Thermal Stability and Dynamic Mechanical Behavior of Acrylic Resin and Acrylic Melamine Coatings

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ABSTRACT: Acrylic polyols of different hydroxyl numbers consisting of hydroxy ethyl methacrylate, methyl methacrylate, butyl acrylate, and styrene were prepared by free-radical solution as well as suspension polymerization techniques in the presence of benzoyl peroxide initiator. These polyols were crosslinked with butoxy methyl melamine at a ratio of 85 : 15 in the presence of acid catalyst. The thermal stability of polyols and their corresponding crosslinked films was studied by thermogravimetric (TG) technique. The Broido and Coats–Redfern methods were used to calculate the activation energy of thermal decomposition from standard TG curves. Dynamic mechanical thermal analysis was used to study the dynamic mechanical properties and determination of glass-transition temperature of acrylic/melamine crosslinked films. The results indicate that the thermal stability of polyols and crosslinked films strongly depends on the hydroxyl number of the acrylic polyols. It was found that acrylic polyols synthesized by suspension polymerization methods upon crosslinking yield more thermally stable and flexible films than polyols prepared by solution polymerization methods. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 27–34, 2004

Key words: thermosets; thermal properties; mechanical properties; crosslinking; films

INTRODUCTION

In recent years, the focus of research in coatings and other allied industries has been shifted toward the study of thermal and dynamic mechanical properties of the coatings as well as the resins/oligomers used in their formulation. The cause of this shift is the demand for high-performance coatings for various applications. To develop such coatings one has to take into account the dimensional and thermal stability of the network. The network chain of thermoset formed upon crosslinking of prepolymer with a crosslinker and the degree of crosslinking can be increased by using a higher functionality prepolymer, increasing the crosslinkers and catalyst concentration, and/or baking time or temperature[1–5]: all these factors influence both the thermal and the dynamic mechanical properties of the ultimate material. The thermal stability of the network chain is related to the thermal stability of the prepolymer and the nature of crosslinker, the former of which depends on several factors: monomer selection, constitution, and ratio of monomeric units and their arrangements, the molecular weight of the copolymer, molecular weight distribution, and the method of polymerization. Thermogravimetric analysis (TGA) is a reliable tool to study

thermal stability and provides valuable data to calculate the kinetic parameters[6–9] of thermal degradation. In the present study the Broido[10] and Coats–Redfern methods[11] were used.

The network structure and viscoelastic behavior of thermoset coatings can be understood and more readily be interpreted in structural and molecular terms[12,13] by dynamic mechanical measurements. A better understanding of the mechanical properties can be acquired from the analysis of the viscoelastic spectra of coatings.

The thermosetting system used for the present study was acrylic/melamine. Various studies have examined the effect of chemical crosslinking on the material properties of acrylic–melamine films. There have been studies on the effect of crosslink density on dynamic mechanical property,[12] effect of hydrolysis on network structures,[14–16] and extent of crosslinking and rate constant for crosslinking by kinetic models.[17,18] The thermal stability and dynamic mechanical properties of acrylic–melamine networks constitute the main focus of this investigation. Butoxy methyl melamine was used as crosslinker.

EXPERIMENTAL

Materials

The monomers styrene (St; Fluka Chemicals, Buchs, Switzerland); methyl methacrylate (MMA; E-Mark Chemicals); butyl acrylate (BA) and hydroxyl ethyl

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methacrylate (HEMA; both from Aldrich Chemicals, Milwaukee, WI) were used as received without any additional purification and benzoyl peroxide (BPO) was purified by precipitation with methanol from chloroform solution before use.

Melamine resin

The melamine resin used in this study was butoxymethyl melamine (molecular weight: 68,455; polydispersity: 1.46; 60% solids content in butanol) obtained from Synthetics and Polymer Industries (India).

Synthesis of acrylic resin

Acrylic copolymers with different amounts of pendent hydroxyl groups were synthesized by using both solution and suspension polymerization methods. In both polymerization methods, the variant was HEMA content.

The resin kettle was equipped with a dropping funnel, stirrer, thermometer, and reflux condenser. Methyl isobutyl ketone was added to the kettle and a monomer mixture containing 10 g St, 32 g MMA, 30 g BA, and 19–40 g HEMA, along with 1 g BPO initiator, was charged dropwise from the dropping funnel for 1 h into the kettle. The reaction temperature was maintained at 72 ± 2°C and the reaction was allowed to proceed for a period of 4–5 h. In solution copolymerization, the reactions stopped as soon as the dramatic increase in viscosity of the reaction mass was observed. These polyols were purified by precipitating in nonsolvent, filtered and washed several times, and finally dried at 80°C for 6 h under vacuum. The purified polyols were subjected to molecular characterization. Synthesized polyols were coded 1 to 4.

For suspension polymerization, a kettle equipped like that for solution polymerization was immersed in a water bath. It was charged with 250 mL distilled water and heated to 75°C. Poly(vinyl alcohol) stabilizer was added to the kettle and dissolved by stirring. The monomer mixture (10 g styrene, 32 g MMA, 30 g BA, and 19–40 g HEMA), 2 g BPO, and 0.1% dodecyl mercaptan chain-transfer agent were put into the dropping funnel and introduced to the kettle. Polymerization was carried out at 72 ± 2°C for a period of 4–5 h with a stirring rate around 400 rpm. The polymers thus prepared were filtered, washed with distilled water, and dried at 80°C for 6 h. Synthesized polyols were coded 5 to 8.

Preparation of crosslinked free films

Acrylic polyol and butoxymethyl melamine in the stoichiometric ratio of 85 : 15 w/w, methyl isobutyl ketone, and acid catalyst were mixed and viscosity was adjusted to 40–50 s with Ford Cup No. 4. A coating of 8 mills wet thickness was cast onto a smooth surface of tin foil using a film applicator and backed for 20 min in an air-circulating oven at 120°C. The cured supported films were placed in a clean mercury bath to amalgamate the tin substrate and after cleaning, the unsupported films were removed.[19] Crosslinked films derived from polyols 1–8 were dubbed as 1C–8C, respectively.

Characterization

The molecular weights of acrylic polyols were determined by gel permeation chromatography (GPC C-R4A Chrotopac; Shimadzu, Kyoto, Japan) with phenomenex (100 Å) columns. The polyols were dissolved in THF at about 0.1 g/10 mL and the experiment was carried out at 1.0 mL/min flow rate with THF as the mobile phase. The columns were calibrated with Aldrich polystyrene standards crosslinked with divinyl benzene.

Thermogravimetric analysis

TGA analyses were performed using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851ᵉ) controlled by a computer at a heating rate of 15°C/min under a dry flow of nitrogen. The sample weight was about 8–10 mg. The TGA data were used to fit into kinetic models to calculate various parameters. The details of the kinetic models are given here.

Kinetic methods

The rate of conversion, $d\alpha/dt$, in a dynamic TGA experiment at a constant heating rate can be expressed as

$$d\alpha/dt = Af(\alpha)\exp(-E/RT) \qquad (1)$$

where A is the preexponential factor, E is the activation energy, R is the universal gas constant, and $f(\alpha)$ is the conversion functional relationship.

The integral form of this rate equation in a dynamic heating experiment may be expressed as[20]

$$g(\alpha) = (AE/QR)\int_{\infty}^{Z}\left[\exp(-Z/Z^2)\right]dz \qquad (2)$$

where $Z = E/RT$, Q is the heating rate, and $g(\alpha)$ is the integral form of conversion dependency function.

Several methods using different approaches have been developed for solving this integral equation.

TABLE I
Molecular Weight of Acrylic Polyols Along with Hydroxyl Value and Polydispersity

	Formulation							
	Solution polymer				Suspension polymer			
Parameter	1	2	3	4	5	6	7	8
Hydroxyl number (mg KOH/gm)	93	105	136	153	87	106	125	147
M_n	45472	40415	45360	45058	35330	37785	40594	42130
M_w/M_n	2.16	2.17	2.16	2.17	2.2	2.22	2.21	2.2

Broido equation[10]

$$\ln \ln(1/Y) = E/R \, (1/T) + \text{Constant}$$

where $Y = (w_0 - w_t)/(w_0 - w_\infty)$ is the fraction of the number of initial molecules not yet decomposed; and w_t, w_∞ (=0), and w_0 are the weight at time t, the weight at infinite time, and the initial weight, respectively. The slope of the plot of $\ln \ln(1/Y)$ versus $1/T$ is related to the activation energy.

Coats–Redfern equation[11]

Coats and Redfern provide an approximation to the integral of eq. (2), thus obtaining the following expression:

$$\text{Log}_{10}[g(\alpha)/T^2] = \text{Log}_{10}(AR/QE)[1 - (2RT/E)]$$
$$- E/2.303RT$$

Thus a plot of $\text{Log}_{10}[g(\alpha)/T^2]$ versus $1/T$ should result in a straight line whose slope equals $-E/2.303R$ for the correct chosen value of n, the order of degradation.

Dynamic mechanical study

The dynamic mechanical properties of acrylic polyol/melamine cured coating films (15 × 10 × 0.5 mm) were determined by using a dynamic mechanical thermal analyzer (DMTA IV; Rheometric Scientific) in ten-sile mode at a frequency of 10 Hz at a heating rate of 3°C/min. In principle, DMTA techniques detect the viscoelastic behavior of polymeric materials and yield quantitative results for the tensile storage moduli (E') and the corresponding loss moduli (E''), the loss factor (tan δ) as the quotient of loss and storage, E''/E'. E' and E'' characterize the elastic and viscous compo-nents of a viscoelastic material under deformation. Usually, the maximum of tan δ is reported as the glass-transition temperature of the materials.

RESULTS AND DISCUSSION

The molecular weight and hydroxyl values of acrylic polyols are reported in Table I. The absence of mono-mer impurities in acrylic polyols (1 to 8) prepared by both solution and suspension polymerization methods was confirmed from IR and ^{1}H-NMR spectra.

The relative thermal stability of various acrylic poly-ols and crosslinked films was evaluated from TGA data. The values of T_{id} (initial decomposition temper-ature), T_{df} (final decomposition temperature), T_{max} (temperature of maximum rate of weight loss), per-centage weight remaining at 330°C, char yield at 450°C, and activation energy of thermal decomposi-tion are tabulated in Table II for acrylic polyols and in Table III for crosslinked films; the corresponding TG curves of different polyols and their crosslinked films are shown in Figure 1.

TABLE II
Thermal Analysis Results of Acrylic Polyols Prepared by Solution and Suspension Polymerization Methods

Sample	T_{id} (°C)	T_{max} (°C)	T_{df} (°C)	% Weight at 330°C	% Weight at 450°C (char yield)	E_a (kJ/mol) Broido method	E_a (kJ/mol) Coats–Redfern method
1	336	387	424	96.8	5.0	168.18	167.99
2	316	368	420	80.1	—	91.95	91.77
3	337	390	418	95.9	4.2	154.03	153.86
4	334	387	425	94.3	3.8	137.36	137.2
5	350	407	431	91.7	4.8	126.51	126.36
6	339	403	428	90.3	4.7	123.39	123.25
7	338	406	431	88.8	3.9	114.28	114.16
8	336	402	429	90.8	3.8	112.85	112.72

TABLE III
Thermal Analysis Results of Acrylic Polyol/Melamine-Cured Films

Sample	T_{id} (°C)	T_{max} (°C)	T_{df} (°C)	% Weight at 330°C	% Weight at 450°C (char yield)	E_a (kJ/mol)	
						Broido method	Coats–Redfern method
1C	344	401	429	91.7	9.5	121.39	121.26
2C	331	407	430	98.9	17.2	144.61	144.45
3C	335	401	428	93.6	10.3	118.67	118.53
4C	337	402	433	86.1	10.9	90.87	90.77
5C	357	417	438	93.7	8.7	136.18	130.03
6C	348	414	435	92.1	9.5	127.88	127.74
7C	352	409	433	91.4	10.5	123.57	123.44
8C	343	410	436	93.3	12.3	123.4	123.26

Thermal stability of acrylic polyols

The thermal stability of polyols plays a important role in determining the final film properties and is greatly influenced by the structure, chemical composition, monomer distribution, and different interaction parameters. Thermograms of all the acrylic polyols were found to have a similar nature, showing a single-step degradation. Most polyols were stable up to 330°C and started to lose weight above this temperature. The good thermal stability could be attributable to the absence of unsaturation in the polyol backbone.[21] The decomposition observed is perhaps a result of the breakdown of polyol or random scission initiated from the weak side (bulky groups and ester groups).[22] The degradation followed first-order kinetics, as observed from the Coats–Redfern equation. The correlation coefficient values in both the Broido and Coats–Redfern plots were greater than 0.99.

The char yield values at 450°C and activation energy of decomposition decreased with increase of hydroxyl value for acrylic polyols, except for sample 2. That means the thermal stability decreases with an increase of hydroxyl value. The overall stability of sample 2 was less than that of samples 1, 3, and 4, as shown in Figure 1(a). This fact may be attributed to its lower molecular mass (Table I) or may be an experimental error.[23] Among samples 5 to 8, sample 5 was most stable and T_{id} decreases with increase of hydroxyl number, as shown in Table I and Figure 1(c). Generally the weight fraction at 330°C decreases with an increase in hydroxyl value.

An increase in molecular mass from polyol 5 to polyol 8 is the reason for the increase in thermal stability, whereas the increase in hydroxyl number leads to a decrease of thermal stability. These two opposing factors are responsible for the lesser difference in activation energy between polyols 5 and 6 or polyols 7 and 8, whereas for polyols 1, 3, and 4, the only variable parameter is the hydroxyl number and thus there is a substantial decrease in activation energy of thermal decomposition as we proceed from polyol 1 to polyol 4.

In other cases, no systematic correlation was found between T_{id}, T_{max}, or T_{df} with hydroxyl number in these polyols.

Thermal stability of crosslinked films

The thermal properties of thermoset resin depend primarily on the network structure and the stability is a function of more than one variable than just the extent of crosslinking: both the kind and concentration of remaining polar groups, cohesive energy between molecular chains, molecular chain rigidity, and other chemical structural factors such as, for example, steric strain and conformational arrangements of groups.[21] In addition, the degradation mechanism of these complex systems changes during degradation and so activation energy not only is a function of chemical structure but also changes with conversion for a single crosslinked film.[24] All these factors complicated the understanding of the relationship between crosslinking density and thermal stability of cured resins.

In the present study, the basic composition was almost the same for cured resins, where the crosslink densities were changed by varying the HEMA concentration to study the effect of crosslink density on the thermal properties.

The degradation followed first-order kinetics and the linearity of the Coats–Redfern and Broido plots were found to be in good agreement with correlation coefficients greater than 0.99.

Generally for highly crosslinked polymers, one can expect first the scission of highly strained crosslinks as well as weak links in the polymer chains. The second step represents the random scission of the free linear chains formed during the first degradation step into still smaller fragments.[25] The result of our study shows that more crosslinked films were less stable, given their need for less energy of activation for decomposition. The bulky character associated with excessive crosslinking in the three-dimensional networks of the films is expedient because the hydrogen bond (O—H—O) between two hydroxy functional
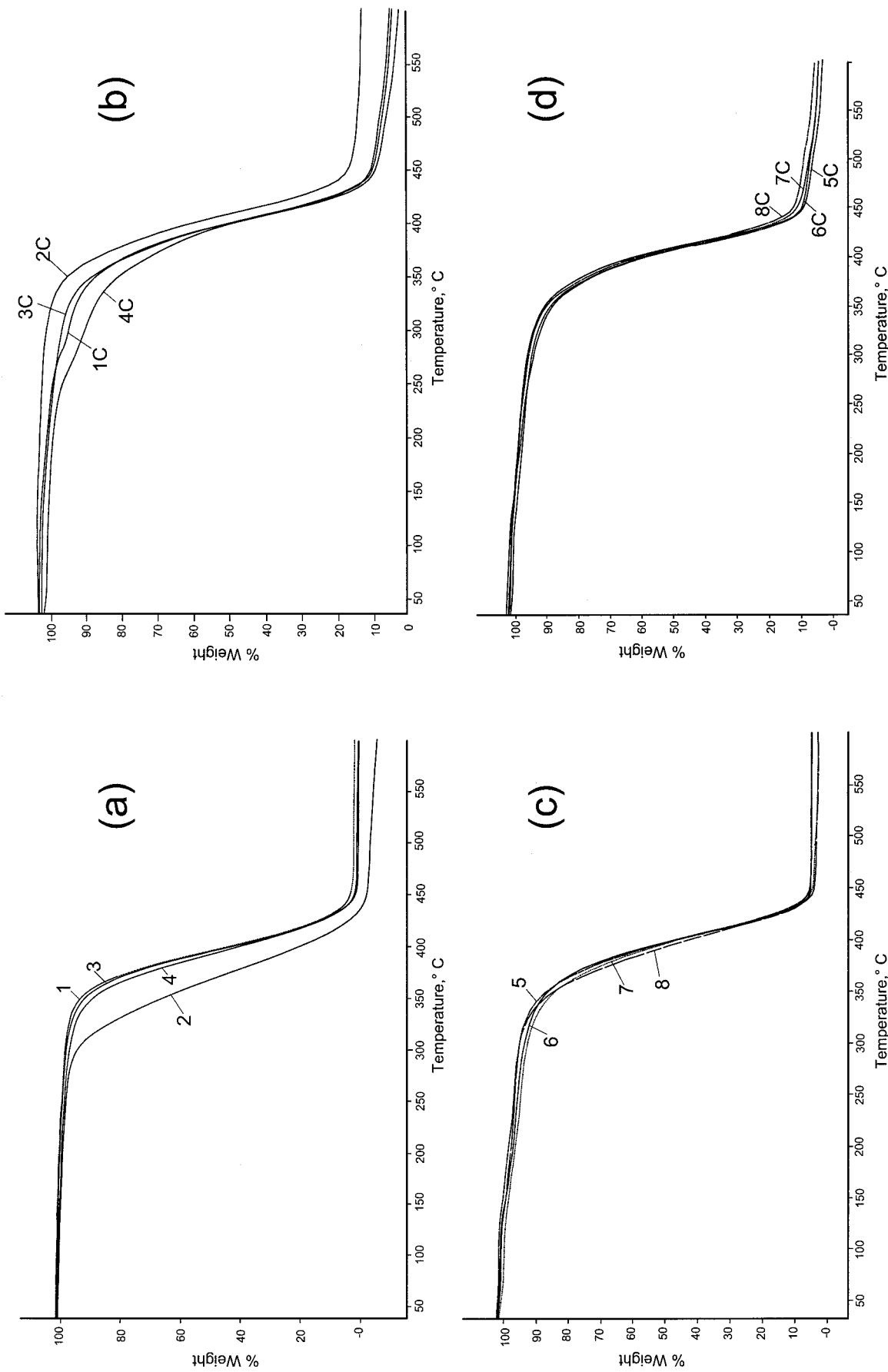
Figure 1 Thermogravimetric curves of different polyols and crosslinked films: (a) polyols prepared by solution polymerization methods (1–4); (b) corresponding crosslinked films (1C–4C); (c) polyols prepared by suspension polymerization methods 5–8; and (d) corresponding crosslinked films (5C–8C).

polyacrylic molecules is replaced with OH–melamine bonds.

The polyols upon crosslinking with melamine gave greater char yield values at 450°C and this value increased with increase of crosslinking for cured systems (i.e., a high degree of crosslinking was found to have a favorable influence on increasing the weight residues at high temperature).[26,27] The increase of char yield at 450°C upon crosslinking of polyols showed that crosslinked films were more stable than the respective acrylic polyols at high temperature. On comparing crosslinked films 5C to 8C, percentage weight remaining at high temperature T ($T > T_{df}$) increases with increase of crosslink density, although the T_{id} value is greater for sample 5C. This phenomenon is of practical importance because of less strain and more efficient packing of the corresponding crosslinked resin.

The cause of higher thermal stability and activation energy of thermal degradation of the crosslinked resin (sample 2C) derived from the least stable acrylic polyol (polyol 2) may be attributed to an increase in the amount of melamine–melamine crosslinking. The lower functionality resulted from the respective lower molecular mass polyol, which contains less OH–melamine crosslinking and sufficient amounts of melamine–melamine crosslinking.

The crosslinked films 5C, 7C, and 8C were more stable than 1C, 3C, and 4C because the values of T_{id}, T_{max}, T_{df}, and activation energy of degradation are greater for crosslinked films prepared from the suspension polymerization method. With respect to crosslinked films 4C and 8C, the molecular mass (M_n) values of the corresponding acrylic polyols were 45,058 and 42,130 and the hydroxyl numbers were 153 and 147, respectively.

On comparing, based on the molecular mass of acrylic polyol, 4C is more stable than 8C. On the other
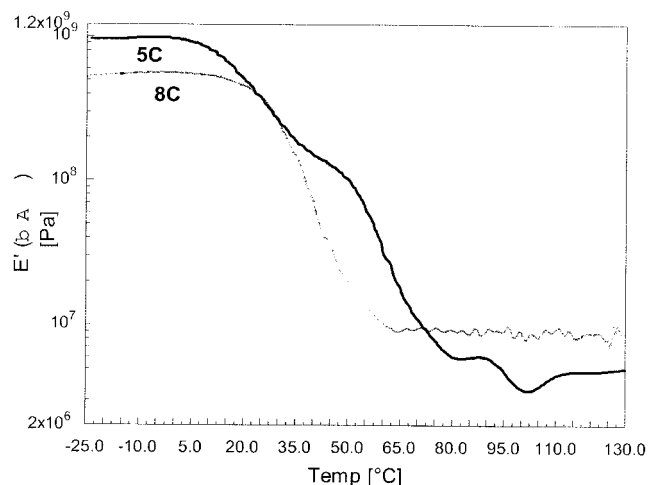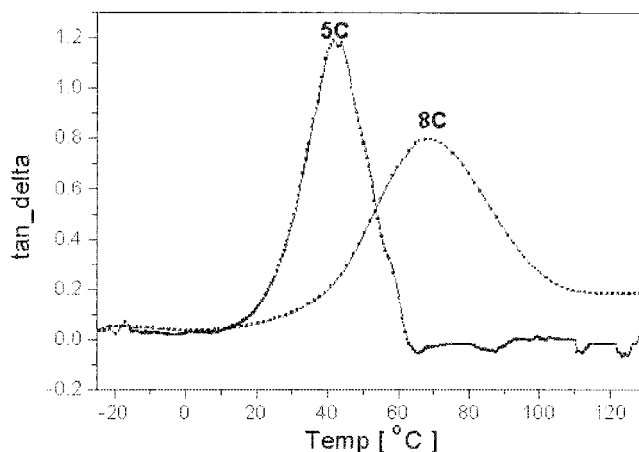

Figure 3 Plot of tan δ versus temperature of the crosslinked films 5C and 8C.

hand 8C is more stable when we compare only the melamine–melamine linkages. Because the amount of melamine–melamine linkage is greater in 8C, the same 15% w/w melamine was used for both crosslinked films. Differences between these two opposing factors, however, are considerably less than differences in activation energy of thermal decomposition; such a large difference in activation energy may be attributed to the change in polymerization technique.

Dynamic mechanical property

The dynamic mechanical properties of all the crosslinked films were determined. The elastic storage modulus versus temperature and the loss factor versus temperature spectra of representative films are shown in Figures 2–4.

The room-temperature E' is regarded as a measure of hardness for coating materials and depends on intermolecular forces, intramolecular forces, molecular structure (e.g., crosslink concentration and molecular weight), temperature, and relaxation phenomenon of materials.[28,29] Usually hard materials have a higher room-temperature modulus than that of rubbery materials. Interestingly, based on the hydroxyl numbers the film 8C was expected to have greater room-temperature modulus than that of film 5C, but as shown in Figure 2 this is not the case, which signifies the anomalous behavior of thermoset coating films.[30–32]

The decrease in modulus in the glassy state with increasing crosslinking may be the result of structural effects (i.e., that increasing crosslinking and molecular weight prevent efficient structural packing) or the result of relaxation (kinetic) effects.[30]

The modulus for samples with lower crosslink density, such as 5C, decreased at a lower temperature and the length of this decrease was greater than that for
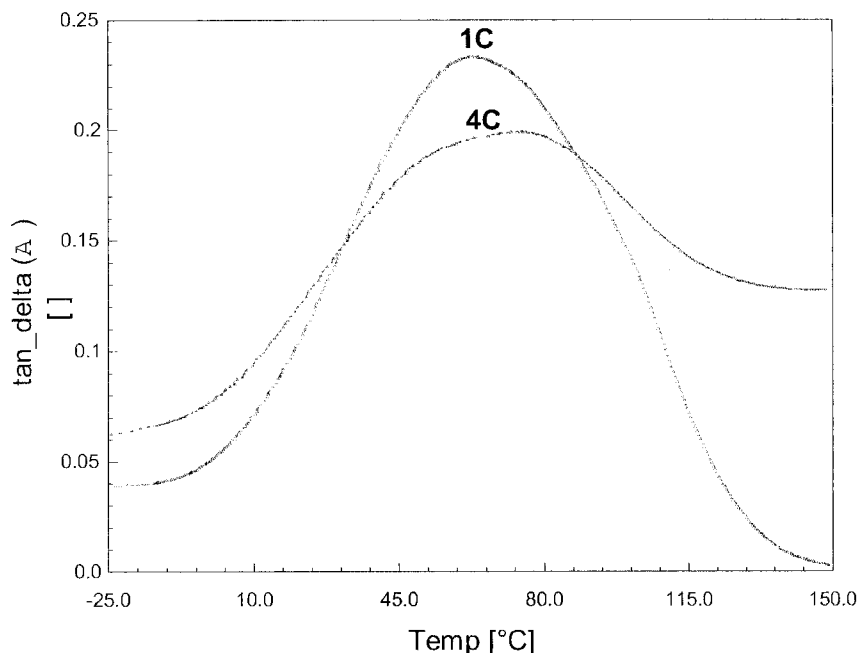

Figure 2 Plot of E' versus temperature of the crosslinked films 5C and 8C.

Figure 4 Plot of tan δ versus temperature of the crosslinked films 1C and 4C.

samples with higher crosslink density, such as 8C (as shown in Fig. 2), which showed the more flexible nature of 5C. Crosslinking increased the storage modulus of film at higher temperature, resulting in improved thermal resistance at high temperature for more crosslinked systems as discussed previously. Increasing the crosslink density affects the loss tangent curves in three different ways. First, the loss tangent peaks shift to higher temperatures. Second, the loss tangent peaks have lower values because samples with higher crosslink densities have larger elastic moduli relative to their viscous moduli. Third, the loss tangent peaks become broader. The breadth and height of the tan δ curve can be used to interpret the crosslink density and flexibility of coatings qualitatively: 1C compared to 8C had a more flexible nature than that of 4C and 5C. The values of tan δ_{max} were greater for crosslinked films 5C to 8C than those of crosslinked films 1C to 4C, as given in Table IV. This shows that polyols prepared by the suspension polymerization method after crosslinking yielded more flexible films than those prepared by the solution polymerization method.

CONCLUSIONS

As shown by TG studies, the presence of HEMA in the polymer backbone does seem to have a significant effect on the thermal stability of the resulting polymer.

The thermal stability of acrylic polyols decreases with increase of hydroxyl value. For polyols with hydroxyl number 115, the activation energy of thermal decomposition was less, which may be attributed to its lower molecular mass.

Crosslinked films are more stable than the respective acrylic polyols and this stability is associated either with the number of crosslinked points or with the crosslinking density. Although it is difficult to propose a clear conclusion in the light of crosslink density on the thermal property, given the overlay of a number of parameters involved, we nonetheless conclude that the activation energy of thermal decomposition decreases with an increase of crosslink density. This decrease was associated with increased steric strain in the three-dimensional network structures arising from increased crosslinking and/or from a decrease in melamine–melamine crosslinking. It was found that acrylic polyols synthesized by suspension polymerization methods upon crosslinking yield more thermally stable films than polyols prepared by solution polymerization methods.

As a result of increased crosslinking, the glassy-state modulus decreases, and the rubbery-state modulus and glass-transition temperature increase. The values of tan δ_{max} were greater for the crosslinked films derived from acrylic resin prepared by suspension poly-

TABLE IV
Values of tan δ_{max} and T_g of Crosslinked Films

Parameter	Crosslinked film			
	1C	4C	5C	8C
tan δ_{max}	0.2	0.2	1.2	0.8
T_g (°C)	62	75	44	69

merization methods. This result shows greater flexibility of the corresponding crosslinked films than that of crosslinked films made of polyols prepared by solution polymerization techniques.

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