Curing of Styrene-Free Unsaturated Polyester Alkyd and Development of Novel Related Clay Nanocomposites

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Summary: Thermoset unsaturated polyesters (UP) are usually obtained by crosslinking of alkyd chains dissolved in an unsaturated reactive monomeric diluent, usually styrene. Recently we found that UP-alkyd chains (without styrene) are intrinsically cured into a crosslinked matrix in the presence of peroxide. The thermal, mechanical, dynamic mechanical and chemorheological properties and the network molecular structure of the crosslinked UP-alkyd are a function of the peroxide content used. All properties change considerably upon the addition of small amounts of peroxide (between 1 and 2%wt.) and change to a lesser extent upon employing higher peroxide concentrations (up to 6%wt.). Due to co-occurrence of crosslinking and scission events, the crosslinked system contains both gel and sol fractions. The sol fraction demonstrates a plasticizing effect on the crosslinked network, affecting the thermal and mechanical properties of the crosslinked polymer. The new materials developed in this work are interesting for utilization in innovative styrene-free UP-alkyd/organo-clay nanocomposites. It was found that inducing high shear levels for prolonged durations promotes the intercalation and exfoliation of the silicate layers, resulting in a better dispersion of clay particles. Crosslinking of the UP-alkyd/organo-clay nanocomposites alters their nanostructure, particularly affected by the peroxide content used. Thus, depending on the content employed, either an exfoliated or a combined intercalated/exfoliated structure may be realized.

Keywords: crosslinking; nanocomposite; peroxide; styrene-free; unsaturated polyester alkyd

Introduction

Unsaturated polyester (UP) resins are often bi-component systems comprising UP-alkyd chains dissolved in an unsaturated reactive monomeric diluent, usually styrene. The alkyd chains are formed by polycondensation of diols with unsaturated and saturated dicarboxylic acids. UP resins are converted into thermosetting matrices in the presence of a peroxide/promoter catalyst system by curing, yielding crosslinked polymers. As curing of an UP system takes place, its molecular weight increases until a group of chains becomes 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 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. Highly crosslinked network polymers are widely used in structural applications such as adhesives and advanced composites.[1–4]

Linear thermoplastic polymers, including polyesters such as Polycaprolactone may be

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converted to thermosets by crosslinking with peroxide or through irradiation.[5,6] Theoretically, a styrene free UP-alkyd containing double bonds within the main chain should be crosslinkable by radicals. Recently we found that UP-alkyd chains (without styrene) are intrinsically cured into a crosslinked matrix in the presence of peroxide.[7] In this paper, crosslinking of styrene free UP-alkyd chains is suggested. The thermal, mechanical and chemorheological properties of the crosslinked UP-alkyd as well as the thermal properties of the isolated gel fraction are studied as a function of the peroxide concentration. This new approach may be utilized in forming related UP/organo-clay nanocomposites.

Experimental

The experimental grade UP-alkyd (without styrene) used in this study was supplied by Makhteshim, Israel. To induce polymerization (curing), 1-6%wt. of a selected free-radical peroxide, tert-Butyl peroxy-3, 5, 5-trimethylhexanoate (Trigonox 42PR) by Akzo Nobel, the Netherlands, was added. Degassed samples were cured in an oven at 110 °C for 24 hours, followed by post curing at 150 °C for 4 hours.

The gel content 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/dry gel weight.

Differential scanning calorimetry (DSC-Mettler DSC 30) was employed at a heating rate of 10 °C/min, under nitrogen atmosphere. Mechanical analysis in the tension mode was conducted on a Rheometric Scientific, MK I11 Dynamic Mechanical Thermal Analyzer (DMTA), at room temperature, in the static tension mode, thus attaining regular stress-strain curves. Dynamic mechanical thermal analysis (DMTA, Perkin Elmer series 7) was conducted in the three point bending mode at 1Hz. 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 was used at 110 °C, 6.28 rad/sec and 35% strain (defined as the angular displacement divided by the sample gap) and typical gap of 800 μm, to study the chemorheological properties of the alkyd undergoing curing.

Results and Discussion

The UP-alkyd was cured using several contents of peroxide, and the heat generated due to the chemical reactions was determined using DSC. The overall heat of reaction evolved during curing of the UP-alkyd with 1%, 2%, 4% and 6%wt. peroxide was estimated from a non-isothermal temperature scan that takes the reaction to completion.[7] In the absence of peroxide, no curing takes place. The peak characterizing the heat of reaction, observed for the uncured alkyd mixed with 2%wt. peroxide, which undergoes curing during heating in a DSC pan, is insignificant for the already cured systems, indicating no residual heat. Thus, all the UP-alkyd peroxide crosslinked systems have been cured to the maximum possible extent. The glass transition temperature, T_g, is often used as an empirical measure of the crosslink density. An increase in the molecular weight of the polymer and in its crosslink density results in an increase in the T_g of the polymer, due to reduced mobility of chain segments. The T_g values of the systems are summarized in Table 1. The T_g of the uncrosslinked alkyd is −2 °C, and it increases by 14–18 °C upon crosslinking.

Rheological properties such as viscosity and dynamic modulus are sensitive to the variation of molecular structure during curing, associated with the process of chemical conversion. Oscillatory shearing flow measurements have been used to investigate the rheological behavior of resins undergoing curing. The gel time may be realized as the time at which the storage modulus (G′) and the loss modulus (G″) coincide.[8,9] The gel time values are depicted in Table 1. At short curing times the loss modulus values

are higher than those of the storage modulus, due to the polymer chains' viscous dominant behavior. As curing progresses, both the storage and loss moduli increase, until their values coincide, i.e. the gel point of the alkyd is reached. Beyond the point of gelation the trend is changed and the storage modulus values are higher than those of the loss modulus, due to the dominant solid elastic behavior of the polyester gel. As observed in Table 1, the gel time decreases with increasing peroxide content.

Free radicals acting on polymers may cause scission and formation of branched and crosslinked structures. Above the gel point, the progress of gel content with peroxide concentration may be expressed according to the modified Charles by- Pinner method modified by:[10] $S + S^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 \overline{X_n} I}$, 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 concentration, respectively; $\overline{X_n}$ 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 Fig. 1 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 reasons preventing the gel content from reaching 100%, other reasons are spatial limitations exerted upon the crosslinking reaction.

The gel content of the cured UP-alkyd as a function of peroxide concentration is summarized in Table 1. Generally, the gel content increases with 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. Free radicals acting on polymers may cause scission and formation of branched and crosslinked structures. The occurrence of both crosslinking and scission events is one of the reasons preventing the gel content from reaching 100%, other reasons are spatial limitations exerted upon the crosslinking reaction.[17] The sol and the gel fractions of the crosslinked UP-alkyd are expected to exhibit different properties, e.g. thermal and mechanical properties. The T_g of all gel fractions (after extraction in MEK) of the cured UP-alkyd containing 1%, 2%, 4% and 6%wt. peroxide as exhibited from DSC thermograms are summarized in Table 1. The T_g of all gel fractions is higher than that of the whole system (containing both sol and gel fractions, Table 1). Long chains are predominantly incorporated into the gel,[12] thus yielding a sol fraction of low molecular weight. Moreover, the sol fraction may include polymer chains which had undergone multi-scission events. Thus, the sol fraction may 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 addition of the peroxide (from zero peroxide to 1%wt), 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 pro-

Table 1.
Properties of peroxide cured UP-alkyd

Peroxide content	Gel time	Cured UP-alkyd	Gel		Swelling degree	$\overline{M_c}$[a]	$\overline{M_c}$[b]
[%]	[hr]	T_g [°C]	Weight fraction	T_g [°C]	[%]	[g/gmol]	[g/gmol]
0		−2	—	—	—	—	—
1	3.5	12	0.51	20	350	13677	21538
2	1.5	16	0.67	23	250	6787	8852
4	0.9	16	0.75	25	200	4420	2614
6	0.5	16	0.78	26	170	3342	2238

[a] Calculated from swelling data according to the Flory-Rehner equation.
[b] Calculated from DMTA data according to $E' = 3\frac{\rho}{M_c}RT$.

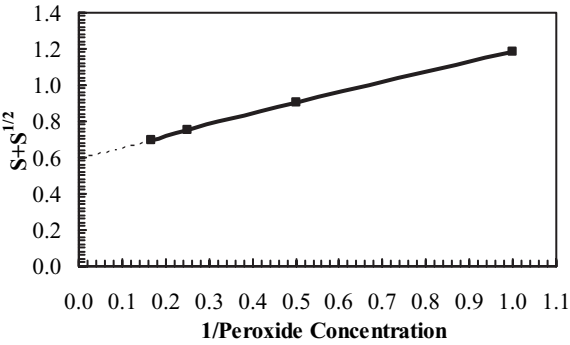

Figure 1.
Plot of $S+S^{1/2}$ versus reciprocal peroxide concentration of crosslinked UP-alkyd.

foundly with the addition of low peroxide contents. This behavior was also observed for the gel content and T_g of the whole system (Table 1).

The crosslink density, $\overline{M_c}$, is an inverse function of the average molecular weight between crosslinks. The degree of swelling in boiling MEK, summarized in Table 1, is a measure of $\overline{M_c}$, decreasing upon increasing the degree of crosslinking.[13] As observed in Table 1, the degree of swelling decreases significantly with the extent of crosslinking up to 2%wt. peroxide, and further decreases through the addition of up to 6%wt. peroxide. At equilibrium swelling, $\overline{M_c}$, can be estimated by the Flory-Rehner equation:[13]

$$\overline{M_c} = \frac{V_1\rho_2\left(v_{2m}^{1/3} - \frac{v_{2m}}{2}\right)}{-(\ln(1-v_{2m}) + v_{2m} + \chi_1 v_{2m}^2)}$$

where V_1 is the molar volume of the solvent; ρ_2 is the density of the gel fraction; v_{2m} is the volume fraction of the gel in the swollen mass; and χ_1 is the polymer-solvent interaction parameter. In this case, the interaction parameter of crosslinked UP-alkyd – MEK was taken as 0.4, which is the average value for both PCL (polycaprolactone) – MEK[14] and crosslinked vinyl ester (containing styrene) – MEK[15] systems. The $\overline{M_c}$ values calculated from the Flory-Rehner equation as well as $\overline{M_c}$ values calculated from the theory of rubber elasticity (will be discussed later) are presented in Table 1. The average molecular weight between crosslinks is highest for the UP-alkyd crosslinked with 1%wt. peroxide, and as expected it decreases with the peroxide content. The $\overline{M_c}$ value decreases significantly between the 1 and 2%wt. peroxide-containing systems and further decreases as the peroxide content increases.

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 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, e.g., a distribution in the molecular weight between crosslinks.[16] The storage and loss moduli of the cured UP- alkyd systems are depicted in Figs. 2a and 2b, respectively. The rubbery modulus, the T_g and the breadth of the loss modulus peak are all shown to increase with peroxide concentration, reflecting a restriction of segmental mobility. The small difference found between the foregoing properties of the 4 and 6%wt. peroxide crosslinked systems implies the small difference in crosslink density and gel fraction between the two samples, as was already shown in Table 1.

The increase in T_g with peroxide concentration is in agreement with the DSC thermograms (Table 1). However, the T_g

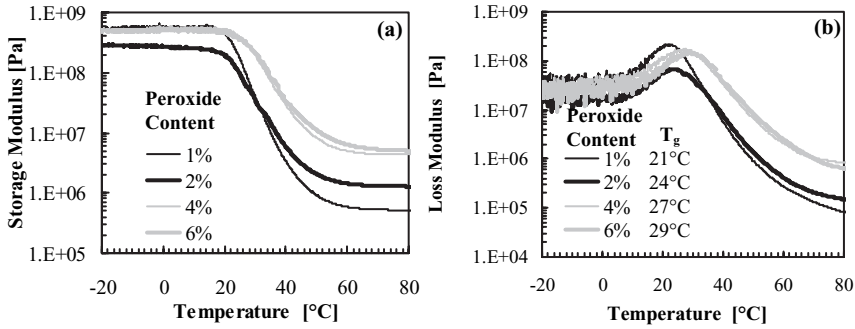

Figure 2.
Storage (a) and loss (b) moduli of crosslinked UP-alkyd cured with various peroxide contents.

values depicted from 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 the Young's modulus E on the crosslink density is given by: $E = 3\Phi nRT$, where n represents the number of active network chains per unit volume, sometimes called the network or crosslink density (n equals $\frac{\rho}{\overline{M_c}}$, where ρ is the density and $\overline{M_c}$ the average molecular weight between crosslinks); R is the universal gas constant; T is the absolute temperature; and Φ is a correction factor, i.e. a ''front factor''. For an ideal rubber, Φ is unity at all temperatures.[16] The molecular weight between crosslinks calculated from the E′ values at 80 °C (which is above the T_g of all cured UP-alkyd systems), taking Φ as 1 is shown in Table 1. The calculated $\overline{M_c}$ values range from 21,500 to 2,200 g/gmol for the 1 and 6%wt. peroxide crosslinked UP-alkyd, respectively. The $\overline{M_c}$ values obtained by the two methods, i.e. 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 calculated by the Flory-Rehner equation when a low peroxide concentration is used (1 and 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. Since the E′ values are affected by both the gel and sol fractions, it is feasible that upon reduction in sol fraction, i.e. at a high peroxide content, the difference between $\overline{M_c}$ values obtained by the two methods will decrease. Another reason for the diminishing discrepancy in $\overline{M_c}$ values would be the changing molecular structure of the crosslinked network. The average molecular weight of the neat UP-alkyd chains is about 1,600, with an average unsaturation level of about 2.5 C=C bonds per oligomer chain. The high $\overline{M_c}$ 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 formation of a network through crosslinking. Thus, it is feasible to assume that only part of the C=C double bonds have reacted in this system. This may result in a higher content of chain ends dangling in the crosslinked network, leading to $\overline{M_c}$ 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 $\overline{M_c}$ values. Thus, network formation is more pronounced

than branching. During network formation trapping of physical entanglements may occur which contributes to the storage modulus and affects the $\overline{M_c}$, resulting in a higher apparent crosslink density (lower $\overline{M_c}$ values).

Figure 3 illustrates the tensile stress-strain curves of the various UP-alkyd/peroxide systems. The sample containing 1%wt. peroxide could not be analyzed due to its high softness imposing clamping problems; all the tested samples broke in the clamps. The elongation at break of the 2, 4 and 6%wt. peroxide crosslinked samples is 55, 40 and 35%, respectively. The elongation at break decreases as the peroxide concentration increases, i.e. as $\overline{M_c}$ decreases. The high elongation values may be attributed to the structure of the gel network, co-existing with the sol fraction. A more facile elongation is expected from species with lower crosslink density, having 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 sol fraction through a common plasticizing effect.[17] Furthermore, the tensile modulus increases with peroxide content, in agreement with all other measured polymer properties.

The new materials developed in this work may be interesting for utilization in innovative styrene-free UP-alkyd/organo-clay nanocomposites. These nanocomposites were synthesized through several mixing processes, and several processing parameters were studied.[18] It was found that inducing high shear levels for prolonged time durations promoted the intercalation and exfoliation of the silicate layers, resulting in a better dispersion of clay particles. The high shear level effects were achieved by vigorous mechanical mixing and were intensified by using large amounts of clay and appropriate matrix viscosity.[18] As previously observed for neat UP-alkyd, the UP-alkyd/organo-clay nanocomposites may be cured without styrene, using the new procedure developed in our laboratory, thus attaining thermoset UP-alkyd/organo-clay nanocomposites.

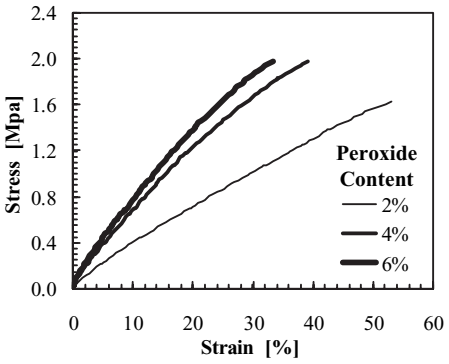

Figure 3.
Tensile stress - strain curves of crosslinked UP-alkyd cured with various peroxide contents.

UP-alkyd/24wt% I.28MC-clay nanocomposites processed under high shear rates and 80 °C for 20 h[18] were diluted into UP-alkyd/5wt% clay and UP-alkyd/2.5wt% clay systems, which were further cured using various amounts of peroxide. Upon curing using 2%wt. peroxide, XRD patterns (not shown) of both systems (containing 2.5wt% and 5wt% clay) show no peak, meaning that the interlayer spacing has increased beyond the measuring ability of XRD (ca. higher than 88Å). However, curing with 6%wt. peroxide results in a peak corresponding to an interlayer spacing of 42Å corresponding to an intercalated nanocomposite. There may be various reasons for the exhibited different structures: the peroxide may intercalate into the galleries, causing crosslinking of the alkyd chains located there and further penetration of alkyd chains into the interlayer region, as was previously suggested by Pinnavaia et al.[19] in an epoxy/clay system. Another reason could be that during the curing process alkyd chains further intercalate into the galleries, again resulting in a higher intercalation extent. A combination of both may also occur. As previously discussed, crosslinking of UP-alkyd with increasing amounts of peroxide results in a decreasing gel time. Thus, the high peroxide content results in a shorter gel-time, hence a fast viscosity increase is realized which kinetically

hinders the above mentioned occurring processes. Thus, crosslinking of the UP-alkyd/organo-clay nanocomposites alters their nanostructure, particularly affected by the peroxide content used. Depending on the content employed, either an exfoliated or a combined intercalated/exfoliated structure may be realized.

Conclusions

Styrene-free UP-alkyd may be crosslinked into a thermoset network in the presence of peroxide. The thermal, mechanical, dynamic 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 2wt% peroxide, followed by a slight change upon further increase of the peroxide concentration up to 6wt%. As the peroxide concentration increases, the gel content, crosslink density, T_g of both the crosslinked UP system and the gel fraction, rubbery storage modulus and tensile modulus increase, while the gel time and the elongation at break decrease. Due to 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.

This new method of crosslinking UP-alkyd into a thermoset crosslinked network may be implemented in the formation of novel UP-alkyd/organo-clay nanocomposites, whose structure and properties widely depend on the processing conditions employed.

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