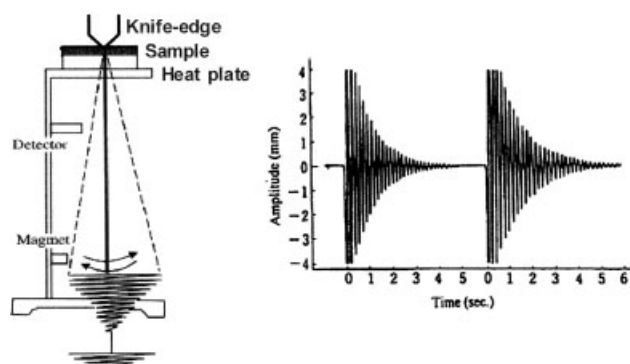

Figure 4 Oscillation pattern of the pendulum.

pieces could be obtained with the following equation:

$$t = \frac{t_1 + t_2 + \ldots + t_n}{n} \qquad (1)$$

where t is the oscillation period (s) and n is the number of oscillations.

The oscillation pattern of the pendulum is shown in Figure 4.

The viscosity (η) of the test substance had a function of stopping the oscillation of the pendulum, which was in contact with the test samples. It could be evaluated with the following equations:

$$\eta = kM^\theta \qquad (2)$$

$$\eta = ke^{\beta/T} \qquad (3)$$

where M is the molecular weight; T is the ambient temperature; and k, θ, and β are constants.

This showed the structural change of the transition process from a liquid to a solid film through the measurement of the frequency of oscillation.

Structural characterization

Fourier transform infrared spectra were recorded with a Nicolet Nexus 870 FTIR instrument (Madison, WI).

Thermogravimetric analysis

The thermal degradation behavior was determined with a thermogravimetric analyzer (TGA-Q500, TA Instruments, New Castle, DE) from room temperature to 800°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Dynamic mechanical property analysis

Dynamic mechanical analysis (DMA; model TA-Q800, TA Instruments) was used at a heating rate of

Figure 3 Device of the rigid-body pendulum rheometer.

5°C/min within the range of −150 to 50°C under a frequency of 1 Hz for temperature scanning.

DMA detected the viscoelastic behavior of the crosslinked PU films and yielded quantitative results for the storage modulus (E') and the corresponding loss modulus (E'') as well as the loss tangent (tan δ = E''/E'). E' and E'' characterize the elastic and viscous components of a viscoelastic material under deformation.

RESULTS AND DISCUSSION

Curing behavior of the PU dispersions with PMMF

In this experiment, a rigid-body pendulum rheometer was used to observe the isothermal cure behavior of poly(urethane urea) dispersions crosslinked with different amounts of PMMF. The effect of the PMMF content on the curing behavior is shown in Figure 5(a,b) at 120 and 150°C, respectively.

In the early stage of curing, the oscillation period reached the tip of inflection very rapidly; the tip of inflection was called the starting point of crosslinking. During the curing period, the oscillation period decreased gradually because the viscosity of the
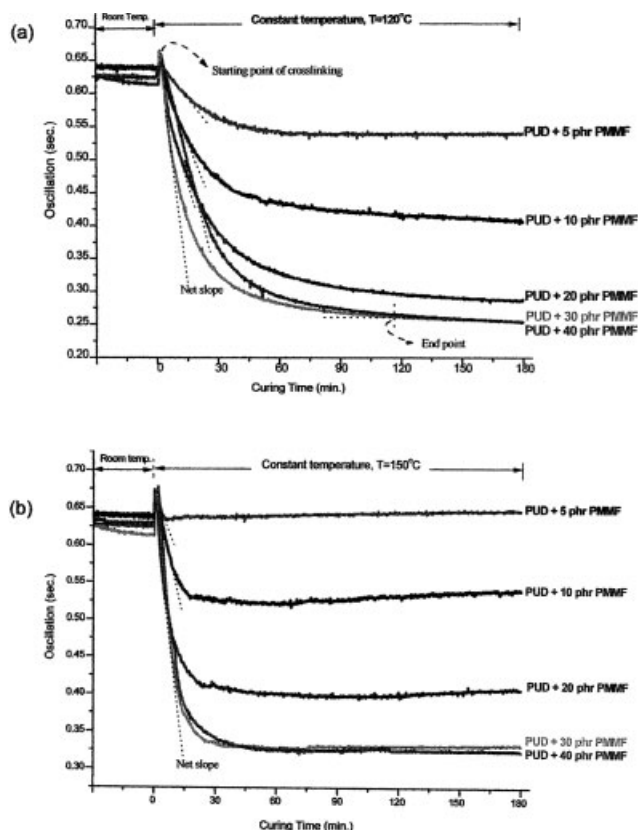

test sample increased, and this depended on the degree of chemical networking (crosslinking) or physical networking (entanglement). Also, the net slope of the isothermal curing curve gave information on the curing speed of the PU dispersions crosslinked with different amounts of PMMF. The higher the PMMF content was, the faster the curing speed was.

In the final stage of curing, the curve became flatter, and the last equilibrium point was called the end point, which indicated that the curing reaction had reached a balanced status. As a result, the higher the PMMF content was, the lower the equilibrium oscillation period was. However, the PU dispersion crosslinked with 40 phr PMMF had a minimum equilibrium oscillation period, which was very close to that of the dispersion crosslinked with 30 phr PMMF. This seems to indicate that 30 phr could be an effective amount of the crosslinking agent (PMMF) for a PU dispersion.

The desired crosslinking reaction of PU dispersions with PMMF results in the loss of hydrogen (—H) in the urethane (∼NHCOO∼) or urea (∼NHCONH∼) groups to react with methoxymethyl (—CH$_2$OCH$_3$) or methylol (—CH$_2$OH) end groups contained in PMMF to form a methylene (—CH$_2$—) bridge. It can be presented as follows:

1. ∼OOC—NH∼ + CH$_3$OCH$_2$N< → ∼OOC—N—CH$_2$—N< + CH$_3$OH
2. ∼OOC—NH∼ + HOCH$_2$N< → ∼OOC—N—CH$_2$—N< + H$_2$O
3. ∼NHCONH∼ + CH$_3$OCH$_2$N< → ∼NHCON—CH$_2$—N< + CH$_3$OH
4. ∼NHCONH∼ + HOCH$_2$N< → ∼NHCON—CH$_2$—N< + H$_2$O

The end groups contained in PMMF are methylol (—CH$_2$OH), methoxymethyl (—CH$_2$OCH$_3$), and imino (>NH) groups, and they have a high tendency toward self-condensation to form methylene (—CH$_2$—) and methylene ether (—CH$_2$—O—CH$_2$—) bridges.[14]

The PMMF self-condensation can be presented as follows:

5. >NCH$_2$OCH$_3$ + HN< → >N—CH$_2$—N< + CH$_3$OH
6. >NCH$_2$OCH$_3$ + HOCH$_2$N< → >NCH$_2$—O—CH$_2$N< + CH$_3$OH
7. >NCH$_2$OH + HN< → >N—CH$_2$—N< + H$_2$O
8. >NCH$_2$OH + HOCH$_2$N< → >NCH$_2$—O—CH$_2$N< + H$_2$O

Figure 5 Isothermal curing behavior of PU dispersions crosslinked with various amounts of PMMF at (a) 120 and (b) 150°C.

Figure 6 shows the FTIR spectra of PU dispersions crosslinked with different amounts of PMMF.
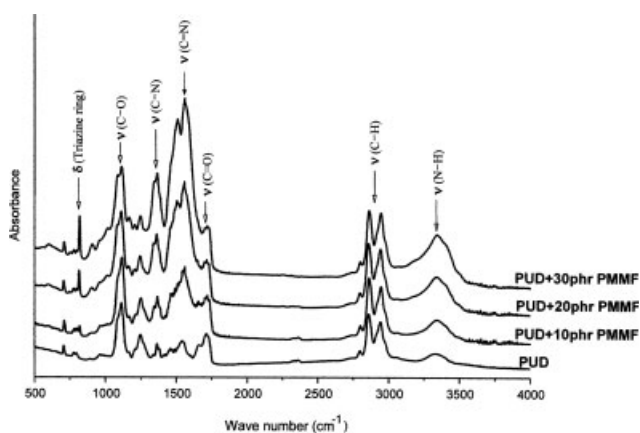
Figure 6 FTIR spectra of PU dispersions crosslinked with various amounts of PMMF.

Six major spectrum regions are presented as follows:

1. 3250–3400 cm^{-1}, N—H stretching, a broad absorption band.
2. 1650–1750 cm^{-1}, C=O stretching. This is assigned to the carbonyl groups in the urethane and urea linkages.
3. 1500–1650 cm^{-1}, C=N stretching. The sharp peak at 1607 cm^{-1} is an indication of the high content of nitrogen in the IR adsorption.
4. 1330–1400 cm^{-1}, C—N stretching. This is assigned to the secondary and tertiary amines.
5. 1050–1150 cm^{-1}, C—O stretching, growth of a shoulder at 1050 cm^{-1} due to methylene ether bridge formation. This band overlaps with the very strong band at 1110 cm^{-1}, the C—O—C stretching vibration of ether groups in the PU soft segment.
6. 815 cm^{-1}, triazine ring bending, out-of-plane deformation of the PMMF triazine ring.

As expected, the increase in the PMMF content causes an increase in the relative intensity of N—H stretching, C=N stretching, and triazine ring bending, confirming the reasonableness of the proposed structure.

Figure 7 shows the curing curves of PMMF self-condensation and PU dispersions crosslinked with PMMF at two different temperatures.

It is clear that the reaction rate of PMMF self-condensation at 150°C is faster than that at 120°C. Therefore, the self-condensation of PMMF can take place simultaneously with the crosslinking of a PU dispersion with PMMF. All the aforementioned reactions (1–8) result in the liberation of not only water but also methanol.

The net slope of the curing curve of a PU dispersion crosslinked with PMMF at 120°C in the early stage is similar to that at 150°C, and this indicates

that the curing speeds are very close. The major difference is that the curing reaction at 120°C can reach a lower oscillation period (more stable balance status) in the final stage than that at 150°C. These results indicate that 120°C is the optimum temperature for the curing process.

A comparison of the curing behavior of PMMF self-condensation and PU dispersions crosslinked with PMMF shows the different reaction rates of these competing reactions. In the early stage, the time required to reach the tip of inflection for PU dispersion crosslinking is shorter than the time required for PMMF self-condensation; this reveals that the reaction rate of a PU dispersion crosslinked with PMMF is generally faster than that of PMMF self-condensation. Furthermore, the curing curve of PU dispersion crosslinking can reach a balanced status and become flatter in the final stage, and this indicates that the crosslinking of a PU dispersion with PMMF goes virtually to completion. However, the curing reaction of PMMF self-condensation occurs to a significant degree but does not approach an equilibrium point or completion.

Thermal degradation behavior

The self-condensation reaction of PMMF also can be monitored by a thermogravimetric method. Fresh PMMF, moderately self-crosslinked PMMF, and highly self-crosslinked PMMF are displayed in Figure 8(a–c), respectively.

It is clear that there are three distinct regions of degradation in Figure 8(c); three successive weight-loss regions appear at (1) 220–400°C, (2) 400–420°C, and (3) temperatures greater than 420°C. The decomposed gas might contain methanol, formaldehyde, and carbon dioxide as well as ammonia and some impurities.[20] By comparing the degradation route shown in Figure 8(a–c), we can notice that the patterns of these three routes are very similar at
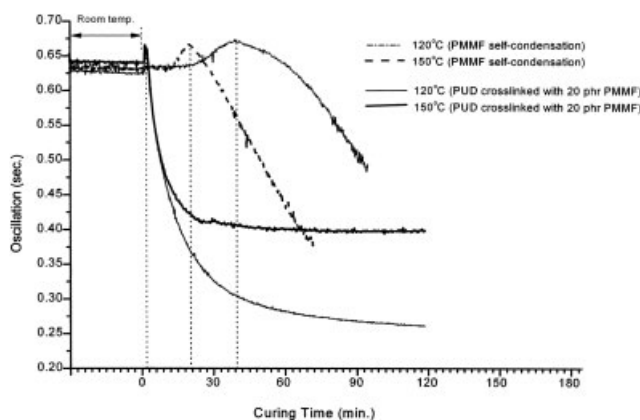

Figure 7 Comparison of the curing curves of PMMF self-condensation and PU dispersions crosslinked with PMMF.
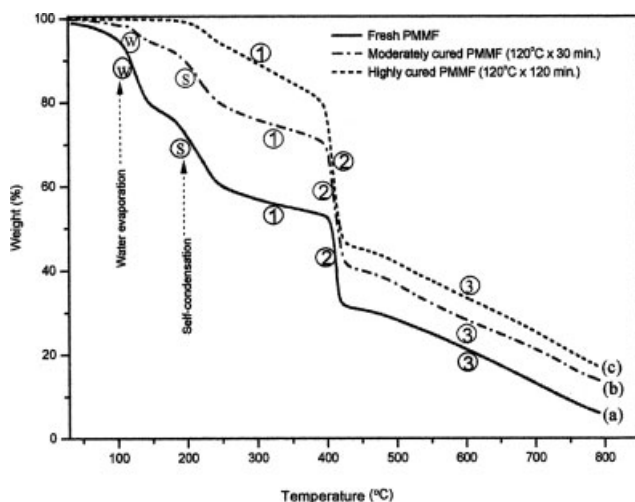
Figure 8 Thermogravimetric curves of PMMF self-condensation.

temperatures scanned from 220 to 800°C, and this is called the thermal degradation behavior of highly self-crosslinked PMMF. Accordingly, it is reasonable to assume that the other two regions of degradation in the early stage (40–220°C) in Figure 8(a,b) can be defined as follows:

The W stage: the initial weight-loss region between 40 and 120°C is mainly due to the evaporation of water contained in fresh PMMF.

The S stage: the second weight-loss region between 120 and 220°C is due to the release of methanol or water, which is a byproduct of PMMF self-condensation.

The thermal degradation behavior of PMMF-crosslinked PU films was measured and is shown in Figure 9. There are two stages of thermal decomposition in the curve of the noncrosslinked PU film (with 0 phr PMMF). The first stage occurs at about 220°C, and the second occurs at about 370°C. Chang et al.[21] reported that the pyrolysis gas product for polyether polyurethane in the first stage is mainly carbon dioxide, which results from the hard segment, whereas the main gas product in the second stage is butyl ether, which results from the soft segment.

In the initial degradation (120–250°C) of PMMF-crosslinked PU films, it can be found that a small amount of weight loss occurs in comparison with the noncrosslinked PU film, and this can be attributed to the further self-condensation of residue end-functional groups contained in PMMF-crosslinked PU films. Focusing on the transition region displayed between 250 and 370°C, we find that with increasing PMMF content, the transition region shifts slightly to higher temperatures. This behavior indi-

cates that with an increase in the PMMF content, the thermal stability of PMMF-crosslinked PU films increases. At the end of degradation above 450°C, melamine residue decomposes gradually.

Dynamic mechanical property analysis

DMA is the most sensitive method for measuring the viscoelastic properties of a polymer as crosslinking proceeds. In this experiment, the effects of the amount of PMMF on the dynamic mechanic properties are shown in Figure 10(a–c), respectively.

The E'–temperature plot is shown in Figure 10(a). A noncrosslinked PU film exhibits a higher E' value than other PMMF-crosslinked PU films at temperatures below −78°C (glassy region), and this can be attributed to the polymer packing ability of molecular chains and the formation of intermolecular hydrogen bonding. The formation of intermolecular hydrogen bonding in aqueous PU dispersions has been reported.[22] The —NH groups in urethane or urea linkages can form a hydrogen bond with the carbonyl group (C=O) of the hard segment or with an ether group (C—O—C) of the soft segment, and this makes a higher ordered structure in the molecular chains. However, the crosslinking reaction of a PU dispersion with PMMF results in the loss of hydrogen (—H) in the urethane or urea groups to react with methylol or methoxymethyl end groups contained in PMMF to form a methylene bridge. Thus, with the disappearance of hydrogen bonding, the packing ability of the polymer decreases. Once the glass-transition temperature is reached, E' decreases rapidly as the polymer chains begin to move. E' continues to decrease until it plateaus around −50°C. However, a turning point occurs at temperature higher than −20°C: PMMF-crosslinked PUs exhibit higher E' than noncrosslinked PU. Also,
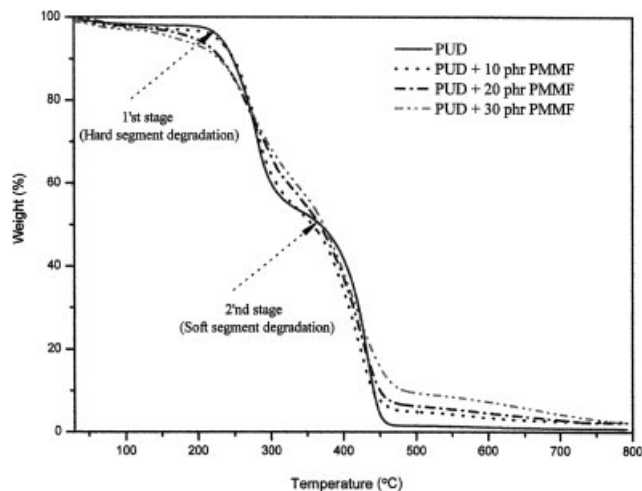

Figure 9 Thermogravimetric curves of PU dispersions crosslinked with PMMF.
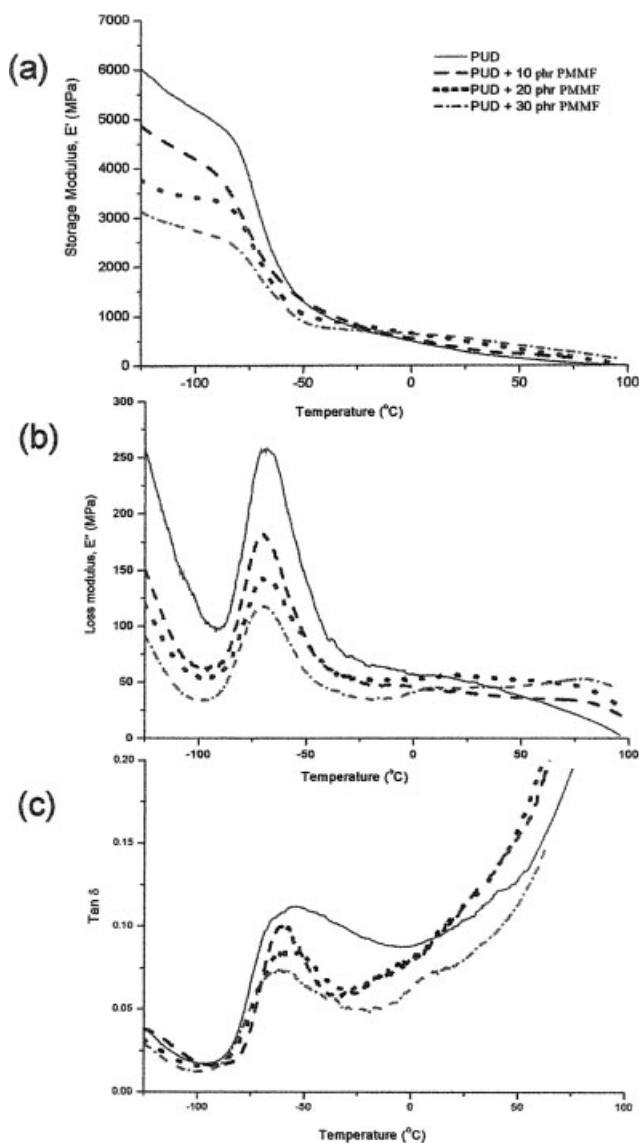
Figure 10 (a) E', (b) E'', and (c) tan δ versus the temperature for PU dispersions crosslinked with PMMF.

TABLE I
Glass-Transition Temperatures of PU Dispersions Crosslinked with PMMF

	Glass-transition temperature (°C)		
PMMF (phr)	Onset of E'	Maximum peak of E''	Maximum peak of tan δ
0	−78	−69	−57
10	−86	−70	−60
20	−83	−70	−58
30	−81	−70	−63

film is broader than that of other PMMF-crosslinked PU films. This broadening is attributed to the higher chain mobility.

In an effort to simplify the determination of the glass-transition temperature, it is commonly defined as tan δ_{max} or the maximum of E''. However, a more accurate determination can be derived from the extrapolated onset of E'. A comparison of these calculation techniques is shown in Table I. A noncrosslinked PU film (with 0 phr PMMF) exhibited a

when a larger amount of PMMF is used, E' of PMMF-crosslinked PU is slightly higher. One possible interpretation is that a highly PMMF branched PU can be formed with a partial crosslinking structure that can restrict the motion of the polymer chains. These measurements provide evidence that cured films are more flexible at higher temperatures. These results are consistent with the E'' measurements in Figure 10(b); the higher values of E'' suggest the great mobility of the polymer chains associated with the dissipation of energy when the polymer is subjected to deformation.

In Figure 10(c), the value of the maximum of the loss tangent (tan δ_{max}), that is, the peak height, is a direct measure of the degree of crosslinking. The lower tan δ_{max} is, the higher the degree of crosslinking is. Also, the tan δ peak of a noncrosslinked PU
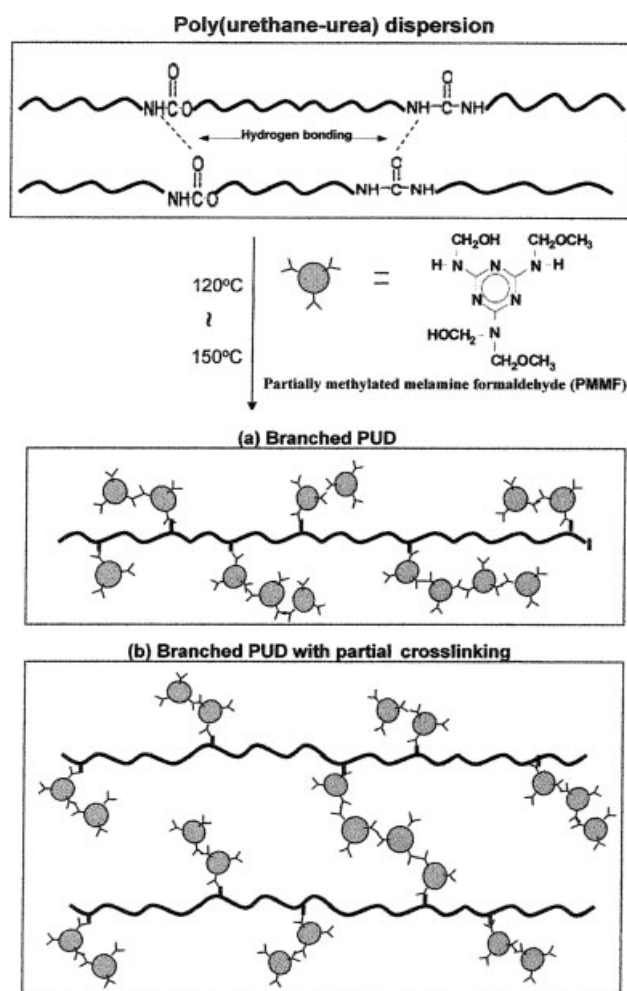

Figure 11 Possible approaches of PU dispersions crosslinked with PMMF.

higher glass-transition temperature than PMMF-crosslinked PU films because of the formation of intermolecular hydrogen bonding. The single glass-transition temperature for each sample suggests that phase separation did not occur in this experiment.

On the basis of this curing behavior and the DMA test results, it is reasonable to assume that a highly PMMF branched PU with a partial crosslinking structure can be formed. Possible approaches are presented in Figure 11.

CONCLUSIONS

The isothermal cure behavior of anionic poly(urethane urea) dispersions crosslinked with different amounts of PMMF was observed with a rigid-body pendulum rheometer. The results showed that the higher the PMMF content was, the faster the curing speed was, and they indicated that 30 phr could be the optimum amount of the crosslinking agent (PMMF) and that 120°C was the optimum temperature for the curing process. In addition, PMMF self-condensation could take place during the curing process. The self-condensation of PMMF also could be monitored by a thermogravimetric method. Moreover, the reaction rate of a PU dispersion crosslinked with PMMF was faster than the self-condensation of PMMF. From the DMA test results, it was clear that a noncrosslinked PU film exhibited a higher E' value than PMMF-crosslinked PU films at the temperatures below the glassy region, and this could be attributed to the packing ability of the polymer. However, a turning point occurred at temperatures higher than $-20°C$; PMMF-crosslinked PUs exhibited higher E' than noncrosslinked PU. One possible interpretation is that a highly PMMF branched PU can be formed with a partial crosslinking structure that can restrict the motion of the polymer chains.

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