Structure–Property Relationship and Influences of Phenolic Compounds on the Mechanical and Thermomechanical Properties of UV-Cured Acrylic Resin Networks

S. Yin,[1] A. Merlin,[2] A. Pizzi,[2,3] X. Deglise,[2] B. George,[2] M. Sylla[2]

[1]College of Wood Science and Technology, Nanjing Forestry University, China
[2]LERMAB, UMR INRA/ENGREF/UHP 1093 University of Nancy 1, Nancy, France
[3]ENSTIB, University of Nancy 1, Epinal, France

ABSTRACT: Trimethylolpropane triacrylate (TMPTA) resin was cured under UV radiation, with 2,2-dimethoxy-2-phenylacetophenon (DMPA) and a mixture of benzophenone and methyl-diethanolamine (BP/MDEA) as initiators and three phenolic compounds as inhibitors, respectively. For each formulation, the curing enthalpy was measured by photocalorimetry and the modulus of elasticity (*MOE*) of cured resin films by thermomechanical analysis. The DMPA resulted in networks with higher rigidity that was slightly reduced by the addition of a phenolic compound; while the networks were more flexible and the effects in reducing the *MOE* by the phenols were much more pronounced when the BP/MDEA was used as an initiator. For the three phenolic compounds, their importance in reducing the *MOE* can be ranked in the order of eugenol > dimethoxyphenol > phenol. Three equations are proposed to model the structure–property relationship of TMPTA networks. These models suggest that *1)* the *MOE* increases with the crosslinking density, which is proportional to the conversion degree to a power of about 1/3, indicating that cyclization becomes progressively more important as the photopolymerization advances; *2)* the decrease of the *MOE* with temperature is mainly due to relaxation of pending chains and chain segments, and the activation energy needed to overcome such an energy barrier is greater for a less crosslinked network than for a more crosslinked one; and *3)* the overall contribution of the crosslinking and the interactions between pending chains (secondary forces) can be expressed by a simple equation in which the network rigidity (*MOE*) is a function of the degree of conversion, the activation energy and the temperature. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3499–3507, 2004

Key words: acrylic resin; phenols; networks; crosslinking; mechanical properties

INTRODUCTION

UV-curable coatings have found manifold industrial applications owing to their distinct advantages, such as short curing time, excellent energy balances, and lack of organic solvents, and are becoming increasingly attractive with the introduction of ever more stringent environmental demands on the limitation of volatile organic content (VOC). Great efforts have been made since 1980s to improve the durability of UV-cured coating films, especially in the field of automobile body finishing. Nowadays, many formulations with excellent performance have been commercialized for metallic surface protection. In the wood industry, the use of UV-curable resins as a top and/or undercoating layer to protect wood materials has also aroused interest, especially for furniture protection.[1–3] However, the wood industry usually adopts existing formulations optimized for metallic surface finishing, which do not always perform as well as expected when applied to wood materials. To obtain the desired protection performance for wood materials, these types of resins need to be finely tuned to accommodate the special features of wood.

Compared with metals, wood is porous and dimensionally unstable. When applied on the surface of wood, a liquid resin may migrate into the porous structure to a depth higher than that of UV light penetration. For some species, this loss by migration can become significant and increase greatly the cost of treatment. Thus the viscosity of coatings must be tailored so that the penetration can be limited by an appropriate extent while the coatings themselves can still be handled easily enough to meet the requirements of the application. This is achieved at present by adding a reactive diluent, i.e., a low vapor pressure monomer that lowers the coating viscosity and can polymerize under UV irradiation.

The dimensional instability is an inherent characteristic of wood diminishing the durability of protection coating films. When subjected to variations of moisture, the expansion or contraction of wood creates internal stress at the coating/wood interface that may

cause an interface fracture and/or rupture of the coating layer. To obtain a durable protection layer, a coating film must remain sufficiently flexible to follow the dimensional alteration without rupture and separation from the substrate.[4] Two strategies can be envisaged for this purpose:

- Formulate a flexible coating by lowering the glass transition temperature (T_g) of the cured film to a range below the service temperature. In the case of UV coatings, however, the addition of a reactive diluent necessary to adjust the viscosity usually leads to films being too rigid. Although aqueous resins can be formulated with low viscosity while being capable of forming flexible films, their application on wood poses other problems, as excessive water may cause swelling, staining, and roughening of the wood surface.
- Improve the dimensional stability of wood before the application of a coating. These types of treatments make it possible to limit, in a durable way, the dimensional variations of wood but may modify the surface energy and reduce the adhesion of the coating.

Furthermore, wood is not "inert" vis-à-vis the curing reaction of UV-curable resins. Some species contain extractives capable of interfering with the polymerization process of UV-curable resins. Drying of polyester or alkyd coatings, for example, is delayed to such an extent on certain exotic species that it is incompatible with the production rate of a finishing line.[4,5] This behavior has been attributed to the content and especially to the nature of phenolic extractives.[6–9] A previous study[10] showed that phenolic compounds could also inhibit and/or retard the polymerization reactions of an acrylic resin (trimethylolpropane triacrylate, TMPTA). The importance of these effects depends on the types of the photoinitiators, hence on the mechanism of initiation as well as the type of phenols. For the TMPTA resin with different initiators, the kinetics of TMPTA/DMPA (2,2-dimethoxy-2-phenylacetophenon) systems was only slightly affected by the incorporation of phenolic compounds, but the final degree of conversion decreased to some extent. On the other hand, the retardation and inhibition phenomena were much more pronounced and the final degree of conversion was reduced significantly when the BP/MDEA (benzophenone/methyldiethanolamine equimolar mixture) was used as an initiator. By using nanosecond transitory absorption spectroscopy (NTA) and electron spin resonance (ESR) analysis techniques, the mechanism of inhibition and retardation effects by phenols was elucidated and attributed to the interactions between the triplet state [3]BP and the phenolic compounds added into the resin or abstracted from the wood surface.

The durability of acrylic resins on a wood substrate depends rather on the interfacial adhesion between the coating and the wood than on the cohesion of the coating itself. It was demonstrated that the adhesion was better on a softwood surface at the beginning of accelerated aging tests. However, when the aging tests were prolonged, the resin films on hardwood surfaces seemed much more durable,[11] probably owing to the presence of more extractives in the latter case. From the point of view of industrial application of an acrylic coating, the presence of phenols seems to have two antagonistic effects: *1*) it requires more time to cure the resin and hence decreases the productivity and increase the cost of production and *2*) it results in films with higher flexibility and durability. With phenols, a "gradient modulus interface" or "rubber bumper" that reduces the stress concentration at the interface or interphase may be formed.[12] Consequently, better understanding of the relationship between the mechanical properties and the molecular structure of cured coating films of different formulations is needed, as well as the role of phenols in the photopolymerization process. This is necessary to optimize the formulations of acrylic coatings and to establish appropriate drying procedures for wood-based materials.

In this article, the modulus of elasticity (*MOE*) of UV-cured acrylic resin films of different formulations was measured at different temperatures using a thermomechanical analyzer (TMA) and the conversion degree of these films was evaluated with a photocalorimeter in a deoxygenated media. Based on the correlation of the *MOE*s and the corresponding degrees of conversion, as well as the temperature dependence of the *MOE*s, interesting information about the structure–property relationship was drawn for acrylic coatings of different formulations containing phenols. It has been found that the *MOE* of a cured acrylic film depends on the type of initiator, the incorporation or not of a phenolic compound, and the type of the latter. Both chemical bonding (namely, crosslinking density) and secondary forces contribute to the viscoelastic behavior of cured TMPTA films in a relatively wide range of temperatures.

EXPERIMENTAL

Chemicals and formulations

The chemicals and formulations were the same as in the previous study.[10] Trimethylolpropane triacrylate (Aldrich technical grade, 3.7 mol L^{-1}) was used as a model acrylic resin. The photopolymerization was initiated either with DMPA (Aldrich 99.1%) or an equimolar mixture of BP (Fluka best-available grade) and MDEA (Aldrich 99.1%). Three phenolic compounds, namely phenol, 2,6-dimethoxyphenol (DMP), and eugenol (2-methoxy-4-propenyl phenol) provided

by Aldrich at best-available grade were used as models of phenolic wood extractives. All the chemicals were used as received.

The concentration of initiator was 2×10^{-2} mol L^{-1} and that of phenols was 5×10^{-2} mol L^{-1} (0.55 and 1.35% in molar proportion based on that of TMPTA), respectively.

Thermomechanical analysis (TMA)

The *MOE* of cured resin films was measured with a METTLER thermomechanical analyzer TMA40, using a three-point bending device and rectangular specimens. The specimens were prepared by pouring the resin into a Teflon mold with thick adhesive bands as removable sidewalls and then cured under UV radiation. The radiation was carried out with a drying system equipped with a conveying belt and two mercury vapor lamps at medium pressure (average flow at sample level 30 mW/cm^2 at 360 nm). Preliminary tests showed that the *MOE* of all films increased with the irradiation time (number of passages) for the first 1 to 5 passages at a speed of 5 m/min, depending on the formulation, and then leveled off until 10 passages. This indicated that further polymerization became impossible under the experimental conditions (10 passages), hence the films reached their maximum possible degree of polymerization without appreciable degradation. After cooling, the cast films were separated from the mold and cut to length of 21 mm. Finally, the films were sanded carefully, first using 180-mesh followed by 400-mesh sandpaper to smooth the edges and surfaces and to remove the outer layer of specimens that might have lower degree of polymerization due to the inference of oxygen presented in the atmosphere. The actual dimensions of the films used for TMA tests were $21 \times 6 \times 0.5–0.6$ mm.

The *MOE* was isothermally measured at a 20 or 10°C interval starting at 25°C and ending at 125°C. A probe touching the center of the specimen provided an oscillatory load that varied from 0.1 to 0.5N ($\Delta F = 0.4N$) over a cycle of 12 s (6 s/6 s). The specimens had been conditioned before the measurement started for 1 to 6 min to thermal equilibrium, depending on the testing temperatures. The *MOE* was calculated using the classical mechanics relationship $MOE = [L^3/(4bh^3)][\Delta F/(\Delta f)]$, in which L (18 mm) was the spacing between the two support points; b and h were the width and thickness of specimens, respectively; ΔF was the difference of force exerted by the probe and Δf was the deflection caused by ΔF. The reported *MOE* values were all the average of five samples, measured over a period of 60–120 s.

The evolution of *MOE* was also evaluated with the same types of specimens in the temperature range –80 to 190°C. In this case, the specimens were heated at 5°C/min and the measurements were carried out continuously with the increase of temperature. A 15-min thermal stabilization time was given to the specimens at −80°C before the measurement started.

Photocalorimetry

The photocalorimeter was a Perkin–Elmer DSC 7 in which the sample and reference were irradiated with a continuum Xenon UV lamp Osram XBO (450 W). A Pyrex filter, cutting the wavelengths under 310 nm, was used to avoid direct excitation and dry nitrogen gas to avoid oxygen inhibition. Irradiation was maintained at 25°C (298 K) until the sample resin reached its maximum possible conversion degree (actually for 5 min). The total amount of enthalpy change, ΔH, proportional to the maximum possible conversion degree of the resin, was calculated from the corresponding thermograms. As a reference to compare the maximum possible conversion degree of different formulations, the thermograms of one formulation with 2,2'-azobis(2-methylpropionitrile) (AIBN) as a thermal initiator were also recorded and the ΔH was calculated.

RESULTS AND DISCUSSION

Influences of initiators and phenols on the curing enthalpy and the modulus of elasticity

Table I shows the curing enthalpy ΔH and the *MOE* of cured TMPTA films measured at different temperatures. It can be seen that the two initiators have a different effectiveness in hardening the TMPA resin. The ΔH and *MOE* of the films with DMPA as initiator are always much higher than those of the films with BP/MDEA, all other conditions being the same. For instance, at 25°C, the *MOE* of the BP/MDEA reference film (2,487 MPa, 0.55% initiator without phenol) is about 78% of that of a DMPA reference (3,186 MPa); Correspondingly, the ΔH of the BP/MDEA reference (97.9 J/g) is only about 40% of that of DMPA (245 J/g). This trend holds true for other formulations and at other temperatures.

The three phenols have all negative effects on the ΔH and *MOE* of TMPTA films and their importance in reducing the ΔH and *MOE* can be ranked in the order: eugenol > DMP > phenol. Furthermore, it is noted that this effect is more pronounced for the BP/MDEA systems than for the DMPA systems. At 25°C, the *MOE*s in the latter cases are only slightly decreased (less than 10%) by the incorporation of the phenols, while the *MOE*s for BP/MDEA systems with eugenol, DMP, and phenol represent only 63, 69, and 82% of that of their reference (without phenolic compounds), respectively.

A previous study[10] has shown that the two initiators work through different mechanisms and the phenolic compounds play different roles in the polymerization

TABLE I
Enthalpy Change of the UV-Curing and *MOE* of UV-Cured TMPTA Resins Measured at Different Temperatures

Formulation	Modulus of elasticity (MPa)								Enthalpy (J/g)
	25°C	35°C	45°C	55°C	65°C	85°C	105°C	125°C	
DMPA	3,186	—	2,674	—	2,396	2,184	2,039	1,962	245.0
DMPA + P	3,066	—	2,569	—	2,258	2,039	1,877	1,783	210.0
DMPA + DMP	3,057	—	2,557	—	2,262	2,058	1,907	1,805	216.0
DMPA + E	3,038	—	2,593	—	2,299	2,095	1,964	1,859	185.0
BP/MDEA	2,487	—	2,061	—	1,784	1,576	1,438	1,367	97.9
BP/MDEA + P	2,046	—	1,598	—	1,365	1,228	1,145	1,091	78.7
BP/MDEA + DMP	1,704	1,522	1,359	1,254	1,217	1,161	1,124	1,087	49.4
BP/MDEA + E	1,564	1,349	1,238	1,160	1,109	1,055	1,018	981	49.2
AIBN	—	—	—	—	—	—	—	—	408.3

P, phenol; DMP, 2,6-dimethoxyphenol; E, eugenol.

of TMPTA. DMPA produces benzoyl and dimethoxy-benzyl radicals through an α-cleavage process (Scheme 1), which is much faster than the reaction between the DMPA triplet and the phenolic compounds, hence no inhibition or delay effect due to the incorporation of a phenolic compound was observed in the polymerization of the TMPTA/DMPA systems.

While for the TMPA/BP/MDEA systems the formation of effective initiating radicals MDEA°$_{-H}$ is assured by the photoreduction of the benzophenone triplet ^{3}BP (Scheme 2), the rate of hydrogen transfer is comparable with that of the reaction between a triplet ^{3}BP and a phenolic compound (ArOH). Consequently, a noticeable induction period and a decrease in the rate of curing were detected when a phenolic compound was added in the latter case.

These findings are helpful to interpret the observation made on the mechanical property measured with the TMA. A common feature of free-radical polymerization involving multivinyl monomers is that an increase in the concentration of free radical species results at an early stage in an increase in polymerization rate and degree of polymerization. Subsequent polymerization proceeds by diffusion control and the formation of long chains favors a decrease in the diffusivities of the macroradicals and decreases also the probability of meeting of two groups on the same chains.[13, 14] Thus, it would be expected that the number of crosslinking nodes between the already formed chains increases with the number of effective initiating radicals, hence a hypothesis can be advanced to explain the effects of different initiators and phenols:

- DMPA produces more effective initiating radicals than BP/MDEA, more chains can be formed at an early stage, and hence further crosslinking nodes can be formed after the gel point. This in turn results in an increase in the *MOE* of the network.
- The addition of phenols decreases the concentration of effective initiating radicals and reduces the number of chains, hence of crosslinking nodes and therefore the *MOE* of the network.

The total enthalpy change of polymerization, ΔH, of the TMPTA/DMPA systems is higher than that of the TMPTA/BP/MDEA systems and it decreases in both cases with the incorporation of phenolic compounds into the resin. Although the mechanism involved in the determination of the final degree of polymerization has not been completely understood, a close look at the values of *MOE* and those of corresponding ΔH (Table I) suggests that these two characteristics may well be correlated to each other. This will be discussed more in depth in the paragraphs that follow.

Correlation between the *MOE* and the degree of conversion

Structure–property relationships are a subject of great interest in studies of polymer networks. The curing of TMPTA under UV is, in fact, a chain polymerization leading to crosslinking. This is a rather complicated way of forming a network. The conditions under which this occurs are far from ideal, from the very beginning of polymerization. For example, strong cyclization, excluded-volume effects, steric hindrance effects, and specific diffusion control[13,14] do occur. No existing theoretical approach can give a reliable prediction of network buildup and the molecular structures formed. Nevertheless, as already noted above,
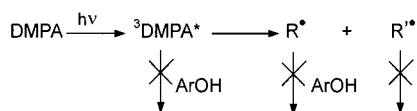
Scheme 1

Scheme 2

TABLE II
Values of the Parameters a, ΔH_{gel}, and q Determined by Using Equation (1)

Parameters	25°C	35°C	45°C	55°C	65°C	85°C	105°C	125°C
a	541.4	478.1	449.8	402.0	397.1	361.3	336.7	320.9
ΔH_{gel}(J/g)				←	22.2	→		
q				←	3	→		

the higher the total enthalpy change, ΔH, the higher the *MOE* of the cured films. Based on this observation, one can try to establish a relationship between the mechanical properties and some features of the molecular structure of TMPTA networks. The following assumptions need to be made:

1. the enthalpy change ΔH at the gel point, ΔH_{gel}, is constant for all the TMPTA systems,[15] regardless of the initiator type and incorporation or not of a phenol compound;
2. the *MOE* before the gel point is negligible and it starts to increase and become measurable only after the gel point has been reached;
3. the *MOE* is proportional to the crosslinking density, hence to the molar number of crosslinking nodes N_c per unit volume, i.e., $MOE = k_1 N_c$;
4. the molar number of crosslinking nodes N_c is proportional to the molar number of bonds formed after the gel point N_t to a power of $1/q$, i.e., $N_c = k_2 N_t^{1/q}$, where q is a constant greater than 1 to account for the importance of nonidealities in the network, such as the formation of elastically inactive loops and growth of pending chains;
5. the molar number of bonds formed per unit volume after the gel point N_t is proportional to the enthalpy change per unit volume $(\Delta H - \Delta H_{gel})'$ and approximately to the enthalpy change per unit mass $\Delta H - \Delta H_{gel}$ (the difference in density of all the TMPTA films was found to be negligible in our experimental conditions), i.e., $N_t = k_3(\Delta H - \Delta H_{gel})$, then the *MOE* can be expressed as:

$$MOE = k_1 k_2 [k_3 (\Delta H - \Delta H_{gel})]^{1/q}$$

or

$$MOE = a(\Delta H - \Delta H_{gel})^{1/q} \qquad (1)$$

in which q is a constant and hence the proportional factor $a = k_1 k_2 k_3^{1/q}$ is also a constant that does not depend on the conversion degree and hence by inference not on the term $\Delta H - \Delta H_{gel}$. It should pointed out that a may be temperature dependent if the contribution of network structure characteristics other than the crosslinking density, such as the interactions

between nonbonding chains or chain segments, is significant.

Three unknown constants must be determined in eq. (1), namely, q, a, and ΔH_{gel}, and this can be carried out by using the nonlinear least squares fitting (NLSF) method with some reasonable constraints. First, among these constants, only the parameter a may change with the temperature. The other two parameters q and ΔH_{gel} are only associated with the structure of the networks and could not be altered by the measuring temperature once the films have been cured under UV. Hence, q and ΔH_{gel} are specified as shared parameters, that is, they are the same for all the datasets whereas each dataset (corresponding to each measuring temperature) may have its own "version" of the remaining parameter a. Second, the range of ΔH_{gel} can be reasonably set between 0 and 49.2. The lower bound 0 is evident and the upper bound is defined based on the fact that the smallest value of ΔH obtained in this study is 49.2 J/g, associated with the curing of the TMPA/BP/MDEA plus eugenol system. The cured films of this formulation have a *MOE* of 1,564 MPa, an obvious proof that their polymerization has proceeded far beyond the gel point.

By using the nonlinear regression method based on the Levenberg–Marquardt algorithm, the values of q and ΔH_{gel} fitting the experimental data the best were found to be 3 and 22.2 J/g, respectively, with a varying with the temperature listed in Table II. The comparison of the experimental values with those calculated by eq. (1) are presented in Figure 1, which demonstrates that an equation $MOE = a(\Delta H - \Delta H_{gel})^{1/3}$ can well describe the experimental values of *MOE*, with the parameter a assigned an appropriate value for each temperature.

Compared with the ultimate conversion degrees, the conversion degree of TMPTA resin at the gel point seems extremely low. By definition and convention in the DSC technique, the conversion degree can be expressed as $p = \Delta H / \Delta H^*$, where ΔH^* is the enthalpy change corresponding to the 100% conversion. Although ΔH^* is unknown and cannot be obtained experimentally, its value must be constant for the same resin transforming to a fully cured network. Taking the $\Delta H_{gel} = 22.2$ and assuming the $\Delta H^* = 408.3$ as reference (maximum ΔH obtained in this work for the TMPTA/AIBN system, Table I), the de-
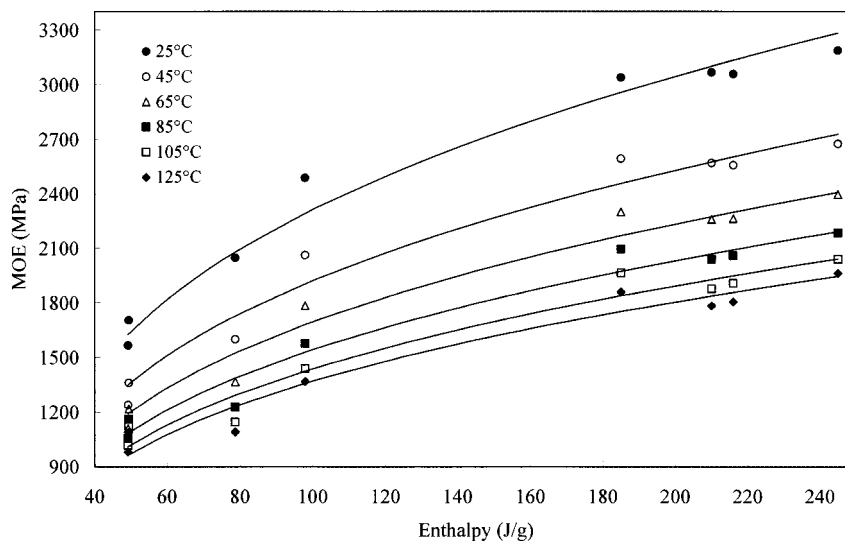
Figure 1   Nonlinear regression of *MOE* as a function of ΔH ($q = 3$, $\Delta H = 22.2$ J/g).

gree of conversion at gel point p_{gel} for the TMPTA can be estimated to be about 5%. This shows a striking contrast with a nonlinear polycondensation system of which the predicted gel point is much higher. However, this should not be surprising, as even for the cured films of TMPA/BP/MDEA plus eugenol system ($\Delta H = 49.2$), the so estimated final degree of conversion is only about 12%. Since the actual ΔH^* is certainly greater than 408.3, the actual value of p_{gel} should be even lower.

Equation 1 expresses the dependence of the *MOE* on the curing enthalpy. If the ΔH^* is known, the terms ΔH and ΔH_{gel} can be replaced by the conversion degree $p = \Delta H / \Delta H^*$ and $p_{gel} = \Delta H_{gel} / \Delta H^*$, and then eq. (1) can be written as:

$$MOE = a^*(p - p_{gel})^{1/3}$$

with $a^* = a \, (\Delta H^*)^{1/3}$. For the value $\Delta H^* = 408.3$, the values of a in Table II should be multiplied by a factor of 7.42 to keep the above equation valid.

The fact that $q = 3$ describes best the relationship between *MOE* and ΔH suggests that a great part of the bonds formed in the networks did not produce crosslinking points, rather the formation of elastically inactive loops and pending chains might be predominant at a higher degree of conversion. Nevertheless, this does not mean that the crosslinking density in a network with a higher conversion degree is lower than in a network with a lower conversion degree. The crosslinking density still increases with the conversion degree, but the ratio of the number of crosslinking nodes or bonds (N_c) to the total number of bonds (N_t) will decrease.

Temperature dependence of the modulus of elasticity

Figure 2 shows the variation of *MOE* as a function of temperature at constant heating rate (5°C/min) for TMPTA films cured with two different initiators and in one case with the addition of a phenol, namely eugenol. The presence of a viscoelastic transition zone from −60°C to a certain temperature and a plateau above this temperature can be seen there. Both the rate of decrease in *MOE* and the temperature at which the *MOE* tends to level off depend on the formulations, indicating that the nature and/or concentration of the elastically active network chains (EANCs)[16] are different for different systems and at different temperatures.

The viscoelastic behaviors of a polymeric material are associated with the motion of units of different sizes, such as specific groups, side chains, and main chain segments. In general, the *MOE* of a material will decrease several orders in magnitude when its state changes from glassy to rubbery. However, the *MOE* in Figure 2 decreases only to about 1/3 to 1/5 of its initial value from −80 to 185°C. Furthermore, all the samples broke suddenly at temperatures higher than 125 to 200°C depending on their formulation, and the strain at rupture was less than 0.5%. This indicates that the TMPTA films remained very brittle at higher temperatures and behave as energetic systems. The viscoelastic behavior of TMPTA is more likely associated with a γ or β transition, corresponding to the motion of specific groups, pending chains or smaller chain segments in the network structure due to the increase of free volume. Hence, although the crosslinking density is unlikely affected by the temperature, the interactions between noncrosslinking chains, including entanglements, may be significantly altered by such a
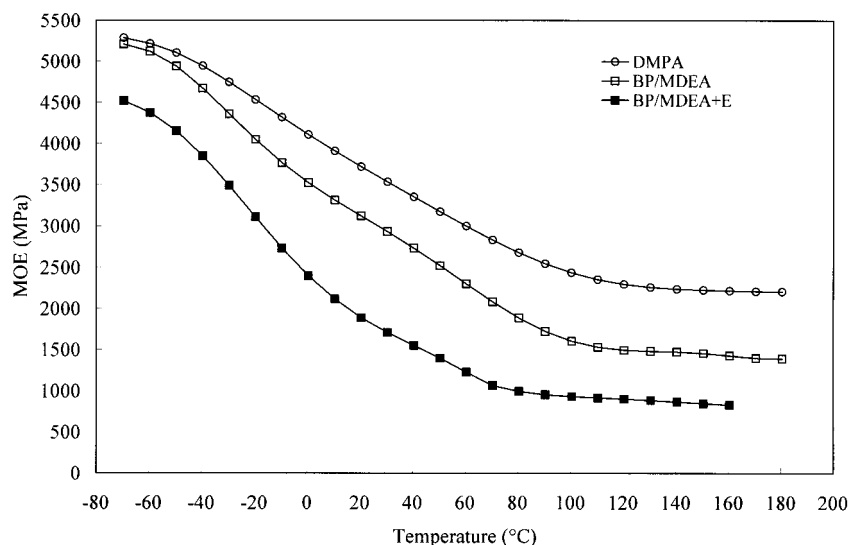
Figure 2 Evolution of the modulus of elasticity of three acrylic resin films.

transition and therefore play an important role in determining the rigidity (or inversely the flexibility) of the TMPA networks.

Based on the β transition model of Simon and Ploehn,[17] an Arrhenius type equation is proposed to express the temperature-dependence of the MOE for a TMPA network with a given formulation:

$$MOE = A \exp(E/RT) \qquad (2)$$

In the above equation, E is the average activation energy for the relaxation process and A is a preexponential factor and both of them are associated with the specific formulation while independent of the temperature in, at least, a given temperature range. By drawing Ln*MOE* versus $1/RT$ plots with the MOE experimental data obtained under different isothermal conditions, the best-fitting values of A and E have been

obtained for each formulation and eq. (2) with these values can describe the MOE experimental data with excellent coefficients of correlation (Table III). Except for the two TMPTA/BP/MDEA systems with DMP or eugenol as inhibitor, all others can be well described with a single A and a single E in the temperature range of 25–125°C. In the former cases, it is found that eq. (2) can also hold for different temperature ranges if we use the piecewise regression with the temperature 65°C as a switch point to calculate separately the corresponding values of A and E. Apparently, for these two systems, the mechanisms involved in the transition process are different at different temperature ranges. The values of A and E obtained are shown in Table III.

Although the correlation is very clear, it is rather difficult to decide to what physical parameters A and

TABLE III
Parameters A, E, and c in Equations (2) and (3) for TMPTA Networks

Formulation	E (J/mol)	A	R^2	c	Temperature range (°C)
DMPA	4,791.9	441.6	0.989	72.8	25–125
DMPA + P	5,355.8	339.2	0.995	59.2	25–125
DMPA + DMP	5,286.3	357.5	0.995	61.8	25–125
DMPA + E	4,931.4	410.6	0.995	75.2	25–125
BP/MDEA	6,128.8	207.7	0.994	49.1	25–125
BP/MDEA + P	6,344.3	150.3	0.976	39.2	25–125
BP/MDEA + DMP	7,314.0	87.7	0.973	29.2	25–65[a]
BP/MDEA + E	7,084.6	87.1	0.963	29.0	25–65[a]
BP/MDEA + DMP	2,083.7	578.8	0.997	192.5	65–125[b]
BP/MDEA + E	2,263.9	494.9	0.998	165.0	65–125[b]
BP/MDEA + DMP	4,258.7	257.3	0.923	85.6	25–125
BP/MDEA + E	4,737.8	221.4	0.920	73.8	25–125

[a] Temperatures at 25, 35, 45, 55, and 65°C.
[b] Temperatures at 65, 85, 105, and 125°C.

E correspond.[18] In general, *A* is greater while *E* is smaller for a TMPTA network with a higher conversion degree in the transition temperature range (25–125 or 25–65°C). Consequently, we can hypothesize that the preexponential factor *A* is a parameter referring to the crosslinking density[18] of a network and *E* is the average activation energy of the units capable of participating the transition process. By inference, for the TMPTA/DMPA systems, the networks are more crosslinked while the units participating the transition are smaller. On the other hand, the networks of the TMPTA/BP/MDEA systems are less crosslinking while the units participating the transition are larger, and this is especially accentuated by the addition of phenols.

Modeling of the dependence of the *MOE* on the conversion degree and temperature

Equation 1 not only fits the data well but also gives a mechanistic explanation of the relation between the *MOE* and the conversion degree, with the factor *a*, however, being assigned different values for different temperatures at which the *MOE* was measured. This implies that *a* must be a temperature-dependent parameter reflecting the contribution of network structure characteristics other than the crosslinking density, which are unlikely affected by the temperature under the experimental conditions. If *a* can be correlated with the temperature, a more accurate model will be obtained to account for both the influences of the conversion degree and the temperature, by inference for both the contributions of the crosslinking density and the interactions between the nonbonding chains or chain segments.

For a given formulation, both eqs. (1) and (2) give calculated values almost the same as those of the measured *MOE*, that is,

$$a(\Delta H - \Delta H_{gel})^{1/3} \approx MOE \approx A \exp(E/RT) \,,$$

with ΔH on the left side and T on the right side as an independent variable, respectively. Therefore, the temperature dependence of the parameter *a* can be determined by combing eq. (1) with (2), and a model relating the *MOE* and the conversion degree as well as the temperature can be established as:

$$MOE = c(\Delta H - \Delta H_{gel})^{1/3} \exp(E/RT) \qquad (3)$$

where $c = A/(\Delta H - \Delta H_{gel})^{1/3}$ is a constant for a given formulation and its values are presented in Table III.

As to the physical meaning of the parameter *c*, it may integrate both the contributions of the network crosslinking density and the interactions between the nonbonding chains and chain segments. One can imagine that *c* can be divided into two parts, i.e., $c = c_1 c_2$; then eq. (3) may be expressed as $MOE = [c_1(\Delta H - \Delta H_{gel})^{1/3}] [c_2 \exp(E/RT)]$. The first term could be considered as the contribution of the network crosslinking density that is not sensitive to the temperature variation, and the second term as the contribution of all the secondary forces, i.e., the interactions between noncrosslinking chains or chain segments of which the mobility depends on the temperature. However, it is impossible to determine their relative importance with this model and the experimental data. In the temperature range at which the *MOE* decreases gradually (25–125 or 25–65°C), what is certain is that the overall contribution (parameter *c*) of a TMPTA network increases with the degree of conversion.

To check the validity of eq. (3), the experimental *MOE*s and data fitting curves of the films for five formulations are shown in Figure 3 (other formulations are not shown for reason of clarity). It proves that eq. (3) does describe well the relationship between the *MOE* and the degree of conversion, as well as the temperature. For all the TMPA resin formulations in this study, the maximum deviation of the calculated values from the measured ones is about ± 5%.

CONCLUSION

The conversion degree and *MOE* of UV-cured TMPTA resin films depend on both the type of initiators and the addition or not of phenolic compounds. As the two initiators participate in the photopolymerization of TMPTA through different mechanisms, their effectiveness in hardening the resin are quite different. The DMPA results in a higher degree of conversion and produces films with higher *MOE,* while the BP/MDEA mixture yields a lower degree of conversion and more flexible films. The three phenols have all a negative effect on the ΔH and *MOE* of TMPTA films; their importance in reducing the ΔH and *MOE* could be ranked in the order eugenol > DMP > phenol. This effect is more pronounced for the BP/MDEA systems than for the DMPA systems.

Under the experimental conditions (25–125°C), the networks respond to exercised stress viscoelastically, i.e., their modulus of elasticity decreases with temperature. However, the TMPTA networks seem to not have a T_g below their decomposition or rupture temperature and do not show typical rubber-like elasticity. The decrease in *MOE* with temperature is probably due to a β transition associated with the reorganization of the nonbonding chains.

Three equations are proposed to model the structure–property of TMPTA networks. First, the correlation between the *MOE* and the ΔH and hence by inference the degree of conversion reveals that the *MOE* increases with the crosslinking density, which can be expressed as $MOE = a(\Delta H - \Delta H_{gel})^{1/q}$, with *q*
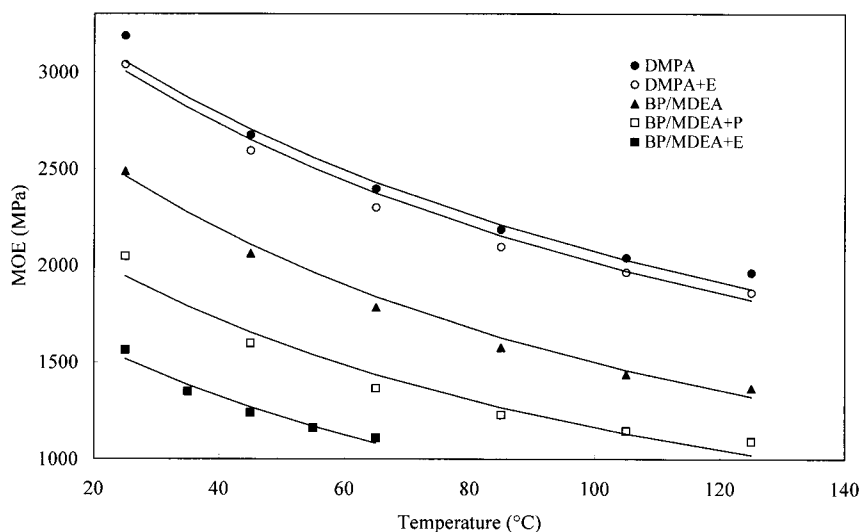
Figure 3 Comparison of the *MOE*s measured with TMA and those calculated by using eq. 3.

being approximately 3. This suggests that cyclization and other nonidealities in the network may be important and the contribution of the interactions between the nonbonding chains to the *MOE* is not negligible, although their relative importance is difficult to determine. Second, the dependence of the *MOE* on the temperature implies that the relaxation of networks may be the main cause of the observed viscoelastic transition, which can be described by an Arrhenius type equation. The activation energy to overcome the energy barrier for the relaxation of these chains seems greater for a less crosslinked network than for a higher crosslinked one, while the number of units participating in the transition appears larger in the former case. Finally, a model relating the *MOE*, the curing enthalpy of network formation (degree of conversion), and the temperature is proposed and can describe well the experimental data. For a given network at a given temperature, its *MOE* depends on the degree of conversion, the activation energy of relaxation, and a proportional factor *c* characterizing the overall effects of the crosslinking density and the secondary forces between the nonbonding chains and chain segments in the networks.

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