

# Peroxide Crosslinking of a Styrene-Free Unsaturated Polyester

I. Mironi-Harpaz,<sup>1</sup> M. Narkis,<sup>1</sup> A. Siegmann<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Technion–Israel Institute of Technology, Haifa 32000, Israel

<sup>2</sup>Department of Materials Engineering, Technion–Israel Institute of Technology, Haifa 32000, Israel

Received 9 September 2006; accepted 16 March 2006

DOI 10.1002/app.25385

Published online 6 April 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Thermoset unsaturated polyesters are usually obtained by the crosslinking of unsaturated polyester chains dissolved in an unsaturated, reactive, monomeric diluent, which is usually styrene. This article describes a new approach in which styrene-free unsaturated polyester chains are intrinsically cured into a crosslinked matrix. The gel time, gel content, swelling degree, glass-transition temperature, dynamic mechanical properties, tensile properties, and molecular weight between crosslinks (calculated according to both the Flory–Rehner equation and the theory of rubber elasticity) of the crosslinked polymer are studied as a function of the peroxide concentration. All properties change considerably upon the addition of small amounts of peroxide (between

1 and 2 wt %) and change to a lesser extent with higher peroxide concentrations (up to 6 wt %). The thermal properties of the isolated gel fraction are studied as a function of the peroxide concentration. The sol fraction demonstrates a plasticizing effect on the crosslinked network, affecting the glass-transition temperature and stress–strain behavior of the crosslinked polymer. In light of the crosslink densities derived from swelling experiments, a molecular structure and crosslinking mechanism are suggested for the gel fractions of 1 and 6 wt % peroxide crosslinked unsaturated polyester chains. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 885–892, 2007

**Key words:** crosslinking; density; polyesters

## INTRODUCTION

Unsaturated polyester (UP) liquid resins are converted into thermosetting matrices in the presence of a peroxide/promoter catalyst system via curing, which yields crosslinked polymers. These UP resins are often bicomponent systems comprising UP alkyd chains dissolved in an unsaturated, reactive, monomeric diluent, which is usually styrene. The alkyd chains are formed by the polycondensation of diols with unsaturated and saturated dicarboxylic acids.

As the curing of a UP system takes place, its molecular weight increases until a group of chains become linked together into a network of infinite molecular weight. This sudden and irreversible transformation from a viscous liquid into an elastic gel, which marks the first appearance of the infinite network, is called the gel point. The formed gel is essentially insoluble in good solvents for the UP polymer chains. The remaining linear and branched, but still soluble, resin is defined as sol. Beyond the gel point, as long as the curing temperature is higher than the glass-transition temperature ( $T_g$ ) of the system, the reaction continues, extending the network and increasing the crosslink density,  $T_g$ , and ultimate physical properties. In most

cases, cured UP resins are relatively rigid, brittle materials. Highly crosslinked network polymers are widely used in structural applications such as adhesives and advanced composites.<sup>1–4</sup>

The network structure of styrene-containing crosslinked polyesters differs noticeably from a homogeneous network because two types of network species, polyester and polystyrene, coexist. The crosslinked structure of cured polyester resins is also inhomogeneous because of the formation of microgel particles, which are formed by both inter- and intramolecular reactions. Because of the strong intramolecular reactions, the primary UP chains may be present in the form of crosslinked coils, and as polymerization proceeds, the crosslinking of the microgels occurs, leading to macrogelation in the system.<sup>5,6</sup>

The crosslink density, an inverse function of the average molecular weight between crosslinks ( $\bar{M}_c$ ), is an important factor governing the physical properties of cured thermoset resins. The crosslink density of a cured, styrenated UP resin can be changed by the variation of the concentration of unsaturation in the UP chain or the styrene content in the resin or by the control of the final double-bond conversion with different amounts of peroxide. Theoretically, a styrene-free UP containing double bonds within the main chain should be crosslinkable by radicals. To the best of our knowledge, the peroxide crosslinking of styrene-free UP chains has never been reported.

Correspondence to: M. Narkis (narkis@tx.technion.ac.il).

In this article, the crosslinking of styrene-free UP chains is suggested. The thermal, mechanical, and chemorheological properties of crosslinked UP alkyds as well as the thermal properties of the isolated gel fractions are studied as a function of the peroxide concentration.

## EXPERIMENTAL

A commercial, experimental-grade UP alkyd (without styrene) was used in this study (supplied by Makhteshim, Beer-Sheva, Israel). The alkyd's average molecular weight was about 1600 g/g mol, and it had an unsaturation level of about 2.5 C=C bonds per oligomer chain, which originated from maleic anhydride. To induce polymerization (curing), a selected free-radical-forming peroxide, *tert*-butyl peroxy-3,5,5-trimethylhexanoate (Trigonox 42PR; Akzo Nobel, Arnhem, The Netherlands), developed for the cure of UP resins, was added at a concentration of 1–6 wt %. Degassed samples were cured in an oven at 110°C for 24 h, and this was followed by postcuring at 150°C for 4 h. The peroxide is a high-temperature peroxide usually used (in the presence of an accelerator) at 80°C. The high curing temperature, 110°C, stems from the system's characteristics; that is, proper mixing of alkyd systems is hard to achieve below 80°C. Because an accelerator was not added, prolonged curing times were needed to complete the crosslinking.

The gel content (averaged from three samples) and the degree of swelling of the cured polyester alkyd were determined after overnight extraction in boiling methyl ethyl ketone (MEK). The degree of swelling is defined as the absorbed solvent weight divided by the gel weight. Density measurements were carried out on a Sartorius balance equipped with a density determination kit. Volume shrinkage upon cure was calculated as follows:

$$\text{Shrinkage (\%)} = \left( \frac{1}{\rho_{\text{uncured}}} - \frac{1}{\rho_{\text{cured}}} \right) / \frac{1}{\rho_{\text{uncured}}} \times 100$$

where  $\rho_{\text{cured}}$  is the density of the cured UP alkyd and  $\rho_{\text{uncured}}$  is the density of the uncured UP alkyd.

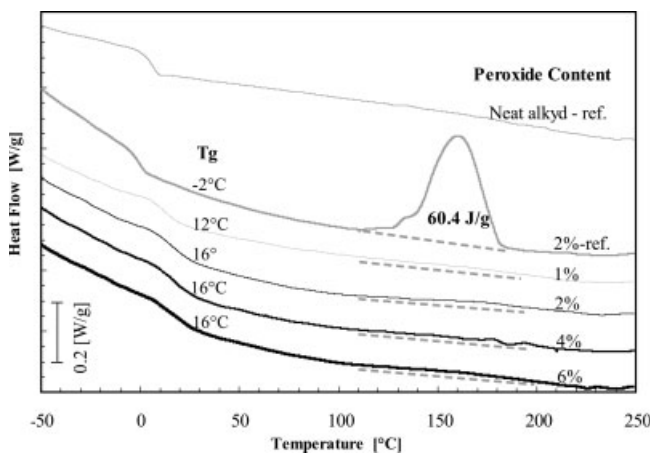
Differential scanning calorimetry (DSC; DSC 30, Mettler, Columbus, OH) was employed at a heating rate of 10°C/min under a nitrogen atmosphere. Mechanical analysis in the tension mode was conducted on a Rheometric Scientific (Piscataway, NJ) MK I11 dynamic mechanical thermal analyzer without an extensometer at room temperature in the static tension mode; thus, the moduli values could not be determined from these stress–strain curves. The samples were rectangular and had typical dimensions of 3 × 1 × 5 mm<sup>3</sup>. The force exerted on the samples was increased at a rate of 0.0083 N/s. Dynamic mechanical

thermal analysis (DMTA; series 7, PerkinElmer, Wellesley, MA) was conducted in the three-point-bending mode at 1 Hz. Heating was carried under an inert nitrogen atmosphere at a rate of 3°C/min under force control. A TA AR1000-N parallel plates rheometer (TA Instruments, New Castle, DE) was used with 2-cm-diameter discs at 110°C and 6.28 rad/s with 35% strain (defined as the angular displacement divided by the sample gap) and a typical gap of 800 μm to study the chemorheological properties of the alkyd undergoing curing.

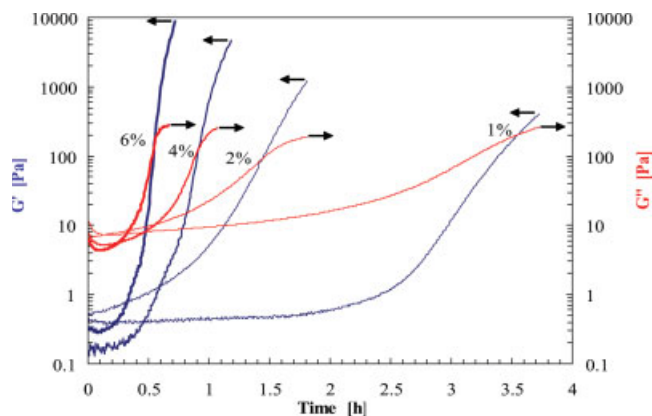
## RESULTS AND DISCUSSION

The styrene-free UP chains were cured with several concentrations of peroxide, and the heat generated by the chemical reactions was determined with DSC. The overall heat of reaction that evolved during curing was estimated from a nonisothermal temperature scan that took the reaction to completion.<sup>7</sup> Figure 1 depicts the DSC thermograms of the already cured UP alkyds containing 1, 2, 4, or 6 wt % peroxide. The reference systems shown are a neat alkyd (without peroxide) and an uncured UP alkyd mixed with 2 wt % peroxide, which underwent curing during heating in the DSC pan. As evidenced by the thermogram of the neat alkyd, in the absence of peroxide, no curing took place. The peak characterizing the heat of reaction (observed for the uncured alkyd/2 wt % peroxide system) is insignificant for the already cured systems, indicating no residual heat. Thus, all the peroxide-crosslinked UP alkyd systems were cured to the maximum possible extent.

$T_g$  is often used as an empirical measure of the crosslink density.<sup>8,9</sup> An increase in the molecular weight of the polymer and in its crosslink density results in an increase in  $T_g$  of the polymer because of the reduced



**Figure 1** DSC thermograms of UP alkyds cured with various peroxide contents at 110°C for 24 h and then postcured at 150°C for 4 h. The reference systems are neat alkyd (without peroxide) and uncured UP alkyd with 2 wt % peroxide. The curves have been shifted for clarity.



**Figure 2** Storage shear modulus ( $G'$ ) and loss shear modulus ( $G''$ ) versus the cure time for UP alkyds containing 1, 2, 4, or 6 wt % peroxide and cured at 110°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

mobility of the chain segments.<sup>8</sup> The  $T_g$  values of the reference and crosslinked systems measured by DSC are shown in Figure 1.  $T_g$  of the uncrosslinked alkyd was about  $-2^\circ\text{C}$ , and it increased by  $14\text{--}18^\circ\text{C}$  upon crosslinking.

Rheological properties such as the viscosity and dynamic modulus are sensitive to the variation of the molecular structure during curing, which is associated with the process of chemical conversion. Oscillatory shear-flow measurements have been used to investigate the rheological behavior of resins undergoing curing. Literature reports indicate several different approaches to determining the gel time from dynamic measurements. According to two approaches, the gel time is the time at which the elastic modulus and dynamic modulus coincide or the time at which the loss modulus maximizes; the latter is more related to the time at which vitrification occurs.<sup>10–13</sup> The dynamic shear-flow behavior during curing is depicted in Figure 2. At short curing times, the loss moduli are higher than the storage moduli because of the polymer chains' viscous dominant behavior. As curing progresses, both the storage and loss moduli increase until their values coincide (i.e., the gelation of the alkyd is reached), and the gel times are determined. Beyond the point of gelation, the trend changes and the storage moduli are higher than the loss moduli because of the dominant solid elastic behavior of the polyester gel. As observed in Figure 2, the gel time decreases with increasing peroxide content. The gel times at 110°C for styrene-free UP cured with 1 and 6 wt % peroxide are about 3.5 and 0.5 h, respectively.

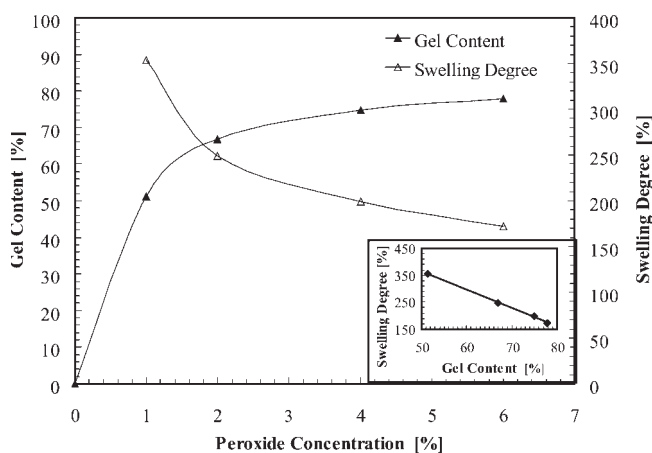
The gel content and the degree of swelling in boiling MEK of the cured UP alkyd as a function of the peroxide concentration are shown in Figure 3. Generally, the gel content increases with the peroxide concentration; however, above 2 wt % peroxide, the gel

content is only slightly further increased until a maximum gel content of about 80% is attained. The degree of swelling is a measure of  $\bar{M}_c$ , decreasing with an increasing degree of crosslinking.<sup>14</sup> As observed in Figure 3, the degree of swelling decreases significantly with the extent of crosslinking up to 2 wt % peroxide and further decreases with the addition of up to 6 wt % peroxide. The insert in Figure 3 shows a linear relationship between the swelling degree and the gel content in the studied range of peroxide concentrations. At equilibrium swelling,  $\bar{M}_c$  can be estimated by the Flory–Rehner equation<sup>14</sup>:

$$\bar{M}_c = \frac{V_1 \rho_2 \left( v_{2m}^{1/3} - \frac{v_{2m}}{2} \right)}{-\left( \ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2 \right)} \quad (1)$$

where  $V_1$  is the molar volume of the solvent,  $\rho_2$  is the density of the gel fraction,  $v_{2m}$  is the volume fraction of the gel in the swollen mass, and  $\chi_1$  is the polymer–solvent interaction parameter. In this case, the interaction parameter of crosslinked UP alkyd/MEK was taken to be 0.4, which is the average value for both polycaprolactone/MEK<sup>15</sup> and crosslinked vinyl ester (containing styrene)/MEK<sup>16</sup> systems. The  $\bar{M}_c$  values calculated from the Flory–Rehner equation as well as the  $\bar{M}_c$  values calculated from the theory of rubber elasticity (discussed later in detail) are presented in Table I and in Figure 4.  $\bar{M}_c$  is highest for the UP alkyd crosslinked with 1 wt % peroxide, and as expected, it decreases with the peroxide content. The  $\bar{M}_c$  value decreases significantly between the systems containing 1 and 2 wt % peroxide and further decreases as the peroxide content increases.

Free radicals acting on polymers may cause scission and the formation of branched and crosslinked structures. Above the gel point, the progress of the



**Figure 3** Gel content and swelling degree versus the peroxide content for the crosslinked UP alkyd systems. The insert shows the swelling degree versus the gel content of the crosslinked UP alkyd systems.

TABLE I  
Properties of Peroxide-Cured UP Alkyd

Peroxide content (%)	Density (g/cm <sup>3</sup> )	Shrinkage (%)	$E'$ at 80°C (Pa)	$\bar{M}_c$ (g/g mol) <sup>a</sup>	Gel density (g/cm <sup>3</sup> )	$\bar{M}_c$ (g/g mol) <sup>b</sup>
0	1.24	—	—	—	—	—
1	1.28	3.0	$5.23 \times 10^5$	21,500	1.25	13,700
2	1.29	3.5	$1.28 \times 10^6$	8,900	1.23	6,800
4	1.28	3.0	$4.33 \times 10^6$	2,600	1.22	4,400
6	1.28	3.0	$5.03 \times 10^6$	2,200	1.22	3,300

<sup>a</sup> Calculated from DMTA data according to  $E' = 3\rho/\bar{M}_cRT$  [eq. (4)].

<sup>b</sup> Calculated from swelling data according to the Flory–Rehner equation [eq. (1)].

gel content with the peroxide concentration can be expressed according to the modified Charlesby–Pinner method:<sup>17</sup>

$$S + S^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 \bar{X}_n I} \quad (2)$$

where  $S$  is the sol fraction;  $p_0$  and  $q_0$  are the probabilities of the main-chain scission and crosslinking reactions per monomer unit per unit of concentration, respectively;  $\bar{X}_n$  represents the alkyd's initial number-average degree of polymerization; and  $I$  is the peroxide concentration. The intercept of the extrapolated value of  $S + S^{1/2}$  at  $I \rightarrow \infty$  is equal to  $p_0/q_0$ . The extrapolation of the  $S + S^{1/2}$  values shown in Figure 5 results in a  $p_0/q_0$  ratio of approximately 0.6, suggesting the occurrence of three scission events per five crosslinking reactions. The occurrence of both crosslinking and scission events is one of the factors preventing the gel content from reaching 100%; other factors are spatial limitations exerted upon the crosslinking reaction. Linear extrapolation of the curve to  $S + S^{1/2} = 2$  gives the critical peroxide concentration necessary for gel formation,<sup>18</sup> which has been calculated to be 0.42 wt %. Thus, all the investigated cured UP alkyd systems are well

above the critical peroxide concentration level, forming a crosslinked styrene-free UP.

The sol and gel fractions of the crosslinked UP alkyd are expected to exhibit different properties (e.g., thermal and mechanical properties). Figure 6 depicts the DSC thermograms of the gel fraction (after extraction in MEK) of the cured UP alkyds containing 1, 2, 4, or 6 wt % peroxide. The  $T_g$  of all gel fractions is higher than that of the whole system (containing both sol and gel fractions; see Fig. 1). Long chains are predominantly incorporated into the gel,<sup>19</sup> thus yielding a sol fraction of a low molecular weight. Moreover, the sol fraction may include polymer chains that have undergone multiscission events. Thus, the sol fraction may even act as a plasticizer, reducing the  $T_g$  of the whole system. The  $T_g$  of the gel fraction increases with the peroxide content, exhibiting a vast increase upon the addition of the peroxide (from 0 to 1 wt % peroxide), and further slightly increases as the peroxide content increases from 1 to 6 wt %. As the crosslink density increases, a less mobile network prevails, its properties changing more profoundly with the addition of low peroxide concentrations. This behavior was also observed

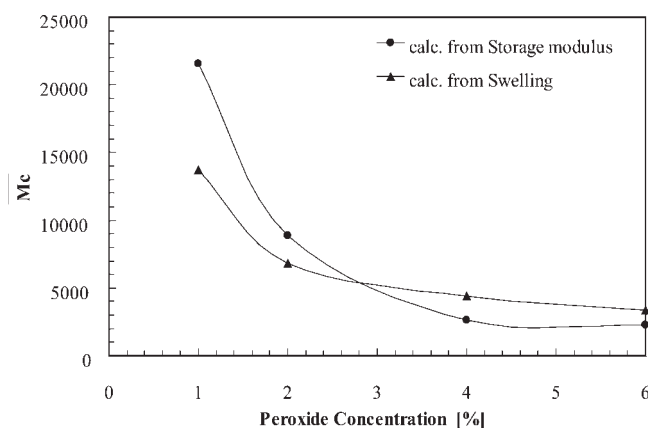


Figure 4  $\bar{M}_c$  of UP alkyds cured with various peroxide contents, as calculated from swelling experiments and from the storage modulus.

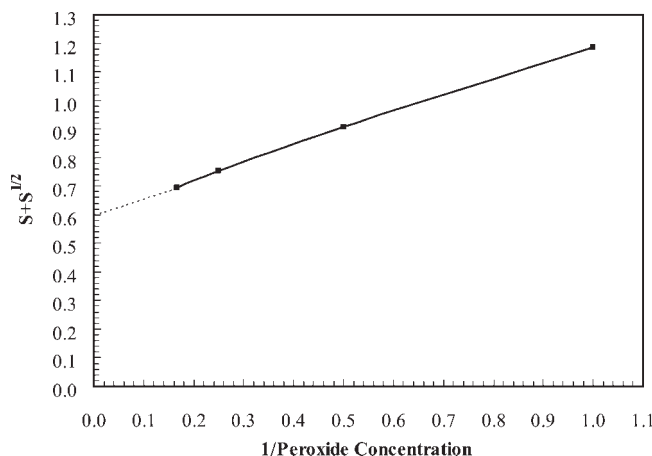
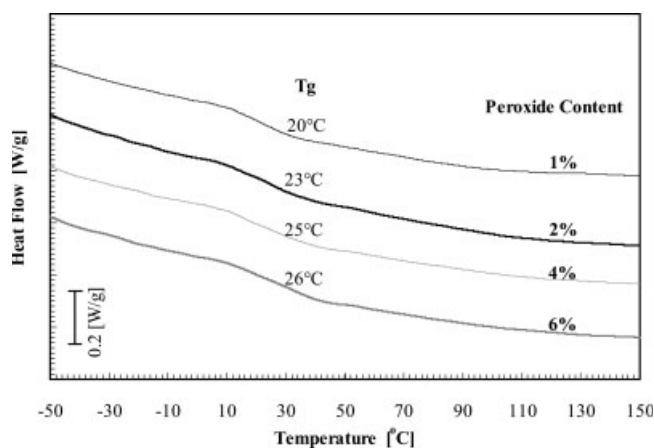


Figure 5 Plot of  $S + S^{1/2}$  versus the reciprocal peroxide concentration of crosslinked UP alkyds.



**Figure 6** DSC thermograms of the gel fraction of UP alkyds cured with various peroxide contents at 110°C for 24 h and then postcured at 150°C for 4 h. The curves have been shifted for clarity.

for the gel content (Fig. 3) and  $T_g$  of the whole system (Fig. 1).

Assuming that the sol fraction acts as a plasticizer for the crosslinked UP alkyd network, we can use the Fox equation to deduce its  $T_g$ . According to the Fox equation<sup>20</sup>

$$\frac{1}{T_{g,blend}} = \frac{w_{gel}}{T_{g,gel}} + \frac{w_{sol}}{T_{g,sol}} \quad (3)$$

where  $w_{gel}$  is the weight fraction of the gel,  $w_{sol}$  is the weight fraction of the sol,  $T_{g,blend}$  is the glass-transition temperature of the cured UP alkyd,  $T_{g,gel}$  is the glass-transition temperature of the gel fraction, and  $T_{g,sol}$  is the glass-transition temperature of the sol fraction. These data are presented in Table II. Interestingly,  $T_{g,sol}$  decreases considerably with the increase in the peroxide content, from 4 to  $-14^\circ\text{C}$  for 1 and 6 wt % peroxide, respectively. As the peroxide concentration in the system increases, the sol content decreases, becoming more degraded and consisting of lower molecular weight chains.

The dynamic mechanical properties of crosslinked systems depend on the degree of crosslinking. The rubbery modulus, that is, the storage modulus magnitude above  $T_g$ , increases with the crosslink density,

the  $T_g$  values increase, and the loss modulus peak becomes broader. The broadening of the glass-to-rubber transition is often assumed to be due to heterogeneity in the network structure, such as a distribution in the molecular weight between crosslinks.<sup>8</sup> The storage and loss moduli of the cured UP alkyd systems are depicted in Figures 7 and 8, respectively. The rubbery modulus,  $T_g$ , and breadth of the loss modulus peak all increase with the peroxide concentration, reflecting a restriction of the segmental mobility. The small difference found between the aforementioned properties of the 4 and 6 wt % peroxide crosslinked systems implies the small difference in the crosslink density and gel fraction between the two samples, as already shown in Tables I and II. The increase in  $T_g$  with the peroxide concentration is in agreement with the DSC thermograms (Fig. 1). However, the  $T_g$  values depicted by DMTA are higher than the values depicted by DSC, as is commonly the case.

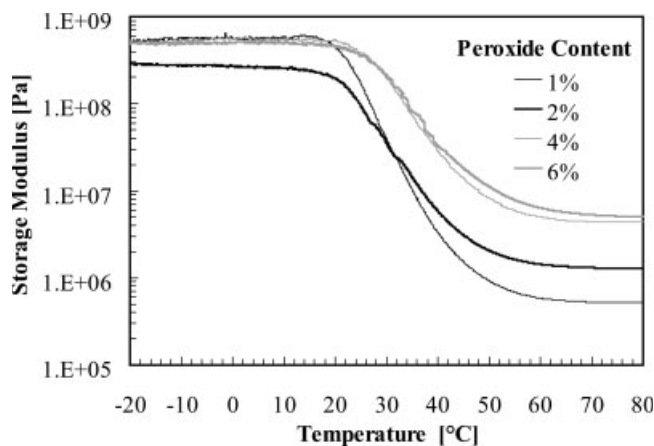
According to the classical theory of rubber elasticity, the dependence of Young’s modulus ( $E$ ) on the crosslink density is given by

$$E = 3\Phi nRT \quad (4)$$

where  $n$  represents the number of active network chains per unit of volume, which is sometimes called the network or crosslink density ( $n = \rho/\bar{M}_c$ , where  $\rho$  is the density);  $R$  is the universal gas constant;  $T$  is the absolute temperature; and  $\Phi$  is a correction factor, that is, a front factor. For an ideal rubber,  $\Phi$  is unity at all temperatures.<sup>8,21,22</sup> Katz and Tobolsky<sup>22</sup> determined that  $\Phi$  is between 2 and 3 for highly crosslinked UP/styrene systems.  $\bar{M}_c$  calculated from the  $E'$  (storage modulus) values at 80°C (which is above the  $T_g$  of all cured UP alkyd systems), with  $\Phi$  taken as 1, is shown in Figure 4 and in Table I. The calculated  $\bar{M}_c$  values range from 21,500 to 2200 g/mol for the 1 and 6 wt % peroxide crosslinked UP alkyds, respectively. The  $\bar{M}_c$  values obtained by the two methods, that is, from swelling experiments according to the Flory–Rehner equation and from DMTA according to the theory of rubber elasticity, are different. The values calculated from dynamic mechanical measurements are higher than those cal-

**TABLE II**  
Thermal Properties of Cured UP Alkyd and Its Sol and Gel Fractions

Peroxide content (%)	Measured $T_g$ of cured UP alkyd ( $^\circ\text{C}$ )	Gel		Sol	
		Weight fraction	Measured $T_g$ ( $^\circ\text{C}$ )	Weight fraction	Calcd. $T_g$ ( $^\circ\text{C}$ )
1	12	0.51	20	0.49	4
2	16	0.67	23	0.33	3
4	16	0.75	25	0.25	-8
6	16	0.78	26	0.22	-14

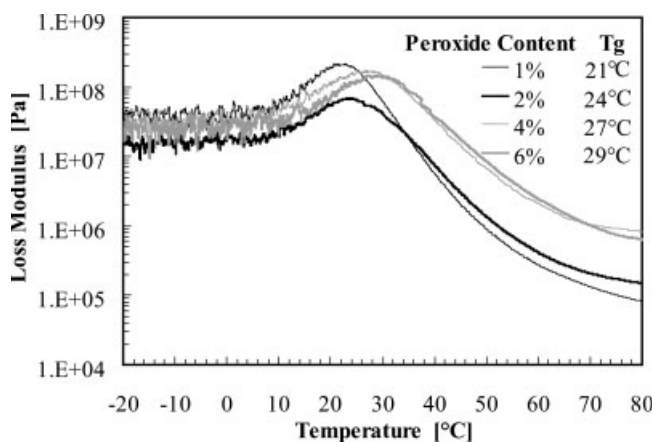


**Figure 7** Storage modulus of crosslinked UP alkyds cured with various peroxide contents.

culated by the Flory–Rehner equation when a low peroxide concentration is used (1 or 2 wt %) and are lower than those calculated by the Flory–Rehner equation for the higher peroxide concentrations (4 and 6 wt %). Although the values are different, the trend is similar. Because the  $E'$  values are affected by both the gel and sol fractions, it is feasible that upon reduction in the sol fraction, that is, at a high peroxide content, the difference between  $\bar{M}_c$  values obtained by the two methods will decrease. Another reason for the diminishing discrepancy in the  $\bar{M}_c$  values is the changing molecular structure of the crosslinked network. The average molecular weight of the neat UP alkyd chains is about 1600, with an average unsaturation level of about 2.5 C=C bonds per oligomer chain. The high  $\bar{M}_c$  values and the low gel content (51%) of the system obtained with 1 wt % peroxide suggest a mechanism that involves more branching of the chains rather than the formation of a network through crosslinking. Thus, it is feasible to assume that only some of the C=C double bonds have reacted in this system. This may also result in a higher content of chain ends dangling in the crosslinked network, leading to  $\bar{M}_c$  values that are actually lower than the ones calculated according to the theory of rubber elasticity without consideration of chain ends. As more peroxide is added to the alkyd, more C=C bonds react to form a denser crosslinked network. Hence, the addition of 6 wt % peroxide results in the reaction of most of the C=C bonds, yielding a highly crosslinked polymer containing a high gel content (78%) associated with low  $\bar{M}_c$  values. Thus, network formation is more pronounced than branching. During network formation, the trapping of physical entanglements can occur, and this contributes to the storage modulus and affects  $\bar{M}_c$ , resulting in a higher apparent crosslink density (lower  $\bar{M}_c$  values).

In association with the  $\bar{M}_c$  values obtained from swelling, which take into account only the gel fraction, the estimation of the gel fraction's molecular structure for UP alkyds cured with 1 and 6 wt % peroxide can be considered. For this estimation, we should consider that one crosslinking reaction is the formation of one new (C—C) bond from two (C=C) bonds, leading to branching and ultimately to network formation. According to Table I,  $\bar{M}_c$  of the UP alkyd crosslinked with 1 wt % peroxide is about 13,500. Because the molecular weight of the neat UP alkyd chains is about 1600, about nine chains are connected to one another. If the starting unsaturation level is about 2.5 (C=C) bonds per oligomer chain, then nine connected chains would leave about three unreacted (C=C) bonds. For the UP alkyd crosslinked with 6 wt % peroxide,  $\bar{M}_c$  is about 3500 (Table I), implying two to three connected chains. Thus, only one unreacted (C=C) bond is included in about nine chains. These calculations may back up the mechanisms suggested earlier; that is, upon crosslinking with low peroxide contents, crosslinking leads mainly to branching, whereas at high peroxide contents, crosslinking leads mainly to network formation.

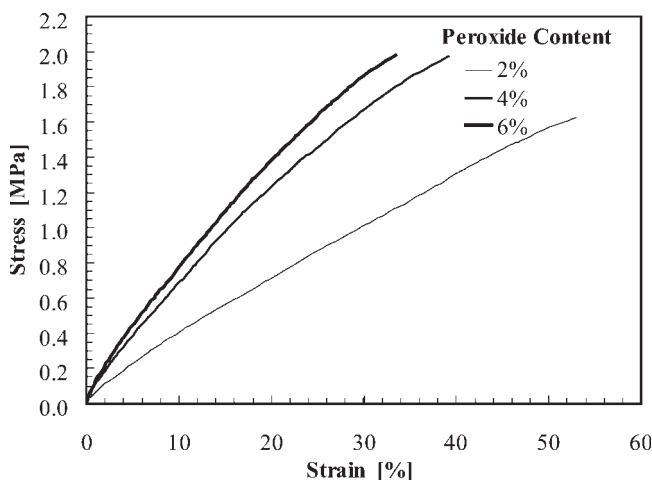
The peroxide crosslinking of styrene-free UP chains involves an intermolecular reaction, as opposed to the crosslinking of styrene-containing UP resins, in which most crosslinking reactions occur between UP chains and styrene. Hence, the intrinsically crosslinked UP alkyd must have properties dramatically different from those of the common styrene-containing thermoset UP. One such property is the low shrinkage values of the cured alkyd–peroxide systems. As illustrated in Table I, the density of the cured alkyd slightly increases because of the alkyd's crosslinking and nearly does not change with the peroxide content, resulting in a small shrinkage of



**Figure 8** Loss modulus of crosslinked UP alkyds cured with various peroxide contents.

about 3%. The curing of the alkyd–styrene systems normally results in shrinkage of up to 17%.<sup>1</sup> Such high shrinkage levels can lead to surface distortion and internal cracks of castings or laminates. Additives such as thermoplastic polymers or fillers are usually used to reduce shrinkage and thus form low-shrinkage, low-profile polyesters.<sup>23</sup> Another property is the elongation at break of the alkyd–peroxide systems. General-purpose crosslinked styrene-containing UP resins are rigid materials that are usually sensitive to brittle fracture, having a characteristic elongation of about 5%.<sup>1</sup> Figure 9 illustrates the tensile stress–strain curves of the various UP alkyd/peroxide systems. The sample containing 1 wt % peroxide could not be analyzed because of its high softness imposing clamping problems; all the tested samples broke in the clamps. The elongations at break of the 2, 4, and 6 wt % peroxide crosslinked samples are 55, 40 and 35%, respectively. The elongation at break decreases as the peroxide concentration increases, that is, as  $\bar{M}_c$  decreases. The high elongation values can be attributed to the structure of the gel network, which coexists with the sol fraction. A more facile elongation is expected from species with a lower crosslink density, which have unreacted double bonds within the polyester chains. The sol fraction was previously shown to act as a plasticizer, affecting the  $T_g$  of the cured UP alkyd. Thus, the elongation at break increases with the sol fraction through a common plasticizing effect.<sup>20</sup> Furthermore, the tensile modulus increases with the peroxide content, in agreement with all other measured polymer properties.

In summary, this article shows the crosslinking feasibility of styrene-free UP chains in the presence of peroxide. The resulting materials exhibit properties that are significantly different from those of common styrene-containing thermoset UP. The new



**Figure 9** Tensile stress–strain curves of crosslinked UP alkyds cured with various peroxide contents.

materials developed in this work may be interesting for the creation of innovative composites and nanocomposites. A future publication will describe the utilization of these materials in the development of thermoset UP alkyd/organoclay nanocomposites.

## CONCLUSIONS

Styrene-free UP chains can be crosslinked into a thermoset network in the presence of peroxide. The thermal, mechanical, and chemorheological properties of the crosslinked UP alkyd as well as the thermal properties of the isolated gel fraction are a function of the peroxide concentration used. All properties change significantly upon the addition of up to 2 wt % peroxide, and this is followed by a slight change upon a further increase in the peroxide concentration up to 6 wt %. As the peroxide concentration increases, the gel content, crosslink density,  $T_g$ 's of both the crosslinked UP system and the gel fraction, rubbery storage modulus, and tensile modulus increase, whereas the gel time and the elongation at break decrease. Because of the co-occurrence of crosslinking and scission events, the crosslinked system contains both gel and sol fractions. The sol fraction acts as a plasticizer, reducing the  $T_g$  of the system and significantly increasing its elongation at break.

The aforementioned change in the properties with the peroxide concentration and estimation of the gel fraction's molecular structure suggest that upon crosslinking with low peroxide contents, the dominating mechanism is the branching of chains, whereas when high peroxide contents are involved, network formation predominates.

The authors are grateful to Michael Silverstein and Janet Zoldan for the use and operation of the Rheometric Scientific MK I11 dynamic mechanical thermal analyzer and helpful discussion.

## References

- Selley, J. Kirk–Othmer Encyclopedia of Chemical Technology; Wiley: New York, 1996.
- Prime, R. B. In Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic: New York, 1981.
- Mussatti, F. G.; Macosko, C. W. *Polym Eng Sci* 1973, 13, 236.
- Gloor, P. E.; Tang, Y.; Kostanska, A. E.; Hamielec, A. E. *Polymer* 1994, 35, 1012.
- Djonlagic, J.; Zlatanic, A.; Dunjic, B. *Macromol Chem Phys* 1998, 199, 2029.
- Yang, Y.-S.; Suspene, L. *Polym Eng Sci* 1991, 31, 321.
- Halley, P. J.; Mackay, M. E. *Polym Eng Sci* 1996, 36, 593.
- Nielsen, L. E.; Landel, R. F. *Mechanical Properties of Polymers and Composites*, 2nd ed.; Marcel Dekker: New York, 1994.
- Alperstein, D.; Narkis, M.; Siegmann, A. *Polym Eng Sci* 1996, 36, 610.
- Han, C. D.; Lem, K.-W. *J Appl Polym Sci* 1983, 28, 3155.

11. Gupta, R. K. *Polymer and Composite Rheology*; Marcel Dekker: New York, 2000.
12. Winter, H. H.; Mours, M. *Adv Polym Sci* 1997, 134, 165.
13. Van Assche, G.; Verdonck, E.; Van Mele, B. *J Therm Anal Calorim* 2000, 59, 305.
14. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1992.
15. Orwoll, R. A.; Arnold, P. A. In *Polymer Handbook*, 3rd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1989.
16. Li, H. Ph.D. Dissertation, Virginia Polytechnic Institute, 1998.
17. Narkis, M.; Raiter, I.; Shkolnik, S.; Siegmann, A.; Eyerer, P. *J Macromol Sci Phys* 1987, 26, 37.
18. Barton, J. *J Polym Sci Part A-1: Polym Chem* 1968, 6, 1315.
19. Bouvier-Fontes, L.; Pirri, R.; Asua, J. M.; Leiza, J. R. *Macromolecules* 2005, 38, 1164.
20. Baiardo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantel, E. *J Appl Polym Sci* 2003, 90, 1731.
21. Sperling, L. H. *Introduction to Physical Polymer Science*, 2nd ed.; Wiley: New York, 1992.
22. Katz, D.; Tobolsky, V. *J Polym Sci Part A: Gen Pap* 1964, 2, 1587.
23. Siegmann, A.; Narkis, M.; Kost, J.; DiBenedetto, A. T. *Int J Polym Mater* 1978, 6, 217.