# **Viscoelastic Properties of Alkyd Ceramers**

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ABSTRACT: The viscoelastic behavior of three alkyd ceramers was studied using dynamic mechanical thermal analysis (DMTA). A commercial product was compared to model alkyds. The model alkyds were prepared from phthalic anhydride, glycerol, and linseed or sunflower seed oil. Three sol-gel precursors, titanium tetra-*i*-propoxide, titanium di-*i*-propoxide diacetylacetonate, and zirconium tera-*n*-propoxide were investigated. The alkyd ceramers were evaluated as a function of both alkyd type and a sol-gel precursor content. The viscoelastic data showed that both E' and  $T_g$  were affected by sol-gel precursor content. Both the crosslink density and  $T_g$  demonstrated a minimum at low sol-gel precursor contents. After this minimum, both the crosslink density and the  $T_g$  increased substantially. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2017–2028, 1999

## INTRODUCTION

Dynamic mechanical thermal analysis (DMTA) has been used extensively in recent years to characterize coatings.<sup>1–3</sup> Viscoelastic materials can be described by the following three parameters: elastic modulus (storage component), loss modulus (viscous component), and tan  $\delta$ . The glass transition  $(T_{\sigma})$  can be derived from DMTA data in several different ways. The first method is by the inflection point of the E' curve. This method is problematic because of the difficulty in determining the inflection point. The second method is the maximum of the E'' plot. This method is sometimes chosen because of the similarity in magnitude to  $T_{\sigma}$ s obtained by differential scanning calorimetry (DSC). The third method is the tan  $\delta$  plot maximum. The tan  $\delta$  maximum is the most widely accepted method of determining  $T_g$ . However, care should be taken as to which peak is chosen, as there may be several peaks within the tan  $\delta$ curve. The maximum of the tan  $\delta$  curve coincides

with a dramatic drop in the E' versus temperature curve. This effect is associated with the transition of the polymer from the glassy to the rubbery region.

The value of the E' curve above  $T_g$  is an indication of crosslink density.<sup>1</sup> Based on work by Flory and others, a general equation relating crosslink density to E' is given in eq. (1), as follows:

$$\nu_e = \frac{E'}{3gRT} \tag{1}$$

Where  $\nu_e$  is the crosslink density, R is the gas constant, T is the temperature in Kelvin, and E' is the value of the elastic modulus in the rubbery plateau. The g term is called a front factor and is an attempt to account for contributions to E' other than crosslink density.<sup>4-6</sup> The value of g is reported to range from 0.5 to unity, with unity representing an ideal elastic network. The physical interpretation and magnitude of the front factor are still subjects of debate. Another result of eq. (1) is that it predicts a linear increase in the elastic modulus with increasing temperature. Experimentally, when the elastic modulus (E') is observed to increase with increasing temperature

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Figure 1 Ceramer concept.

(above  $T_g$ ), it is generally, and often incorrectly, interpreted as a consequence of incomplete crosslinking. A general interpretation is that as the temperature increases, mobility of the reactive groups is enhanced, resulting in more crosslinking reactions.

The rate of increase in E' is the way to determine the formation or destruction of crosslinks. If the rate of increase is such that E'/T is not constant but increases, then crosslinks are being formed. Conversely, if E'/T gets smaller with increasing temperature, crosslinks are being destroyed.

Inorganic–organic hybrid materials, generally referred to as ceramers, have been the subject of recent research.<sup>7–11</sup> Ceramers are materials in which an inorganic matrix is intimately distributed throughout a polymer matrix. A pictorial representation of the ceramer concept is shown in Figure 1. Ceramers differ from interpenetrating networks (IPNs) or semi-IPNs in the magnitude of the phase separation. In ceramers, the phase separation is very limited, and the inter-domain spacings are on the order of nanometers.<sup>12</sup> The possible applications of ceramer coatings range from high-performance coatings for optical polymers<sup>7</sup> to biomedical applications.<sup>2</sup>

The properties of these materials are typically along a continuum between the organic and inorganic phases. The thermal stability of poly(methylmethacrylate)-titania hybrid materials was shown to increase with increased titania amounts.<sup>8</sup> In other work, Roscher and Popall found that coatings with very low near-infrared (IR) loss factors could be produced.<sup>9</sup> Sigel et al. found that the type and amount of cycloaliphatic



Figure 2 Alkyd structure.

epoxide used in their work had a dramatic effect on the overall properties of an abrasion resistant floor coatings.<sup>10</sup> Betrabet found that inclusion of a metal oxide results in an increase in the modulus of the hybrid network as well as a partial restriction in the mobility of the oligomeric chains. Also, the refractive index was found to depend on the size of the inorganic domains as well as their number.<sup>7</sup>

The mechanical properties of a commercial alkyd ceramer coatings system were previously reported.<sup>11</sup> It was found that film properties could be adjusted within a wide range by the addition of sol-gel precursors. An unexpected interaction was also discovered between the sol-gel precursors and the drier system used. Depending on the type and amount of sol-gel precursor used, the addition of sol-gel precursors may accelerate or retard the curing reactions. The titanium tetra-ipropoxide (TIP) and zirconium tera-*n*-propoxide (ZRP) precursors were found to accelerate the crosslinking reactions at high loadings, while the titanium di-i-propoxide diacetylacetonate (TIA) precursor was found to retard the crosslinking reactions at low loadings.<sup>13</sup>

Recently, ceramers based on alkyds with several sol-gel precursors have been reported.<sup>14</sup> These ceramers utilized model resins based on linseed and sunflower oil. The sol-gel precursors consisted of titanium tetra-*i*-propoxide, titanium diisopropoxide, diacetylacetonate, and zirconium tetra-*n*-propoxide. These ceramers showed an improvement in physical properties over the base alkyd when the sol-gel content was greater than 5%. Properties were unchanged or slightly decreased at sol-gel precursor levels in the range of 1–5 wt %.

Alkyds are oligomeric esters based on naturally occurring oils. The basic structure for an alkyd is given in Figure 2. The alkyd can be synthesized via the following two different methods: (1) the monoglyceride or (2) the fatty acid process.<sup>15</sup> The monoglyceride process includes the transesterification of natural oils with glycerol to form monoglycerides. These monoglycerides are essentially diols that are esterified with a diacid to form a polyester with pendant aliphatic chains. The fatty acid process involves the use of freefatty acids, diacids, and triols esterified together in one step to form the polyester. The monoglyceride process has a large cost advantage, whereas the fatty-acid process has better control of the final alkyd composition.<sup>15</sup>

If the appropriate fatty acids are chosen, the alkyds can crosslink via the autooxidative mechanism. A brief outline of some of the reactions leading to crosslinks is given in Figure 3.<sup>16–19</sup> The initial step is the reaction of oxygen with the double bonds on the aliphatic chain. This reaction is possible only where there are activated methylene sites. These sites consist of doubly allylic methylene groups, which make the protons susceptible to abstraction. The initial oxygen addition results in the formation of a peroxide and a conjugated diene species. This peroxide is relatively unstable and can decompose to form free radicals. These radical species may abstract protons from activated methylene sites or they may combine to from crosslinks. There are several combination reactions that can lead to chemical crosslinks, but the ether linkage has been shown to predominate.<sup>18</sup> The carbon–carbon linkage has been shown to be rare. In addition, hydroperoxides can be formed from the combination of two "oxy" radicals.

These reactions are slow at room temperature but can be accelerated by increased temperatures or by the addition of catalysts known as driers. The most widely used driers are cobalt complexes. Cobalt complexes generate both excited state oxygen and free radicals.<sup>19–21</sup> A cobalt complex may loose an electron to oxygen, which then forms the oxygen anion. This anion can follow two paths. The first involves the loss of an electron and results in the formation of singlet oxygen. The second possibility for the oxygen anion is the reaction with a proton resulting in a hydroperoxy radical. A cobalt complex can also undertake re-



Figure 3 Autoxidative crosslinking.

duction-oxidation reactions with peroxides to form free radicals. These reactions are outlined in Figure 4.

Sol-gel reactions are one way to incorporate inorganic regions into organic matrices. Depending on the sol-gel precursor chosen, the reactivity can be moderate to extremely high. The product obtained from a sol-gel reaction is dependant on the nature of the catalyst. If a basic catalyst is used, very dense clusters are formed due to the increased reactivity with substitution. The situation is reversed if an acid catalyst is used. These materials tend to be more porous in nature as the structure is more linear than the branched structure obtained with a basic catalyst. These reactions are outlined in Figure 5.

Three oxidizing alkyds were utilized as the organic phase for these ceramer coatings. The first alkyd to be evaluated was a commercial alkyd based on soya and tall oil. The second and third alkyds were based on linseed and sunflower oil, respectively.

This work is an extension of a previous report on the mechanical properties of three alkyd ceramer systems.<sup>11,14</sup> The viscoelastic properties were investigated as a function of both alkyd and sol-gel precursor type. The rheological properties were obtained via DMTA. Thermal transitions and crosslink density were derived using the elastic modulus and tan  $\delta$ . Comparisons to previously reported mechanical properties will be made to determine a correlation between viscoelastic behavior and bulk material properties.

#### **EXPERIMENTAL**

Ceramer film preparation was described in previous publications.<sup>11,14</sup> The viscoelastic properties of these films were investigated using a Rheomet-



Figure 4 Drier mechanisms.



Figure 5 Sol-gel hydrolysis and condensation.

rics DMTA 3E using the following conditions: a ramp rate of 3°C, a frequency of 1 Hz, an initial temperature of -100°C, a final temperature of 200°C, a strain of 0.5%, a gap length of 3 mm, a sample width of 10 mm, and a sample thickness of approximately 0.025 mm. The test geometry was rectangular tension and compression.

A brief explanation of the ceramer nomenclature is as follows: the alkyd type will be designated as Lin, meaning linseed-oil-based; Sun, meaning sunflower-oil-based; or Glid, meaning a commercial alkyd supplied by Glidden. The alkoxides used are signified as follows: TIP is titanium tetra-*i*-propoxide, TIA is titanium di-*i*-propoxide diacetylacetonate, and ZRP is zirconium tera-*n*propoxide. Numbers signify the weight percent of sol-gel precursor in the system. For example, a system designated GlidTIA10 would stand for a Glidden based alkyd containing 10 wt % TIA.

# **RESULTS AND DISCUSSION**

The physical coatings properties were previously determined for three alkyd ceramer coatings systems.<sup>11,14</sup> It was observed that the hardness and tensile properties of all three alkyd ceramer coatings systems decreased slightly with the initial addition of sol-gel precursor (1–5 wt %). After 5 wt %, both the hardness and the tensile values exceeded the base alkyd. This increase in both hardness and tensile properties is similar to that seen in thermoplastic elastomers.<sup>22–24</sup> It is possible that the inorganic domain is acting as the

hard segment while the alkyd is acting as the soft segment. This would help explain several of the mechanical properties, such as increasing hardness, while maintaining flexibility.<sup>11,14</sup> For the hardness data, the minimum was typically 20% lower than the parent alkyd. As the sol-gel precursor content increased (5-25 wt %), the mechanical properties also increased. At higher solgel precursor loading (5-25 wt %), the hardness of the coating exceeded the parent alkyd by 130%. The bulk tensile properties also demonstrated this minimum. Here, the values of the tensile modulus minimum ranged from 30 to 60% of the parent alkyd. The tensile strength data also showed a similar inflection with increasing solgel precursor content. Consequently, the rheological properties of these ceramers were investigated to elucidate the structure-property relationships responsible for the nonlinear behavior of the bulk mechanical properties.

The objective of this study was to utilize the rheological data to investigate the dependence of extent of cure and crosslink density on the sol–gel precursor content. Three series of alkyds were evaluated as ceramers. Each alkyd ceramer system was evaluated as a function of the sol–gel precursor type and content. The three sol–gel precursors were TIP, TIA, and ZRP ranging from 1–25 wt % loadings. The  $T_g$  derived from tan  $\delta$  data has also been compared to the previously reported  $T_g$  data obtained via DSC.<sup>14</sup>

A typical DMTA plot for these ceramer systems is shown in Figure 6. From Figure 6, the  $T_g$  of the ceramer systems was shown by the large peak in



Figure 6 DMTA plot of sunflower and TIP 25 wt % ceramer.

the tan  $\delta$  centered at approximately 75°C. The high tan  $\delta$  was observed in all of the DMTA results.

The  $T_{\sigma}$ 's for the various alkyd ceramers are given in Figure 7. In general, it was observed that at low sol-gel precursor concentrations (1-5 wt %), the  $T_g$  decreased slightly followed by an increase of the  $T_g$  at higher sol-gel precursor contents (10-25 wt %). This trend is consistant with the previously reported  $T_g$ 's obtained via DSC. As expected, the  $T_g$ 's from  $\widetilde{\mathrm{DSC}}$  are lower than those from DMTA. It was surprising that the difference is around 30°C lower for DSC values. The cause of this large difference is unclear. For all three alkyds, the  $T_g$  was equal to or lower than the parent alkyd until 5 wt % sol-gel precursor loading. After the 10 wt % sol-gel precursor, all but the LinTIP10, GlidTIA10, and GlidZRP10 ceramers had recovered or increased their  $T_g$ 's. This may be an indication of a decrease in crosslink density at low sol-gel precursor loadings (1-5 wt %), followed by an increase in crosslink density at higher sol-gel concentrations (10-25 wt %). For

all of the ceramers at 25 wt % sol–gel precursor, except GlidTIA25, increases in  $T_g$  of at least 10°C over the base alkyd are observed.

The height of the tan  $\delta$  alpha transition was dependant on the extent of cure. The higher the cure, the lower the alpha transition. Figure 8 depicts the tan  $\delta$  data for the sunflower/ZRPbased ceramers. This figure shows that the magnitude of the tan  $\delta$  max decreased with increasing sol-gel precursor content. This supports the precept that ceramers with the higher sol-gel precursor content are reaching a higher degree of cure than those ceramers with lower or no sol-gel precursor content. It is not known by what mechanism this increased cure occurs. The increase could be due to an increase in the organic phase extent of cure due to the presence of sol-gel precursors. It could also be due to the increased contribution from the sol-gel reactions. The possibility of inorganic-organic interactions also exists. Two such interactions are given in Figure 9. Given an inorganic-organic interaction, the inorganic phase could also contribute to the crosslink



**Figure 7**  $T_g$ 's for all alkyd ceramers.

density through the hydrolysis and condensation reactions in Figure 5. Of course, all three of these possibilities may occur simultaneously.

The crosslink density was determined from the E' plot above the  $T_g$ . Two different protocols for calculation were used. The first was a graphical method using a linear fit approach; the second was the use of a single point either at the minimum of the curve, or at  $T_g$  + 55°C. These two methods were compared to determine which, if either was better.

For the linear fit method, eq. (1) was used to calculate a crosslink density for each point on the

E' plot above  $T_g$ . From these values, an average crosslink density is calculated. This average is used to calculate a theoretical E' curve from eq. (1). This theoretical plot and the actual plot are compared for fit. The temperature range was then adjusted to obtain the best fit between the two plots. Examples of these plots are given in Figures 10 and 11. In most cases, the fit is fairly good over a temperature range of about 30°C.

The single point calculation used one point taken at the minimum in the E' plot above  $T_g$ . If no minimum was observed, or if a continuous decline in E' was observed, a point 50°C above the



Figure 8 Tan  $\delta$  for sunflower ZRP-based ceramers.



Figure 9 Possible organic/inorganic interactions.

 $T_g$  was chosen to calculate the crosslink density using eq. (1).

Figure 12 gives the graphical crosslink density calculation, while Figure 13 gives the single point calculation. Figure 14 is a difference plot of the results of the two calculation methods; it is an indication of the agreement of the two methods. The crosslink density given in both Figures 12 and 13 indicate the same basic trends. The difference is that the magnitude of the values changed slightly. For all three alkyds, the crosslink density increased with the increased sol-gel precursor at and above 5 wt %. At 1 wt % sol-gel precursor, the crosslink density is essentially equal to the parent alkyd.

Figure 14 gives a percent difference chart for the two protocols for crosslink density calculation. The data in this figure result from subtracting the single point calculations from the linear fit calculation. This value is then divided by the linear fit calculation and reported as a percentage of the linear fit calculation. From Figure 14, we can see that the linear fit method gives lower values of crosslink density than does the single point method. It should be pointed out that even though there are differences, the magnitude of these differences is typically 5% or less. This would indicate that either method was valid for the calculation of crosslink density.

The commercial alkyd demonstrated the largest increase in crosslink density at a high sol-gel precursor content. Within this series, the TIP solgel precursor afforded the highest crosslink densities. Values were typically 25% higher than the ZRP-based ceramers and up to 50% higher than the TIA ceramers. With the commercial alkyd, the



Figure 10 Experimental fit for linseed alkyd.



Figure 11 Experimental fit for SunZRP 25.

ZRP-based ceramers were second in reactivity, followed by the TIA-based ceramers. The commercial alkyd ceramer coatings afforded the higher crosslink densities than the two model alkyd ceramer systems.

The linseed alkyd ceramers demonstrated similar trends as the commercial alkyd, but subtle differences were observed. One of the major differences was the order of reactivity of the sol-gel precursors. For the linseed alkyd ceramers, ZRP seemed to result in higher crosslink densities, especially at 25 wt % ZRP. The crosslink density was approximately 50% larger than the TIP- or TIA-based ceramers at 25 wt % loading. The TIA ceramers continued, for the most part, to give the lowest crosslink densities than either the TIP- or ZRP-based ceramers.

Unlike the linseed and commercial-alkydbased ceramers, there was no clear difference in the reactivity of the TIP and ZRP sol-gel precursors with the sunflower alkyd. At high sol-gel precursor loadings (25 wt %), the TIP and ZRP systems are almost equal. Unlike the sunflower and linseed oil based alkyds, the commercial



Figure 12 Crosslink density for alkyd ceramers: graphical computation method.



Figure 13 Crosslink density for alkyd ceramers: single point computation method.

alkyd is composed of tall oil. Tall oil based resins have a different crosslinking mechanism as shown in Figure 15. Nonwithstanding, the overall trends for the sunflower-alkyd-based ceramers follow those of both the linseed and commercial alkyd systems (Fig. 15).

The increase in crosslink density with increasing sol-gel precursor could have been due to several interactions. It has been shown that sol-gel precursors do show activity as driers.<sup>14</sup> The increased levels of sol-gel precursors may enhance the crosslink density by acting as a catalyst for the cure of the organic phase. A second possibility is that the sol-gel particles are reinforcing the matrix as pigments have been shown to do.<sup>25</sup> A third possibility is the chemical interaction of the alkyd with the inorganic phase. As the sol-gel precursor is increased, the hydrolysis and condensation reactions result in inorganic crosslinks, hence, higher crosslink density. Figure 16 com-



**Figure 14** Difference between graphical and single point crosslink density calculations. Negative numbers mean that the graphical calculation is lower than single point calculations.



Figure 15 Diels-Alder reaction.

pares the Raman spectra of the linseed oil alkyd ceramer systems with increasing sol-gel precursor (TIP loading). From Figure 16, as the sol-gel precursor increased, an absorption band at 1656 cm<sup>-1</sup> was observed to also increase. Bands in this region are associated with carboxylic acid metal salts. The counter ion in this system would be the metal ion. This complex would lead to a chemical crosslink between the organic and inorganic phases and, therefore, would add to the crosslink density of the ceramer coating.

When the  $T_g$  data and the crosslink data are compared, a discrepancy arose. The tan  $\delta$  data suggests that the  $T_g$  decreases at a low sol-gel precursor content relative to the parent alkyd. One interpretation of this would be a reduction in crosslink density. The crosslink density data, however, does not indicate a reduction in crosslink density at low sol-gel precursor loadings. Another discrepancy is

the fact that while the  $T_g$ 's between the linseed and sunflower alkyd ceramers were substantially different at the same sol-gel precursor type and amount, the crosslink densities are not. One explanation may be the proximity of the functional groups in the alkyds. Linolenic acid has two reactive sites per chain. Furthermore, these reactive sites are fairly close to each other, at most, six carbons apart. Linoleic acid, on the other hand, has only one reactive site per 17 carbon chains. If both reactive sites on linolenic acid react, it would lead to a decrease in the overall chain mobility and a resulting increase in  $T_{\alpha}$ . However, the crosslinks formed may not be far enough apart to result in separate elastically effective crosslinks but may act more like a single crosslink. A second reaction that may result in limited mobility, but not in increased crosslink density is a Diels-Alder addition. This reaction is shown in Figure 15. As with linolenic acid, a "crosslink center" is formed, resulting in decreased mobility, but not increasing the crosslink density.

# **CONCLUSIONS**

The thermo-mechanical properties of alkyd ceramers indicate these systems are very complex. The addition of sol-gel precursors results in



Figure 16 Raman spectra: (A) linseed alkyd; (B) LinTIP5; (C) LinTIP10; (D) LinTIP25.

higher  $T_g$ , extent of cure, and crosslink density. The highest crosslink densities were obtained using the commercial alkyd. Trends in the crosslink density results were independent of the computation method used. A chemical interaction between the inorganic and organic phase was observed.

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