Colloid Polym Sci (2007) 285:1331–1342
DOI 10.1007/s00396-007-1690-0

ORIGINAL CONTRIBUTION

Structure–property relationships of anionic poly(urethane–urea) dispersion cross-linked with partially methylated melamine formaldehyde

Hsien-Tang Chiu · Yi-Chin Huang

Received: 12 February 2007 / Accepted: 27 April 2007 / Published online: 21 June 2007

Abstract An anionic poly(urethane–urea) dispersion (PUD) was cross-linked with different amount of partially methylated melamine formaldehyde (PMMF). The isothermal curing behavior was observed by a rigid-body pendulum rheometer. The test results showed that cure response of PUD cross-linked with PMMF was a function of the concentration of PMMF. Also, PMMF self-condensation could take place during the curing process. In this experiment, the anionic poly(urethane–urea) dispersion has a large number of >N–H cross-linking or branching sites in urethane and urea groups per molecule that allow a large number of PMMF to couple into elastic PUD backbone to form branched structure with partial cross-linking. The dynamic mechanical properties of PUD cross-linked with PMMF were affected by the concentration of PMMF. It was further shown that the tensile properties were strongly influenced by the concentration of PMMF and curing temperature.

Keywords Poly(urethane–urea) dispersion · Methylated melamine formaldehyde · Self-condensation

Introduction

An aqueous polyurethane dispersion is a binary colloidal system in which polyurethane particles are dispersed in a continuous aqueous medium. To be dispersible in water, polyurethane should contain ionic and/or non-ionic hydrophilic segments in its structure [1, 2]. Aqueous polyurethane dispersions can be formulated into coatings and adhesives containing little or no cosolvent, and hence, they are nontoxic, nonflammable, and do not pollute the air. In our previous study [3] on the preparation and characterization of isocyanic acid, *m*-phenylenediiso-propylidene (*m*-TMXDI)-based poly(urethane–urea) dispersions containing various amount of 2,2-bis(hydroxyl methyl) propionic acid (DMPA), the result showed that the average particle size of poly(urethane–urea) dispersions were decreased with an increase in DMPA content, and this led to an increase in viscosity. However, aqueous polyurethane dispersions are deficient in chemical resistance compared to cross-linked, two-pack solvent-based polyurethane because most waterborne polyurethane are linear thermoplastic polymers which allows resolubility in solvents. To improve their properties such as solvent and chemical resistance, many different strategies have been pursued in the cross-linking of aqueous polyurethane dispersions. Aqueous polyurethane dispersions can be cross-linked at room temperature and elevated temperature. Polyaziridines and carbodiimides are available for low-temperature cross-linking through the carboxylic acid groups [4, 5]. For high-temperature cross-linking, methylated melamine formaldehyde resins are the most versatile cross-linking agents for many polymer systems that may include polyurethane dispersions [6–9]. 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 formaldehyde is a complex mixture of melamine with different degrees of hydroxymethylation and methoxymethylation [13]. In spite

H.-T. Chiu (✉)
Graduate School of Polymer Engineering,
National Taiwan University of Science and Technology,
Taipei 106 Taiwan, China
e-mail: jy.tech@msa.hinet.net

Y.-C. Huang
Graduate Institute of Materials Science and Technology,
National Taiwan University of Science and Technology,
Taipei 106 Taiwan, China

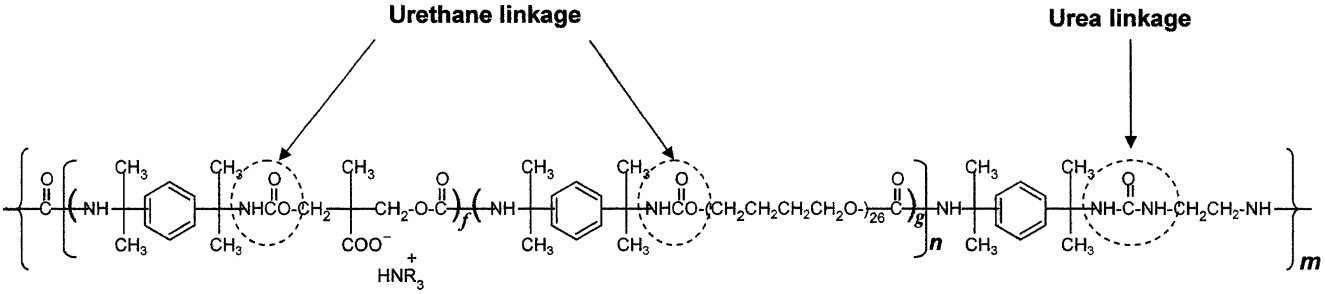


Fig. 1 Chemical structure of anionic poly(urethane–urea) dispersion

of the extensive industrial applications of melamine resins, characterization of these resins has been a difficult task because of their complex compositions. Methylated melamine formaldehyde resins are commonly known as melamine resins. They are widely used in various industries as binder components and cross-linkers. Melamine resins are synthesized by reacting the primary amino groups of melamine with formaldehyde to form hydroxymethyl groups and converting 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 a "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 degrees of hydroxymethylation, *x*, and of methyl end-capping, *y*. The different groups that are found in the melamine formaldehyde resin are methylol ($–CH_2OH$), alkoxymethyl ($–CH_2OR$), imino (>N–H), and acetal ($–CH_2OCH_2OR$) end groups which have a high tendency towards self-condensation [15]. The basic reactions of the functional groups have been discussed by Blank and Hensley [16]. In self-condensation, functional groups on the melamine formaldehyde molecules react with each other, causing undesirable properties. It has been shown that alkoxy groups do not self-condense to any appreciable extent even under strong acid catalysis [17].

It is generally accepted that molecular mobility is an important factor in determining the macroscopic mechanic properties. As far as the networks are concerned, one of the important factors used for changing their properties is the type of cross-linking agent [18–21]. Often enough, in PU system, two kinds of networks can be present: physical and chemical. The physical network is created by the hydrogen bonds, which link the carbonyl groups and NH groups of adjacent chains [22, 23]. Chemical network parameters depend on the cross-linker nature.

In this article, the polyurethane dispersion based on *m*-TMXDI was cross-linked with different amount of partially methylated melamine formaldehyde at constant temperature. The curing behavior was observed by rigid body pendulum rheometer, and the effect of partially methylated melamine formaldehyde content and curing temperature on the dynamic mechanical properties and tensile properties was described.

Experimental

Materials

Isocyanic acid, *m*-phenylenediiso-propylidene (*m*-TMXDI, extra pure grade), was obtained from Tokyo Kasei Kogyo, Japan. 2,2 Bis(hydroxyl methyl) propionic acid (DMPA) was obtained from Lancaster Synthesis, USA. Poly(tetramethylene) ether glycol (PTMEG, M_n=2,000) was obtained from Scientific Polymer Products, USA. Triethylamine (TEA), 1,2-ethylene diamine (EDA), and *N*-methyl 1-2-pyrrolidone (NMP) were obtained from Tedia, USA.

Preparation of anionic poly(urethane–urea) dispersion (PUD)

(1) Preparation of isocyanate terminated prepolymer

In this experiment, PUD-8 was chosen as reported in our previous article [3]; *m*-TMXDI-based anionic poly(urethane–urea) dispersion was prepared by the prepolymer mixing process. The composition of isocyanate-terminated prepolymer is given as follows:

- *m*-TMXDI (wt%): 38.07
- DMPA (wt%): 8
- PTMEG (wt%): 53.93
- NMP (wt%): 10

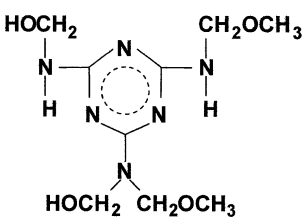


Fig. 2 Chemical structure of partially methylated melamine formaldehyde

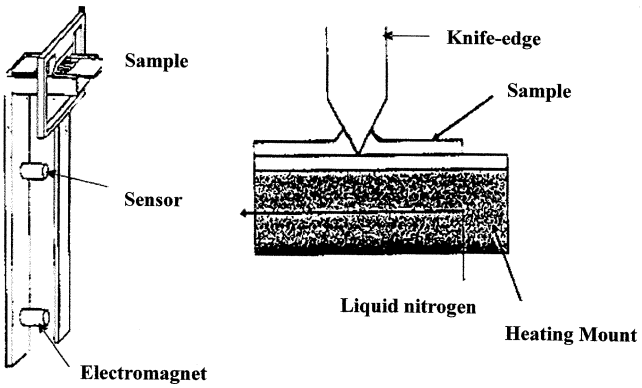


Fig. 3 The device of rigid-body pendulum rheometer

(2) Neutralization

The stoichiometric amount of TEA was added to ensure the complete neutralization of the carboxylic group of prepolymer.

(3) Water dispersion

An aqueous prepolymer dispersion was obtained by adding the neutralized prepolymer into a flask containing distilled water.

(4) Chain extension

Chain extension was carried out by adding stoichiometric amount of EDA.

The chemical structure of anionic polyurethane dispersion is presented as Fig. 1.

Cymel-385, partially methylated melamine formaldehyde (PMMF) was obtained from Cytec, USA. The structures 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. The representative chemical structure of PMMF is shown as Fig. 2.

Samples prepared for rigid-body pendulum rheometer

Samples were prepared by mixing PUD with levels of 0, 5, 10, 20, 30, and 40 phr (parts per hundred) PMMF.

Film preparation for mechanic properties analysis

Films were prepared by casting PUD mixed with PMMF on silicone-coated surface and allowing them to dry at room temperature for 2 days and curing at 120 or 150 °C for 30 min.

Rigid-body pendulum rheometer measurement

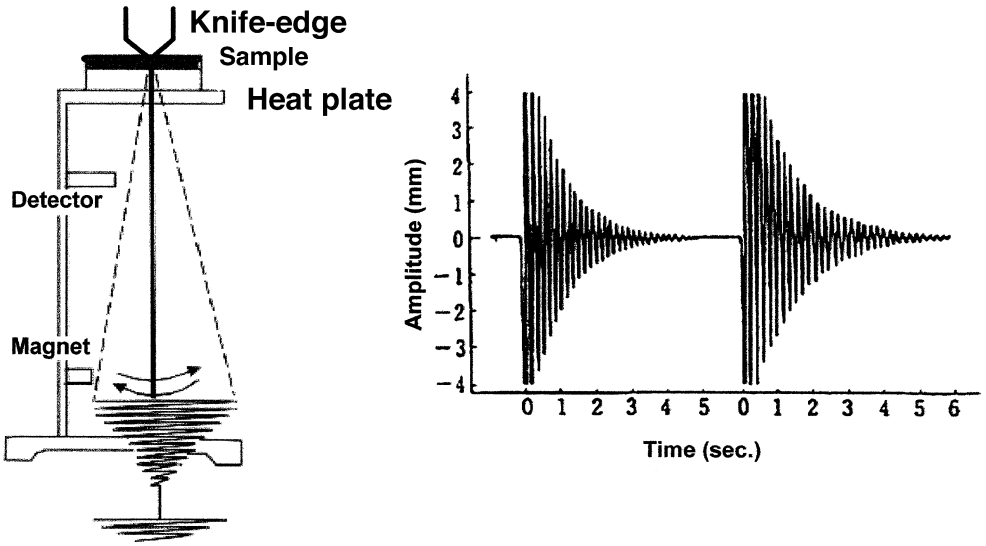
Curing process measurements were taken with a rigid-body pendulum rheometer (Model No. α-100, Tohoku Electronic Industrial, Japan). A frame-type pendulum (FRB-100) with knife edge (RBE-130) was chosen.

Principle of the rigid-body pendulum rheometer

It is possible to use the instrument with free damping pendulum system to observe the drying or curing behavior, which 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 [24, 25]. The test piece was fixed by coating or setting on a plate and placing 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 Fig. 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 piece. As a result, the viscoelastic property of

Fig. 4 The oscillation pattern of the pendulum



the test pieces created swinging period of the pendulum and swing damping action. By measuring the time variation of this period of oscillation (t) of the pendulum, the curing behavior of the test piece could be obtained with the following equation:

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

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

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

The viscosity (η)of test substance had a function of stopping oscillation of the pendulum, which was in contact with the test sample. Viscosity (η) can be evaluated by the following equations:

$$\eta = kM^{\theta} \quad (2)$$

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

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

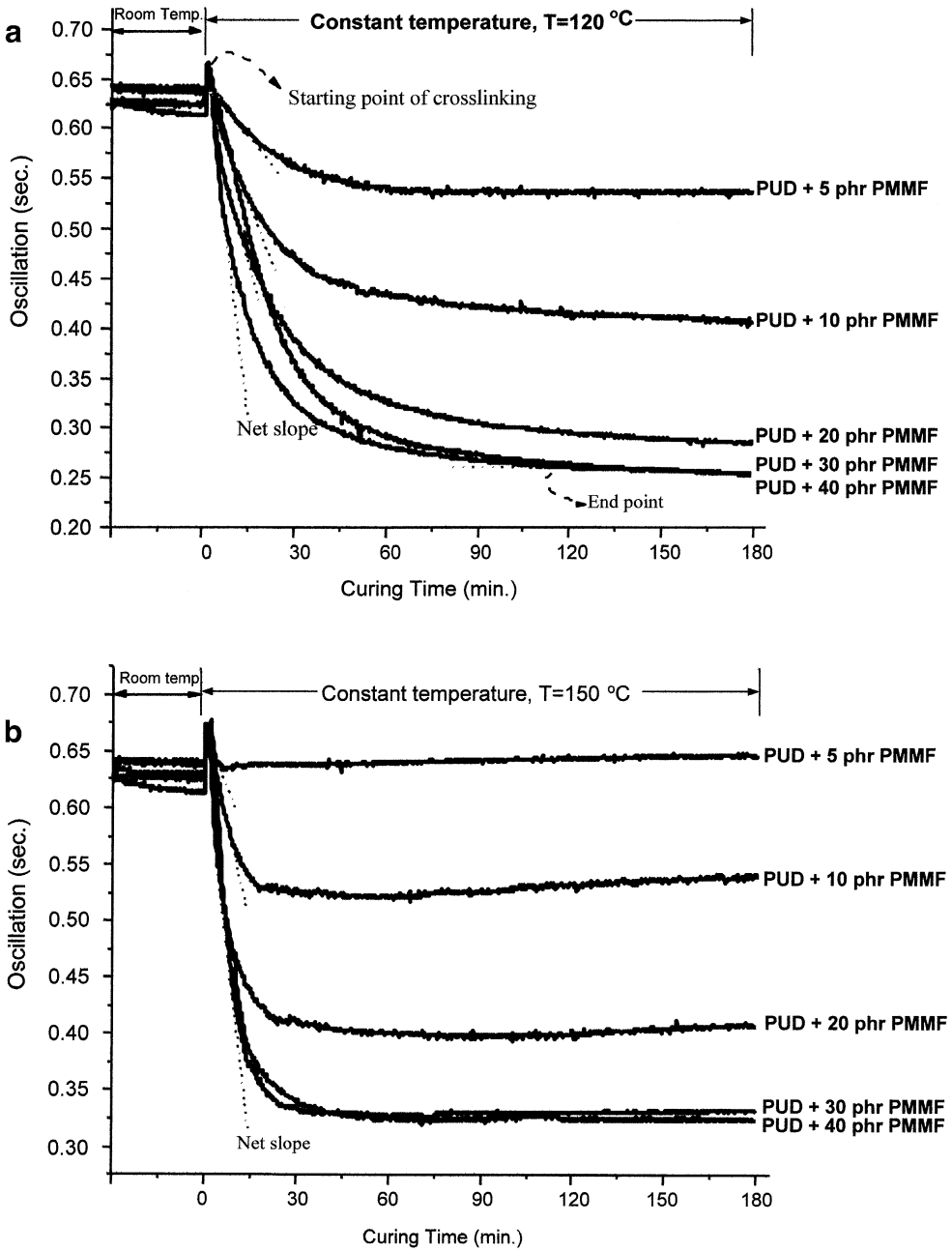


Fig. 5 Isothermal curing behavior of PUD cross-linked with various amount of PMMF: **a** at 120 °C; **b** at 150 °C

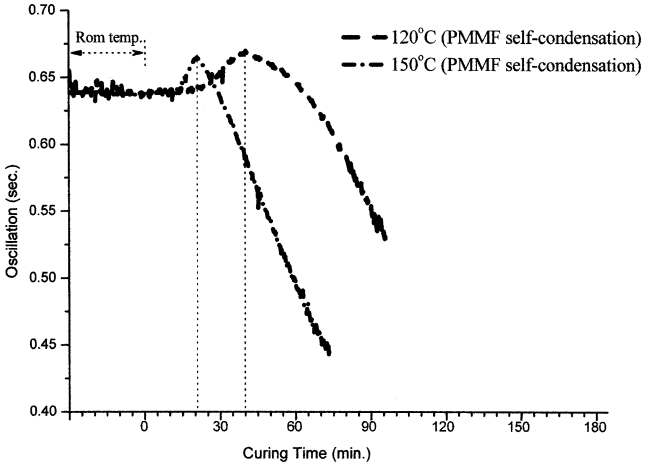


Fig. 6 Isothermal curing behavior of PMMF self-condensation

This realized the structure change of the transition process from liquid to solid film on the measurement of frequency of oscillation.

Thermal gravimetric analysis

The thermal degradation behavior was carried out using thermal gravimetric analyzer (TGA-Q500, TA Instruments) from room temperature to 800 °C at heating rates 10 °C/min under nitrogen atmosphere.

Dynamic mechanical properties analysis

Dynamic mechanical analysis (DMA, Model No. TA-Q800, TA Instruments) was used with a heating rate of 5 °C/min within the range from −150 to 50 °C under a frequency of 1 Hz for temperature scanning.

Tensile mechanical properties analysis

Stress–strain experiments were performed using dog bone samples cut from a die as specified in ASTM D2370, and the tensile testing was performed on a universal tensile testing machine (model AG-IS, Shimadzu) at a crosshead displacement rate of 15 mm/min.

Results and discussion

Curing behavior of poly(urethane–urea) dispersions cross-linked with partially methylated melamine formaldehyde

In this experiment, a rigid-body pendulum rheometer is used to observe the isothermal cure behavior of PUD cross-linked with different amount of PMMF. The effect of PMMF concentration on the isothermal curing behavior is shown in Fig. 5a and b.

During the curing period, the oscillation period (t) was decreased gradually due to the increase of the viscosity (η) of test sample, which is dependent on the degree of physical networking (entanglement) or chemical networking (cross-linking). Also, the net slope of isothermal curing curve gives information on the curing speed of PUD cross-linked with different amount of PMMF. It is obviously to find that the higher the PMMF content the faster the curing speed. At the final stage, the curve becomes flatter; the last equilibrium point is called the end point, which indicates

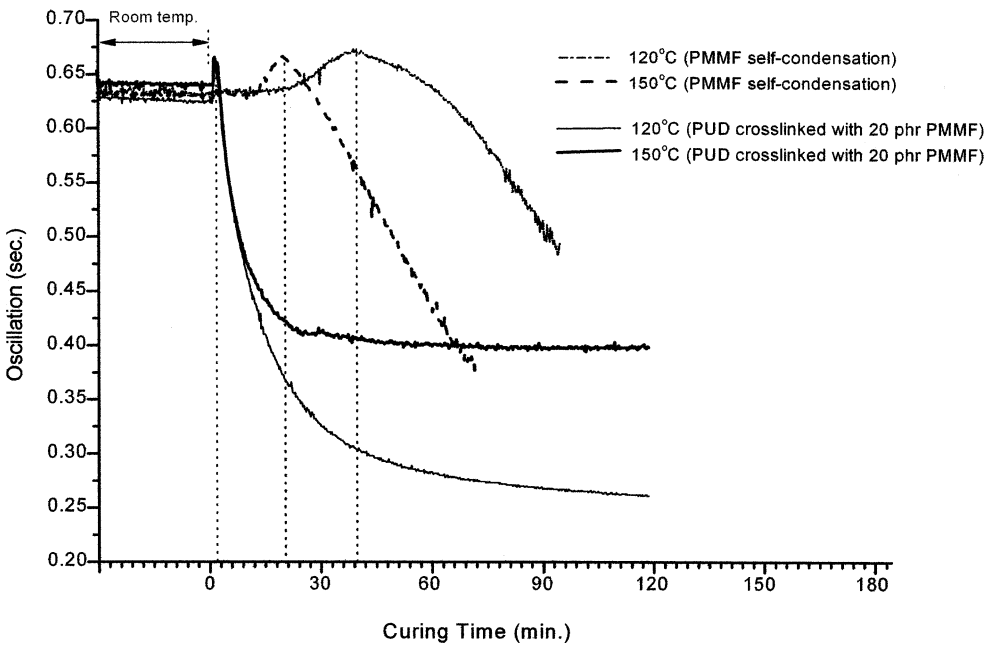


Fig. 7 A comparison of the curing curves of PMMF self-condensation and PUD cross-linked with PMMF

that the curing reaction reaches balance status. As a result, the higher the PMMF content the lower the equilibrium oscillation period (t). However, PUD cross-linked with 40 phr PMMF has a minimum equilibrium oscillation period (t), which is very closed to that cross-linked with 30 phr PMMF. This seems to indicate that the 30 phr PMMF used can be the effective amount of cross-linking agent for PU dispersion.

Owing to the end groups contained in PMMF are imino (>NH), methylol (–CH_2OH) and methoxymethyl (–CH_2OCH_3) groups which have a high tendency towards self-condensation to form methylene (–CH_2–) and methylene ether (–CH_2–O–CH_2–) bridges [15]. Figure 6 shows the curing curves of PMMF self-condensation at constant temperature. It is clear that the reaction rate of PMMF self-condensation at 150 °C is faster than that at 120 °C. In Fig. 7, a comparison of the curing behavior of PMMF self-condensation and PUD cross-linked with PMMF shows the different reaction rates between these competing reactions. At the early stage, the time required to reach the tip of inflection (starting point of cross-linking) for PUD cross-linked with PMMF is shorter than the time required for PMMF self-condensation; it reveals that the reaction rate of PUD cross-linked with PMMF is faster than PMMF self-condensation. Furthermore, the curing curve of PUD cross-linked with PMMF can reach balance status and become flatter at the final stage, which indicates that PUD cross-linked with PMMF goes virtually to completion. In contrast, the curing reaction of PMMF self-condensation occurs to a significant degree, but does not approach balance status.

It is obvious that PMMF self-condensation could take place during the curing process. Higher reaction temperature should promote the reaction of PMMF self-condensation.

Self-condensation of PMMF

The self-condensation reaction of PMMF can also be monitored by thermal gravimetric method. In Fig. 8, the thermal degradation behavior of (a) fresh PMMF, (b) moderately self-cross-linked PMMF, and (c) highly self-cross-linked PMMF are displayed.

It is clear that there are three distinct regions of degradation on curve c, three successive weight loss regions appeared from (1) 220∽400 °C, (2) 400∽420 °C, and (3) T>420 °C. The decomposed gas might contain methanol, formaldehyde, and carbon dioxide as well as ammonia and some impurities [26]. By comparing the degradation route as shown on curves a, b, and c, notice that the pattern of these three routes are very similar at temperature scanned from 220 to 800 °C, which is referred to as the thermal degradation behavior of highly self-cross-linked PMMF. Accordingly, it is reasonable to assume that two regions of degradation at the early stage (40–220 °C) on curves a and b can be defined as follows:

(W) stage— the initial weight loss region occurred between 40 and 120 °C is mainly due to

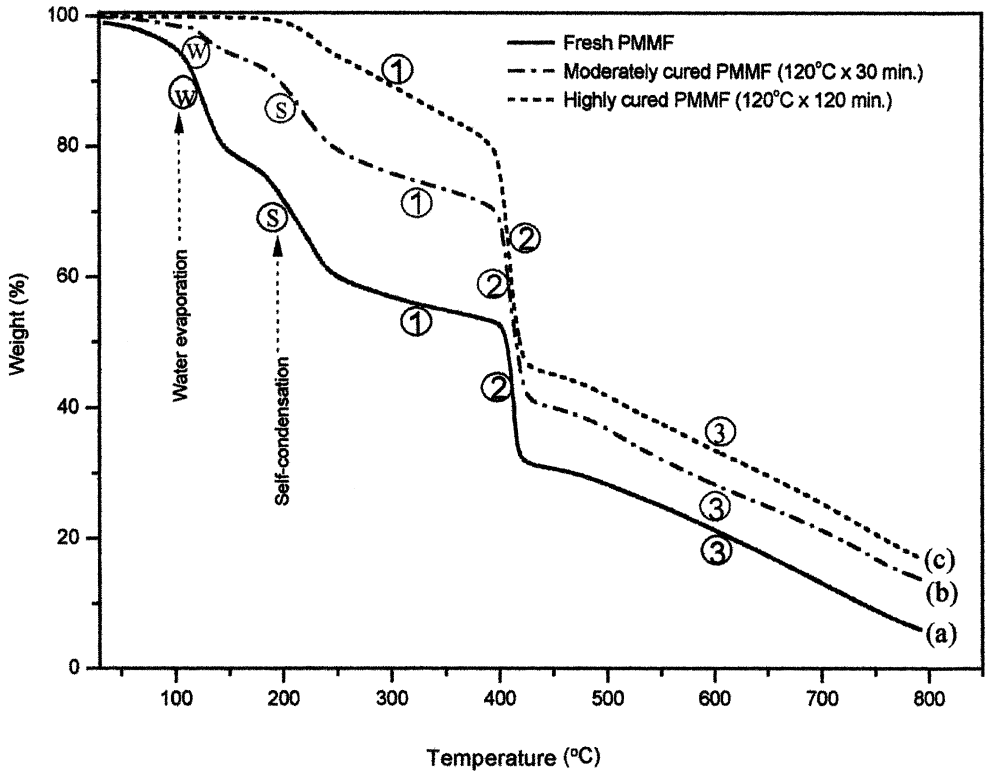


Fig. 8 Thermal gravimetric curves of PMMF self-condensation

the evaporation of water which is contained in fresh PMMF.

(S) stage— the second weight loss region occurred between 120 and 220 °C is due to the release of methanol or water which is a by-product of PMMF self-condensation.

Cross-linking mechanism

The desired cross-linking reaction of PUD with PMMF results in the loss of hydrogen (–H) in the urethane (~NHCOO~) or urea (~NHCONH~) groups to react with methoxymethyl ($–CH_2OCH_3$) or methylol ($–CH_2OH$) end groups contained in PMMF to form a methylene ($–CH_2–$) bridge. It can be presented as follows:

(a) ~OOC–NH~ + $CH_3O\ CH_2N<$ → ~OOC–N–CH_2–N< + CH_3OH

(b) ~OOC–NH~ + $HOCH_2N<$ → ~OOC–N–CH_2–N< + H_2O

(c) ~NHCONH~ + $CH_3O\ CH_2N<$ → ~NHCO–N–CH_2–N< + CH_3OH

(d) ~NHCONH~ + $HOCH_2N<$ → ~NHCO–N–CH_2–N< + H_2O

In this experiment, the anionic poly(urethane–urea) dispersion has a large number of $-\overset{H}{N}-$ sites in urethane and urea linkage per molecule. The average number of cross-linking or branching site per chain ($\overline{X}_s$) can be calculated as follows:

$$\overline{X}s = (N_{NHCOO} \times n \times m) + (N_{NHCONH} \times m) \quad (4)$$

Where

N_{NHCOO} no. of cross-linking or branching site in urethane linkage

N_{NHCONH} no. of cross-linking or branching site in urea linkage

n degree of polymerization of prepolymer

m degree of chain extension,

$$\left\{ m \cong \frac{\overline{M}n \text{ of chain extended poly(urethane–urea)}}{\overline{M}n \text{ of prepolymer+M.W. of chain extender}} \right\}$$

As reported in our previous article [3], $N_{NHCOO}=1$, $N_{NHCONH}=2$, $n \cong 1.25$, and $m \cong 5$. Hence, the average number of cross-linking or branching site ($\overline{X}s$) is approximately 16.

Owing to the end groups contained in PMMF are imino (>NH), methylol ($–CH_2OH$), and methoxymethyl ($–CH_2OCH_3$) groups which have a high tendency towards self-condensation to form methylene ($–CH_2–$) and methylene ether ($–CH_2–O–CH_2–$) bridges [15]. The PMMF self-condensation can be presented as follows:

(e) $>NCH_2OCH_3 + HN< \rightarrow >N–CH_2–N< + CH_3OH$

(f) $>NCH_2OCH_3 + HOCH_2N< \rightarrow >NCH_2–O–CH_2N< + CH_3OH$

(g) $>NCH_2OH + HN< \rightarrow >N–CH_2–N< + H_2O$

(h) $>NCH_2OH + HOCH_2N< \rightarrow >NCH_2–O–CH_2N< + H_2O$

As shown in Fig. 7, the reaction rate of PUD cross-linked with PMMF is faster than PMMF self-condensation, which indicates that the branched PUD could be formed at the early stage. Possible approaches are described in Fig. 9.

Dynamic mechanical properties analysis

Dynamic mechanical analysis (DMA) is the most sensitive method for measuring the viscoelastic properties of a polymer as cross-linking proceeds. In this experiment, the effect of amount of PMMF on the dynamic mechanic properties is shown in Fig. 10a–c, respectively.

The storage modulus (E') versus temperature (T) plot is shown in Fig. 10a. It is clear that non-PMMF-cured PUD film exhibits high storage modulus than other PUD cross-

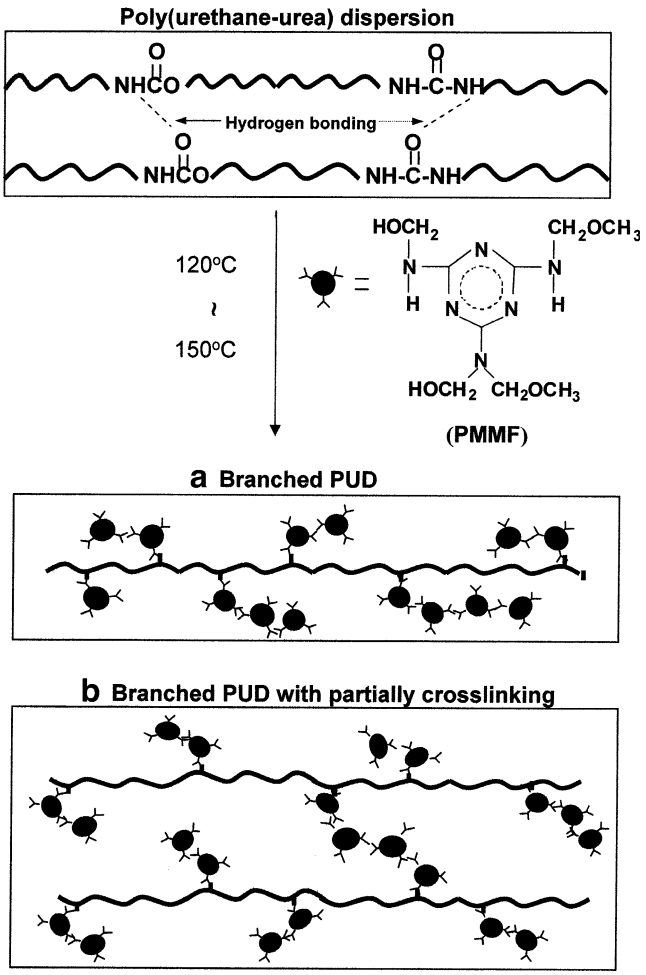


Fig. 9 Possible approaches of PUD cross-linked with PMMF

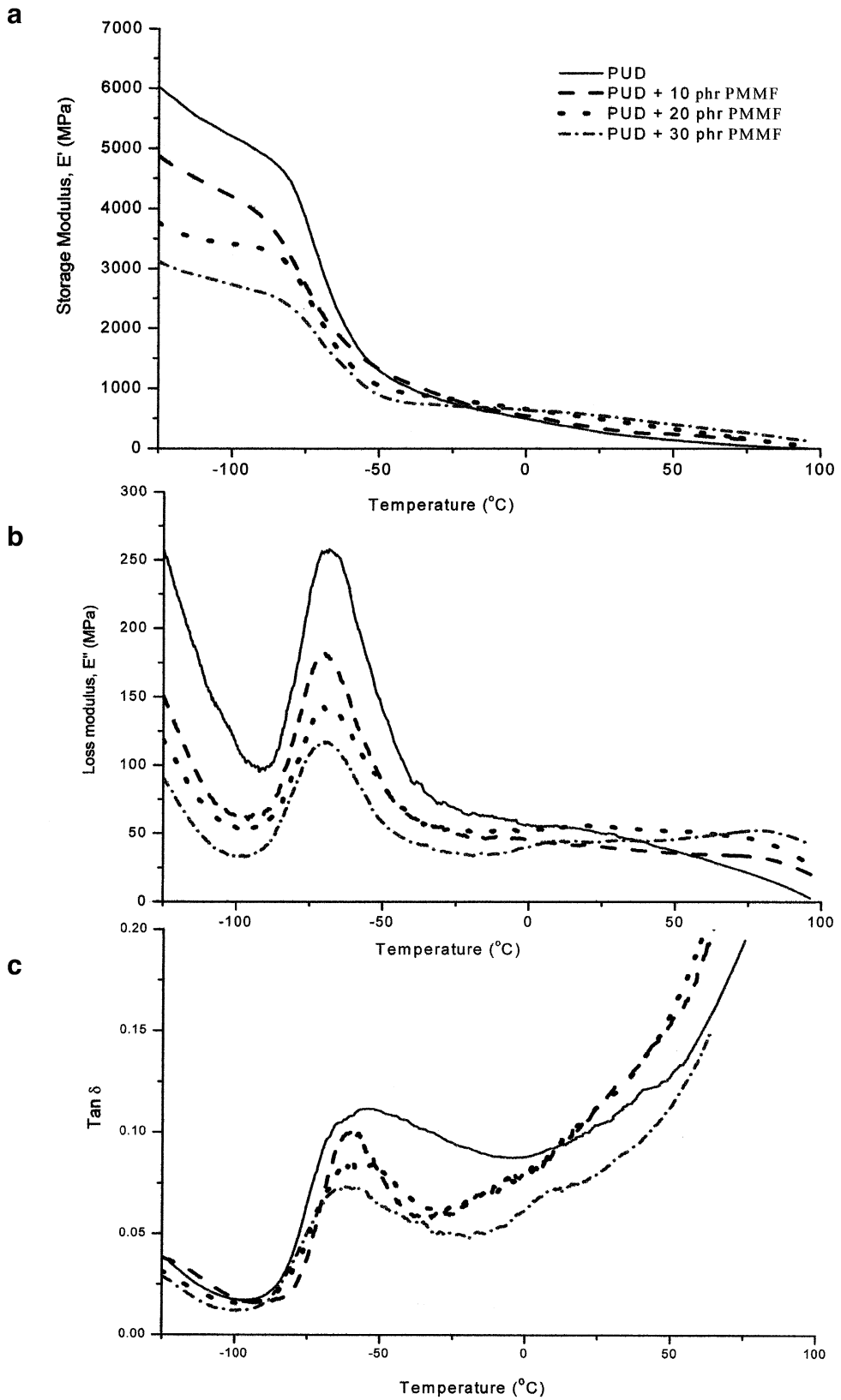


Fig. 10 **a** Storage modulus, **b** loss modulus, and **c** loss tangent versus temperature plots of PUD cross-linked with PMMF

Table 1 The glass transition temperature of PUD cross-linked with various amounts of PMMF

PMMF content (phr)	Onset of E' (°C)	Peak $_{max}$ of E'' (°C)	Peak $_{max}$ of tan δ (°C)
0	−78	−69	−57
10	−86	−70	−60
20	−83	−70	−58
30	−81	−70	−63

linked with PMMF, which scanned at the temperature below −78 °C (glassy region); this is attributed to the polymer packing ability of molecular chains. In non-PMMF-cured PUD, the hydrogen bonds$_H$ are formed between intermolecular chains [23]. The $-N-$ groups in urethane or urea linkage 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, which makes higher ordered structure in molecular chains. However, the cross-linking reaction of PUD 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. Thus, the polymer packing ability decreases due to the disappearance of hydrogen bonding. Once the glass transition temperature is reached, the storage modulus (E') decreases rapidly as the polymer chains begin to move. The storage modulus continue to decrease until it plateaus at around −50 °C. However, a turning point occurs at temperature scanned higher than −20 °C; PMMF-cross-linked PUD exhibit higher storage modulus than non-cross-linked PUD. Also, the higher the PMMF amount used, the slightly higher the storage modulus of PMMF-cross-linked PUD. One possible interpretation is that highly PMMF-branched PU with partial cross-linking structure can be formed, which can restrict the motion of polymer chains. These measurements provide evidence that PUD cross-linked with PMMF is more flexible at higher temperature. These results are consistent with the loss modulus (E'') measurements in Fig. 10b. The higher values of loss modulus suggest the great mobility of the polymer chains associated with the dissipation of energy when the polymer is subjected to deformation.

In Fig. 10c, the value of tan δ_{max}, i.e., peak height, is a direct measure the degree of cross-linking. The lower the tan δ_{max}, the higher the degree of cross-linking. Also, the loss tangent peak of non-PMMF-cured PUD film is broader than other PUD cross-linked with PMMF. This broadening is attributed to the higher chain mobility.

In an effort to simplify the determination of glass transition temperature (T_g), it is commonly defined as the maximum of loss tangent (tan δ_{max}) or maximum of loss modulus (E''_{max}). However, more accurate determination can be derived from the extrapolated onset of the storage modulus (E'_{onsset}). A comparison of these calculation techniques is shown in Table 1. Non-PMMF-cured PUD film exhibited higher T_g than PUD cross-linked with

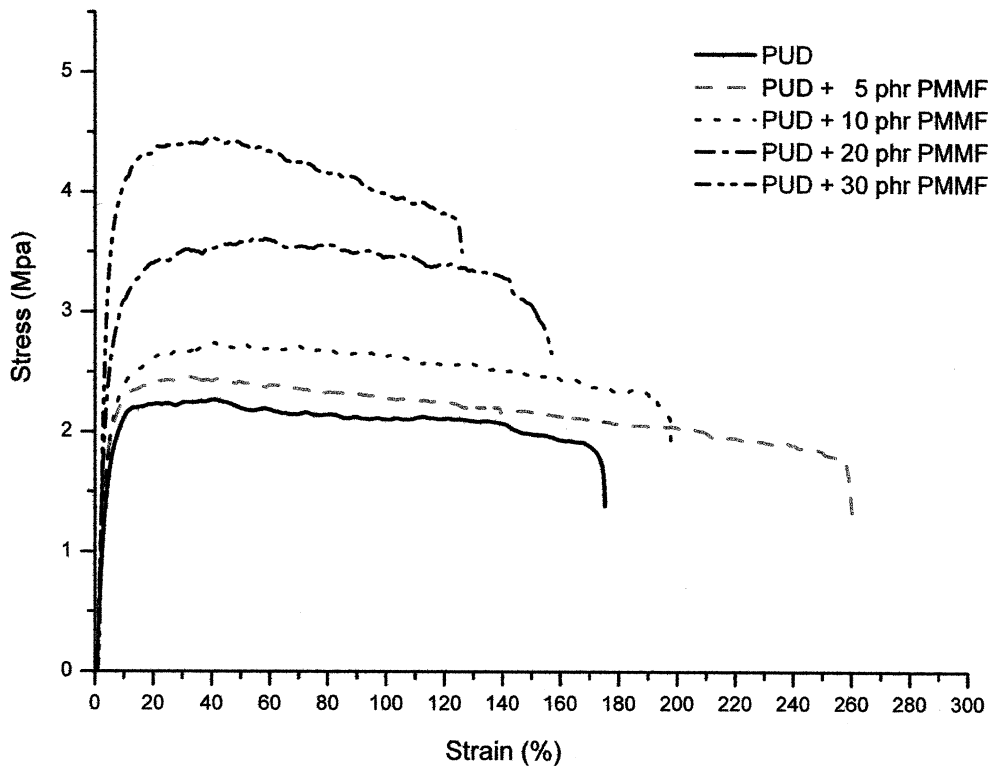


Fig. 11 Stress–strain curve of PUD cross-linked with various amounts of PMMF (120 °C× 30 min)

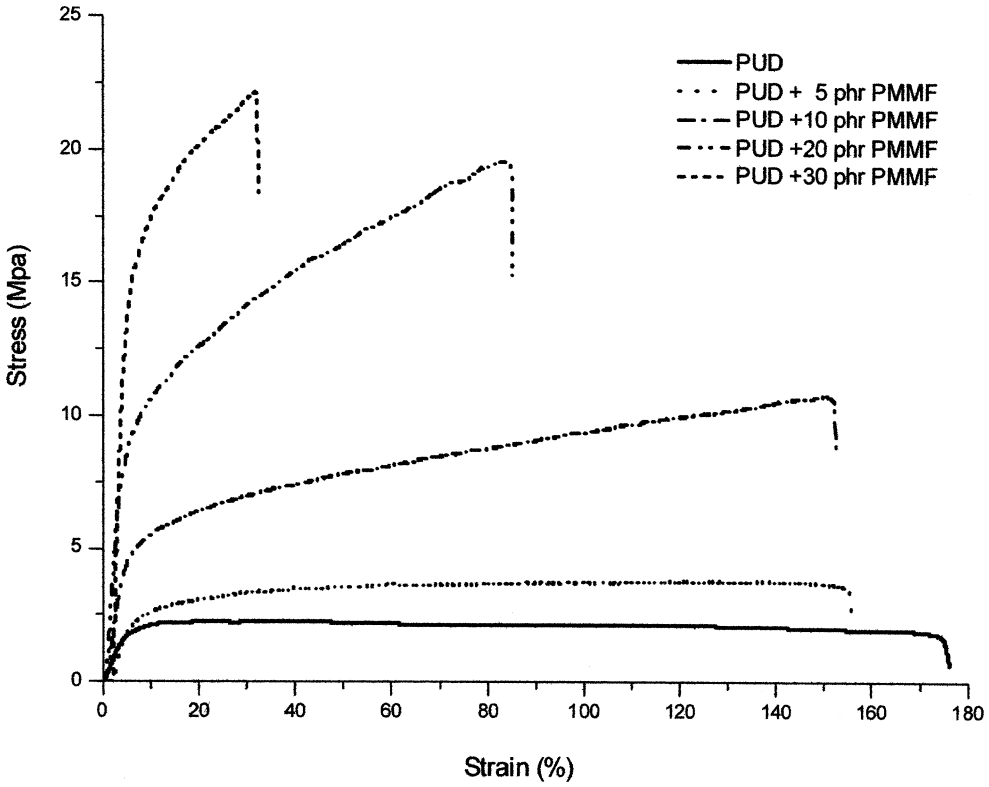


Fig. 12 Stress–strain curve of PUD cross-linked with various amounts of PMMF (150 °C× 30 min)

PMMF due to the formation of physical network by intermolecular hydrogen bonding between the urethane and urea groups, which control the molecular mobility. The single T_g for each sample suggests that phase separation did not occur in this experiment.

Based on the above observation, the various amounts of PMMF used for cross-linking of PUD have a significant effect on the dynamic mechanical properties.

Mechanical properties

The stress–strain curve for PUD cross-linked with PMMF is shown in Figs. 11 and 12. The curve gives information about the tensile strength (σ_b), strain at break (ε_b), and Young's modulus (slope at the initial stage). The experiment data are summarized in Tables 2 and 3. The tensile properties are strongly influenced by the amount of PMMF used and the curing temperature.

It is clear that all PUD cross-linked with PMMF exhibited higher tensile strength (σ_b) and Young's modulus than that of non-PMMF-cured PUD film. The initial slopes of stress–strain curves for PUD cross-linked with various amounts of PMMF are much different. The initial slope increases with increasing the concentration of PMMF due to the formation of branched PUD with partial cross-linking, which causes increase in macromolecular chain entanglement and decrease in chain orientation. Therefore, this chain resistance to orientation gives higher tensile strength at the initial strain.

It should be noted that the test results in Fig. 11, the tensile strength (σ_b), and strain at break (ε_b) for 5 and 10 phr PMMF cured at 120 °C are higher than that of non-PMMF-cured PUD.

It is reasonable to assume that PMMF-branched PUD are formed while cross-linking is absent, which results in the loss of hydrogen bonding between intermolecular chain. So, the macromolecular chains are free to flow and be oriented in the direction of the applied stress; this contributes to the elongation enhancement.

Table 2 Mechanical properties of PUD cross-linked with PMMF (120 °C×30 min)

Sample	Initial strength (MPa)	Tensile strength (MPa)	Strain at break (%)	Young's modulus (MPa)
PUD	2.03	1.89	175	0.35
PUD + 5 phr PMMF	2.24	1.75	260	0.49
PUD + 10 phr PMMF	2.52	2.24	195	0.53
PUD + 20 phr PMMF	3.36	3.15	145	0.84
PUD + 30 phr PMMF	4.34	3.78	125	0.98

Table 3 Mechanical properties of PUD cross-linked with PMMF (150 °C×30 min)

Sample	Initial strength (MPa)	Tensile strength (MPa)	Strain at break (%)	Young's modulus (MPa)
PUD	2.03	1.89	175	0.35
PUD + 5 phr PMMF	2.66	3.64	157	0.42
PUD + 10 phr PMMF	5.25	10.50	152	1.12
PUD + 20 phr PMMF	8.75	18.55	85	2.38
PUD + 30 phr PMMF	16.1	22.4	32	3.64

As shown in Fig. 12, the test films were cured at 150 °C. We found that the tensile strength (σ_b) increased from 1.89 to 22.4 Mpa, and strain at break (ε_b) decreased from 175 to 32% with an increase in the amount of PMMF. This strong decrease in strain at break with high tensile strength is accompanied by PMMF-branched PUD with partial cross-linking. Also, the effect of curing temperature on tensile properties is shown in Fig. 13. PUD cross-linked with PMMF cured at 150 °C possesses higher tensile strength (σ_b) and lower strain at break (ε_b) compared with that cured at 120 °C; this indicated that the further PMMF self-condensation and partial cross-linking reactions are promoted at elevated cure temperature, leading to an improvement of the tensile strength.

Conclusions

An anionic poly(urethane–urea) dispersion was cross-linked with different amounts of PMMF. The results showed that PMMF self-condensation could take place during the curing process. Owing to PUD has a large number of >N–H cross-linking or branching sites in urethane and urea groups per molecule, which allows a large number of PMMF to couple into elastic PUD backbone to form branched structure with partial cross-linking. From the DMA test results, it is clear that non-cross-linked PUD exhibits high storage modulus value than PMMF-cross-linked PUD at the temperature scanned below glassy region; this is attributed to the polymer packing ability. However, a turning point occurs at temperature scanned higher than −20 °C; PMMF-cross-linked PUD exhibits higher storage modulus than non-cross-linked PUD due to PMMF-branched PUD structure formed with partial cross-linking, which can restrict the motion of polymer chains. The tensile properties are strongly influenced by the amount of PMMF used and the curing temperature. This strong decrease in strain at break with high tensile strength is accompanied by PMMF-branched PUD with partial cross-linking.

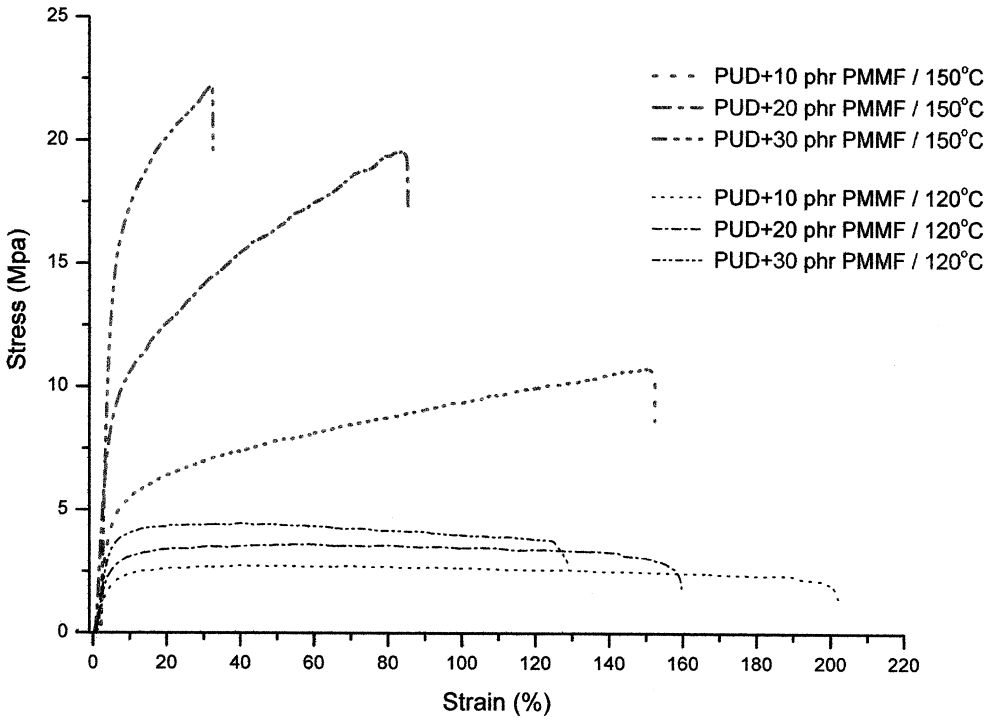


Fig. 13 The effect of curing temperature on the tensile properties of PUD cross-linked with PMMF

References

1. Dieterich D (1981) Prog Org Coat 9:281
2. Kwak YS, Kim EY, Yoo BH, Kim HD (2004) J Appl Polym Sci 94:1743
3. Chiu HT, Huang YC, Hu HY (2006) J Appl Polym Sci 102:5737
4. Lai JZ, Chang YC, Yeh JT, Chen KN (2004) J Appl Polym Sci 97:1997
5. Chen GN, Chen KN (1998) J Appl Polym Sci 67:661
6. Coogan RG (1997) Prog Org Coat 32:51
7. Mequanint K, Sanderson R (2003) Polymer 44:2631
8. Jones FN, Chua G, Samaraweerab U (1994) Prog Org Coat 24:189
9. Blank WJ, Tramontano VJ (1996) Prog Org Coat 27:1
10. Snyder DM, Vuk TJ (1992) J Appl Polym Sci 46:1301
11. Subrayan RP, Jones FN (1996) J Appl Polym Sci 62:1237
12. Narayan R, Chattopadhyay DK, Sreedhar LB, Raju KVSN, Mallikarjuna NN, Aminabhavi TM (2006) J Appl Polym Sci 99:368
13. Blank WJ (1979) J Coat Technol 51:61
14. Chang TT (1994) Anal Chem 66:3267
15. Bauer DR, Dickie RA (1980) J Polym Sci Polym Phys Ed 18:1997
16. Blank WJ, Hensley WL (1974) J Paint Technol 46:593
17. Saxon R, Lestienne FC (1964) J Appl Polym Sci 8:475
18. Chiou BS, Schoen PE (2002) J Appl Polym Sci 83:212
19. Czech P, Okrasa L, Mechin F, Boiteux G, Ulanski J (2006) Polymer 47:7207
20. Sriram V, Aruna P, Tharanikkarasu K, Venkateswarlu U, Radhakrishnan G (2001) J Appl Polym Sci 81:813
21. Munch E, Pelletier JM, Sixou B, Vigier G (2006) Polymer 47:3477
22. Yilgor E, Yilgor I, Yurtsever E (2002) Polymer 43:6551
23. Lu MG, Lee JY, Shim MJ, Kim SW (2002) J Appl Polym Sci 86:3461
24. Tanaka T (1993) Coating films evaluation of physical property. Ricogaka, Japan
25. Tanaka T (1997) Proceedings of the International pressure. Sensitive Adhesive Technoforum, Japan
26. Devallencourt C, Saiter JM, Fafet A, Ubrich E (1995) Thermochim Acta 259:143