# Inorganic−Organic Hybrid and Composite Resin Materials Using Carboxylate-Alumoxanes as Functionalized Cross-Linking Agents

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Chemically functionalized alumina nanoparticles (carboxylate-alumoxanes) are used as the inorganic component of a new class of inorganic−organic hybrid materials. Lysine- or *p*-hydroxybenzoic acid-derivatized alumoxanes are readily prepared from the reaction of boehmite, $[Al(O)(OH)]_n$, with the appropriate carboxylic acid. The peripheral organic hydroxides and amines of these carboxylate-alumoxanes either react directly with epoxide resins, such as the diglycidyl ether of bisphenol A (DER 332), to form a hybrid material, or in the presence of an organic resin and hardener system to form a composite material. SEM with associated EDX analysis, and AFM shows a uniform distribution of alumina nanoparticles within the resin matrix. Solid-state $^{13}$C and $^{27}$Al NMR spectroscopy demonstrates that the carboxylate-alumoxane nanoparticles are chemically bound to the epoxide resin matrix. The model compounds $PhOCH_2CH(OH)CH_2OPh$ (**1**), $PhOCH_2CH(OH)CH_2NH^nPr$ (**2**), and $PhOCH_2CH(OH)CH_2NH^iPr$ (**3**) have been prepared to assist in the NMR characterization of the hybrid materials. The properties and cure times of the alumoxane hybrid and composite materials are distinct from both the pure resins and from a physical blend of the resins with traditional ceramic fillers. A significant increase in thermal stability and tensile strength is observed for both the hybrid and composite resin systems. In addition, both carbon fiber and carbon/Kevlar matting have been successfully incorporated into the hybrid resin systems resulting in further property improvements.

## Introduction

Thermosettable addition polymers are prepared by the irreversible reaction of organic resins with low molecular weight precursors that contain reactive functional groups to form solid, highly cross-linked polymer matrices. One of the more common classes of organic resins contains epoxide-based materials. Epoxy resins are easily extruded and/or molded, have moderate strength, and low hardness.[2] Common resin systems usually consist of two parts, a resin and a hardener, which are mixed and cured at elevated temperatures (50−100 °C).[3]

Cross-linking agents are commonly chosen in an application-directed manner. For example, aliphatic amines are used in adhesive and coating applications where colored products are desired.[4] On the other hand, phenol-based curatives are better for molding complex shapes and provide chemical resistance, hardness, and flexibility.[5] In general, unfilled thermoset polymers tend to be harder and more brittle than thermoplastic polymers. Thus, it is common practice to add fillers to thermosetting polymers to improve their physical properties.

Inorganic ceramic fillers impart a number of desirable properties to the polymer including, but not limited to, tensile strength, stiffness, abrasion resistance, dimensional stability and barriers to gases, solvents and water vapor. The extent to which the fillers modify polymer properties is closely associated with the size, shape, and dispersion uniformity of the filler as well as the degree of interaction between the inorganic filler and the organic matrix. Therefore, an ideal performance is achieved with inorganic fillers consisting of small particles that are uniformly dispersed throughout the polymer and interact strongly with the organic matrix.[6]

Until recently, the particle sizes of fillers used to improve polymeric properties have been on the micrometer length scale or larger.[6] Nanometer-sized particles have higher surface areas and, at the same weight, have higher volume loadings than do larger particles. In addition, smaller particles yield smaller stress concen-

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* To whom correspondence should be addressed (http://python.rice.edu/~arb/Barron.html).

[1] (a) Department of Chemistry. (b) Department of Mechanical Engineering and Materials Science.

[2] Stevens, M. P. *Polymer Chemistry*; Oxford University Press: Oxford, 1990.

[3] Bruins, P. F. *Epoxy Resin Technology*; Wiley: New York, 1968.

[4] Phenolic-type resins tend to be dark in color, whereas amino-type resins are transparent and thus easily colored.

[5] Cowie, J. M. G. *Polymers: Chemistry & Physics of Modern Materials*; International Textbook Company, Ltd.: London, 1973.

[6] (a) Jansen, B. J. P.; Tamminga, K. Y.; Meijer, H. E. H.; Lemstra, P. J. *Polymer* **1999**, *40*, 5601. (b) Becu-Longuet, L.; Bonnet, A.; Pichot, C.; Sautereau, H.; Maazouz, A. *J. Appl. Polym. Sci.* **1999**, *72*, 849. (c) Harani, H.; Fellahi, S.; Bakar, M. *J. Appl. Polym. Sci.* **1999**, *71*, 29.

10.1021/cm990648e CCC: $19.00

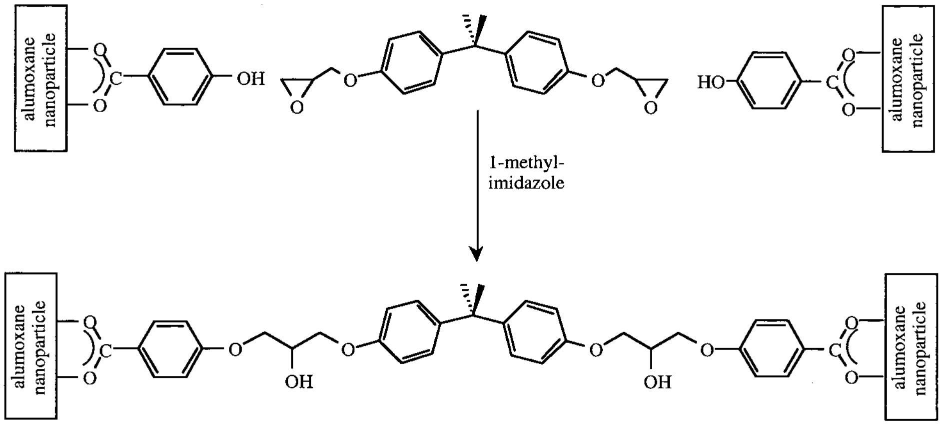


**Figure 1.** Schematic representation of the reaction between *p*-hydroxybenzoate-alumoxane and Dow DER 332 epoxide resin.

trations. Unfortunately, most fillers are hydrophilic inorganic oxides, whereas most polymers are hydrophobic in nature. The result is phase segregation and powder agglomeration which decreases the overall performance of the polymer composite. Thus, it is desirable to use stable, hydrophilic, ceramic, nanoparticles as fillers.

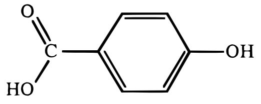
The performance of the polymer–filler composite is strongly dependent on the strength of the interaction between polymer and filler, independent of size. The weakest to strongest interactions between the polymer and the inorganic filler are van der Waals and dipole–dipole interactions, followed by hydrogen bonding, and then finally, covalent bonding.[7] Covalent bonding of the particles to the polymer lattice allows better transfer of mechanical loads to the particles and also promotes toughening of the polymer composite.[6] It is therefore desirable to identify small size (i.e., nanometer scale) chemically functionalized inorganic fillers that can readily be incorporated into polymer matrices through covalent bonds.

We have previously reported that aluminum-oxide nanoparticles may be prepared by the reaction of the mineral boehmite with carboxylic acids:[8,9]

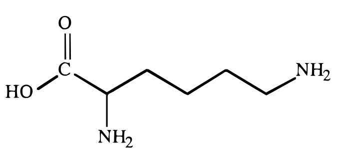
$$[\mathrm{Al(O)(OH)}]_n \xrightarrow{\mathrm{HO_2CR}} [\mathrm{Al(O)}_x(\mathrm{OH})_y(\mathrm{O_2CR})_z]_n \qquad (1)$$

The carboxylate ligand is covalently bound to the aluminum surface[10] and is only removed under extreme conditions. These materials are termed carboxylate-alumoxanes and may be prepared with an almost limitless variety of functional groups. Specifically, carboxylate-alumoxanes formed from *p*-hydroxybenzoic acid (**I**) and lysine (**II**) provide reactive sites (OH and NH, respectively) for epoxide ring opening and thus resin cross-linking. Therefore, these functionalized carboxylate-alumoxanes are ideal candidates to act as nanometer-sized, chemically reactive fillers to be incorporated into thermoset polymers.

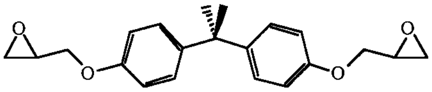
We have investigated two classes of epoxy-alumoxane materials. First, a chemically functionalized carboxylate-alumoxane was directly cross-linked with a common epoxy resin, the diglycidyl ether of bisphenol A (Dow Chemical DER 332, **III**). This material has been termed a "hybrid alumoxane resin". The second class of material, referred to as a "composite alumoxane resin", is formed by the incorporation of the functionalized carboxylate-alumoxane into a commercially available resin/hardener system. Our initial results in these areas are reported herein.



(**I**)



(**II**)



(**III**)

## Results and Discussion

**Synthesis and Characterization of Hybrid Epoxy-Alumoxane Resins.** The diglycidyl ether of bisphenol A (DER 332, **III**) may be cross-linked directly with either *p*-hydroxybenzoate-alumoxane (*p*-HB-alumoxane) or lysine-alumoxane in the presence of a suitable base catalyst (e.g., 1-methylimidazole). By comparison with known epoxide reactivity[11] and model compound studies (see below) it is proposed that the hydroxy group in *p*-HB-alumoxane and the amine groups in lysine-alumoxane undergo a ring-opening reaction with the epoxide groups. A schematic representation of the reaction with *p*-HB-alumoxane is shown in Figure 1.

By reacting varying quantities of *p*-HB- and lysine-substituted alumoxanes with DER 332 an optimal weight ratio, based on a qualitative assessment of the

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[7] The polymer-filler covalent bonding interactions are on the order of 30–100 times greater than those that can be obtained by hydrogen bonding. Whitesides, G. M. *Science* **1981**, *254*, 1312.

[8] Landry, C. C.; Pappè, N.; Mason, M. R.; Apblett, A. W.; Tyler, A. N.; MacInnes, A. N.; Barron, A. R. *J. Mater. Chem.* **1995**, *5*, 331.

[9] Callender, R. L.; Harlan, C. J.; Shapiro, N. M.; Jones, C. D.; Callahan, D. L.; Wiesner, M. R.; MacQueen, D. B.; Cook, R.; Barron, A. R. *Chem. Mater.* **1997**, *9*, 2418.

[10] Koide, Y.; Barron, A. R. *Organometallics* **1995**, *14*, 4026.

[11] May, C. A. *Epoxy Resins: Chemistry and Technology*; Dekker: New York, 1988.

**Table 1. Comparison of the Differences between Hybrid Resins Incorporating Various Carboxylate-Aumoxane Weight Ratios**[a]

| alumoxane:resin ratio[b] | properties of the cured material |
|---|---|
| 1:1 | hard and strong with no flexibility; prior to curing, material is easy to shape, mold, and extrude |
| 1:2 | good balance of strength and hardness with some flexibility; prior to curing, material is easy to shape and mold, but difficult to extrude |
| 1:5 | very flexible with little hardness and moderate strength; prior to curing, shaping is limited to molds and extrusion is impossible |

[a] *p*-Hydroxybenzoate-alumoxane was used for all experiments. [b] Ratio by weight.

**Table 2. Set Times for Hybrid Alumoxane Resin Systems**[a]

| formulation | $T^b$ (°C) | set time (min) |
|---|---|---|
| DER 332 + ethylenediamine[c] | 50 | 19.60 |
| DER 332 + lysine-alumoxane | 50 | 6.03 |
| DER 332 + lysine-alumoxane | 150 | 2.93 |

[a] As determined by differential thermal analysis (DTA). Note that the ratio (by mass) of resin to hardener (ethylenediamine or lysine-alumoxane) is constant for all cited formulations. [b] Constant temperature at which the sample is held during reaction. [c] The diglycidyl ether of bisphenol A (DER 332) was cross-linked with ethylenediamine to form a "blank" resin system for comparative purposes. No alumoxane was present in this formulation, see Experimental Section.

physical properties of the cured materials, was found to be 1 part alumoxane to 2 parts resin, see Experimental Section. Variations of this ratio were found to yield cured materials with slightly different properties as described in Table 1. Neither *p*-HB-alumoxane nor lysine-alumoxane are soluble in DER 332; however, uniform mixtures may be readily prepared by stirring with a mechanical blender. Although reaction occurs over extended times at room temperature, some segregation occurs prior to complete reaction. Thus, it was found that more uniform materials are obtained by heating the samples, due to the reduced cure times. The cure time for the hybrid alumoxane resin (with an alumoxane:DER 332 w/w ratio of 1:2) was found to be 10 h at 50 °C or 2 h at 150 °C.[12] The set times[13] were determined by differential thermal analysis (DTA) as shown in Table 2. Upon mixing of the alumoxane and DER 332 an exotherm is observed in the DTA after an initial inactive period. The time to this exotherm is defined as the set time, and may be related to the point at which the cross-linking reaction is initiated. The time from mixing to the peak of the exotherm was measured for identical samples of lysine-alumoxane/DER 332/1-methylimidazole at 50 and 150 °C. As a reference, a sample of DER 332 was cross-linked with ethylenediamine ($H_2NCH_2CH_2NH_2$).[14] As may be seen from Table 2, the set times for the lysine-alumoxane/DER 332 resins are significantly shorter than for the reference sample. Thus, both set times and temperatures are significantly lower for the alumoxane hybrid resins than traditional, "purely organic", resins.

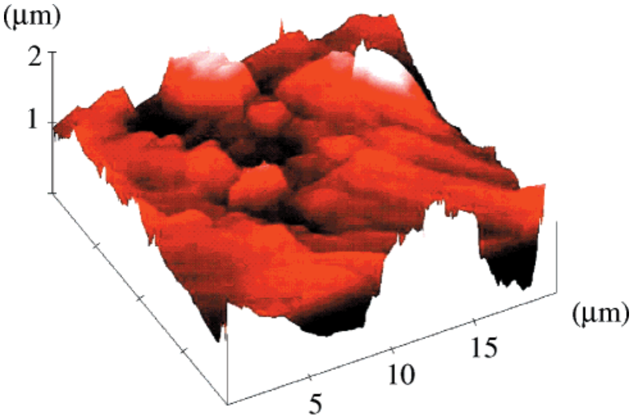

**Figure 2.** AFM image of the surface of the lysine-alumoxane hybrid resin prepared using a 1:2 (w/w) ratio of lysine-alumoxane:DER 332 resin.

Unlike neat organic resins, the carboxylate-alumoxane hybrid resins do not undergo significant mold shrinkage. In particular, complex shapes are conveniently prepared by simple molding techniques. The lack of significant shrinkage thus allows for the fabrication of both flat panels (15 mm × 15 mm × 1 mm) and "dog bones", see Experimental Section. Both shapes were used for tensile strength measurements (see below). In addition, the density of the resultant hybrids is uniform and comparable to, or higher than, that of the neat organic resin.

AFM and SEM analyses of both the *p*-HB-alumoxane and lysine-alumoxane hybrid resins are consistent with a relatively smooth surface (see Figures 2 and 3 for representative examples). As shown in Figure 4, the aluminum content of a *p*-HB-alumoxane resin was mapped by microprobe analysis to further confirm that the carboxylate-alumoxanes are uniformly dispersed throughout the resin. In addition, contact angle measurements revealed that the addition of *p*-HB-alumoxane increased the hydrophillicity of the otherwise extremely hydrophobic material, see Table 3. The similarity of advancing and receding contact angles also points to a uniform composition.

Postcuring, both lysine- and *p*-HB-alumoxane hybrid resins have superior physical properties than were found for a purely organic resin system using ethylenediamine. For example, in the same volume loading, ethylenediamine produced a rubbery material as compared to the rigid one formed with lysine-alumoxane. While the hardness of the hybrid resins is found to be similar to one another, the lysine-alumoxane resin was found to be qualitatively stronger than the *p*-HB-alumoxane resin. Quantitative evaluation of the improved physical properties of the alumoxane hybrid resins over the traditional "organic" resins is obtained from tensile strength measurements. As may be seen from the data in Table 4, a 7-fold increase in the peak load and peak stress is observed with the use of the alumoxane cross-linking agents. This should be compared to a slight decrease observed with the addition

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(12) The effect of different phenolic hardeners on the cure time of biphenyl epoxy resins has been recently reported, see: Han, S.; Kim, W. G.; Yoon, H. G.; Moon, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 773.

(13) The set time of an epoxy resin corresponds to the time it takes for the reaction to initiate, whereas the cure time of an epoxy resin corresponds to the time it takes for the reaction to reach completion.

(14) Aliphatic diamines are commonly employed cross-linking agents, see: Franco, M.; Mondragon, I.; Bucknall, C. B. *J. Appl. Polym. Sci.* **1999**, *72*, 427.

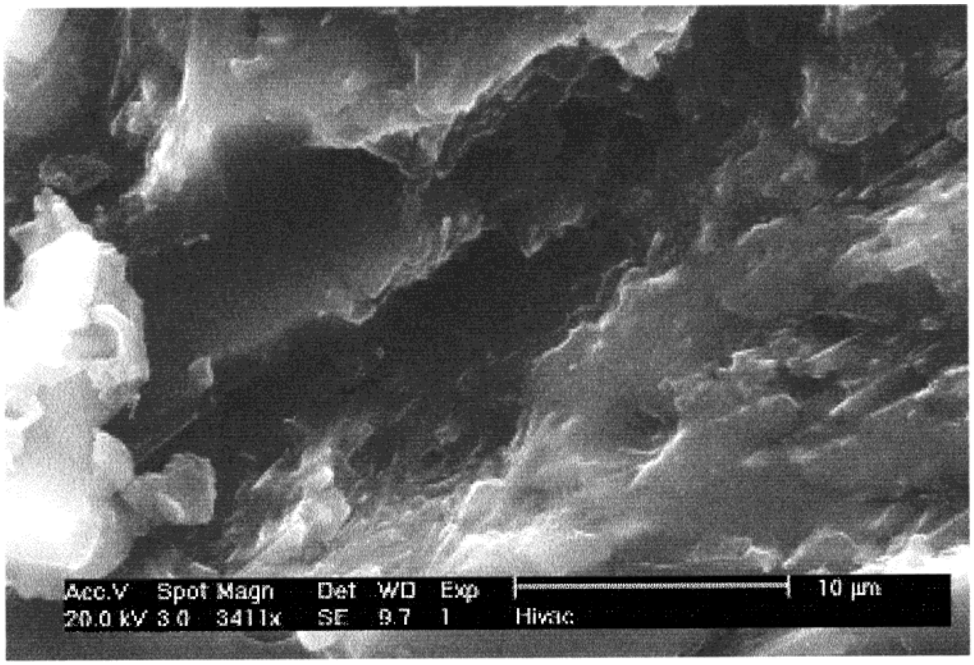

**Figure 3.** An SEI micrograph of the surface of the lysine-alumoxane hybrid resin prepared using a 1:2 (w/w) ratio of lysine-alumoxane:DER 332 resin.

of an "inert" filler such as boehmite (see Table 4). It should be noted that the tensile strength of the alumoxane-based resins are between that of concrete (2 MPa) and aluminum (90 MPa), but with a lower modulus than either. In fact, while the modulus (1000−1700 MPa) is significantly higher than the purely "organic" resins (36−90 MPa), it is still lower than that of concrete (23 GPa) or bone (16 GPa).

Although the physical properties of the alumoxane hybrid resins are consistent with the chemical reaction of the lysine- and *p*-HB-alumoxane nanoparticles with the DER 332 epoxide resin, $^{13}$C CP-MAS NMR has been employed to confirm the reaction and assist in the determination of the optimum reaction conditions. A series of *p*-HB-alumoxane:DER 332 hybrid resins were prepared with varying alumoxane:DER 332 ratios (see Table 1). Each sample was cured under identical conditions (60 min at 150 °C), ground into a fine powder, and the $^{13}$C CP-MAS NMR spectra determined. In this regard, the $^{13}$C CP-MAS NMR spectrum for the *p*-HB-alumoxane epoxide resin prepared from a 1:2 weight ratio of the alumoxane to Dow DER 332 resin is shown in Figure 5a. As a comparison, the $^{13}$C CP-MAS NMR spectrum for *p*-HB-alumoxane and the solution $^{13}$C NMR spectrum for DER 332 are shown in Figure 5b and c, respectively. A comparison of these spectra indicates that the signals at $\delta$ 44.4 ppm and $\delta$ 50.3 ppm due to the epoxide carbons of the DER 332[15] are no longer present in the spectrum of the alumoxane hybrid resin. Instead, a relatively broad asymmetric signal with a maximum at $\delta$ 66.1 ppm appears. On the basis of the $^{13}$C NMR spectrum of the model compound, $PhOCH_2$-$CH(OH)CH_2OPh$ (see below), the signal at $\delta$ 66.1 ppm may be assigned to a combination of the resonances for the O-methylene and O-methine groups created by the

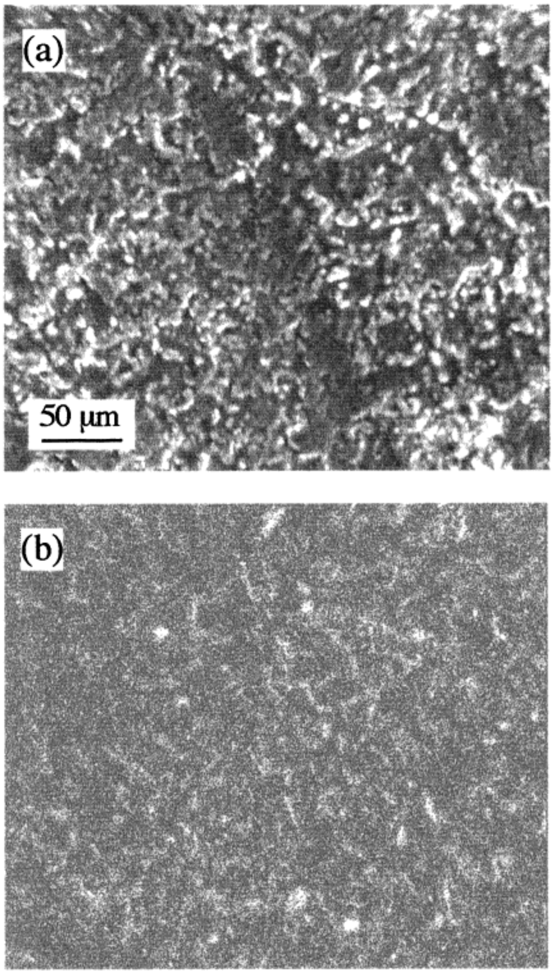

**Figure 4.** SEM image (a) and associated Al elemental maps (b) of *p*-hydroxybenzoate-alumoxane hybrid resin showing uniformity of the alumoxane nanoparticles throughout the resin.

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(15) Garroway, A. N.; Moniz, W. B.; Resing, H. A. Carbon-13 in Organic Solids: The Potential for Polymer Characterization. *Carbon-13 NMR in Polymer Science*; Pasika, W. M., Ed.; ACS Symposium Series 103; American Chemical Society: Washington DC, 1979.

**Table 3. Summary of Advancing Contact Angle Measurements for Various Epoxy Resin Systems**[a]

| formulation[b] | contact angle[c] (deg) |
|---|---|
| Hybrid | |
| “blank” Dow 332 | 152 ± 3 |
| *p*-HB-alumoxane + 332 | 130 ± 3 |
| Composite | |
| “blank” Resin Services (RS) | 150 ± 1 |
| *p*-HB-alumoxane + RS | 167 ± 2 |
| 332 + 201 + *p*-HB-alumoxane | 128 ± 2 |
| 332 + 201 + lysine-alumoxane | 88 ± 2 |
| 4221 + 301 + *p*-HB-alumoxane | 116 ± 1 |
| 332 + 732 + *p*-HB-alumoxane | 137 ± 1 |
| 828 + 732 + *p*-HB-alumoxane | 123 ± 1 |
| 332 + 2426 + *p*-HB-alumoxane | 134 ± 1 |

[a] Deionized/distilled water was used for all measurements. Also note that the surface of the tested materials were cleaned thoroughly to remove any attached mold release agent prior to obtaining the cited measurements. [b] See Experimental Section for specifics of formulation compositions and conditions. [c] Receding contact angle measurements were identical to the advancing angles shown indicating a uniform material.

**Table 4. Summary of Tensile Strength Measurements for Various Epoxy Resin Systems**

| formulation[a] | peak load (kN) | peak stress (MPa) | modulus (MPa) |
|---|---|---|---|
| “blank” Dow 332 | 0.111 | 2.083 | 36.2 |
| “blank” Dow 332 + boehmite | 0.108 | 1.811 | 42.1 |
| *p*-HB-alumoxane + 332 | 0.750 | 15.378 | 1058 |
| “blank” Resin Services (RS) | 0.451 | 8.937 | 905 |
| RS + *p*-HB-alumoxane | 2.251 | 68.022 | 1762 |

[a] See Experimental Section for specifics of formulation compositions and conditions.

cleavage of the epoxide by the *p*-hydroxy group of the carboxylate-alumoxane, see Figure 1. A dipolar dephasing experiment[16] confirms that these overlapping signals result only from O-methylene and O-methine groups (as opposed to O-methyl or quaternary carbons). Similar results are obtained for the reaction of lysine-alumoxane with DER 332. For the lysine-alumoxane case, however, we were unable to follow the reaction by $^{15}$N NMR spectroscopy. Thus, for both alumoxanes, the complete loss of the peaks at $\delta$ 44.4 ppm and $\delta$ 50.3 ppm was used for optimization of the alumoxane:DER 332 ratio and to confirm the curing point of the resin.

The thermal stability of the hybrid resins is significantly enhanced as compared to the purely “organic” resins. A representative thermogravimetric and differential thermal analysis (TG/DTA), shown in Figure 6, indicates that the *p*-HB-alumoxane/DER 332 hybrid resin decomposes at 400 °C, without any prior mass loss. In contrast, the “blank” resin decomposes at 345 °C, but also shows mass loss above 180 °C. The lower temperature mass loss is possible due to the volatilization of either unreacted or short chain species which are clearly not present in the alumoxane-based resin.

**Model Reactions of Hybrid Alumoxane Resins.** Although it is clear from the foregoing discussion that the chemically functionalized alumoxanes react with the epoxide groups in DER 332, there are a number of important questions to be raised regarding the type of chemical interaction occurring between the alumoxane and the resin. For example, does the epoxide react with the core of the aluminum-oxide nanoparticle and can it react with any “free” carboxylic acids that may be physiadsorbed on the surface of the alumina nanoparticle? Or is it that the reaction occurs solely at the

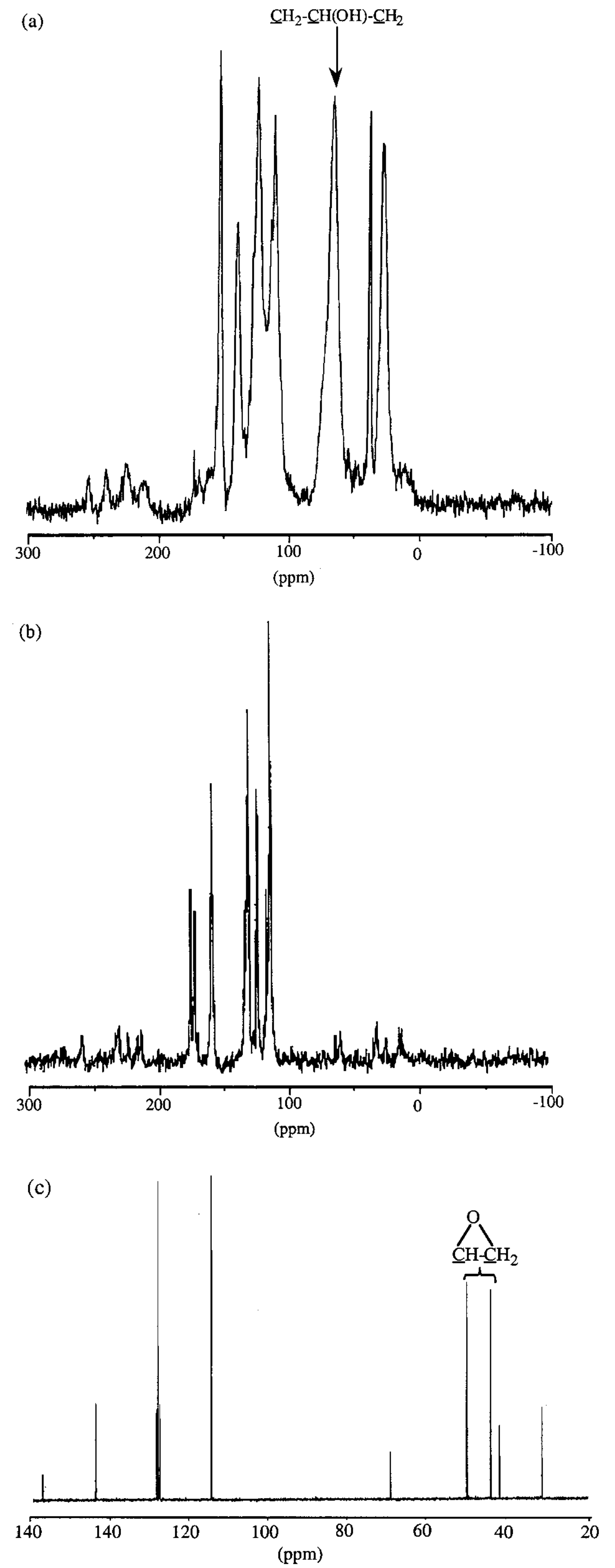

**Figure 5.** $^{13}$C CP-MAS NMR spectrum of (a) hybrid *p*-hydroxybenzoate-alumoxane epoxide resin (fully cured), (b) *p*-hydroxybenzoate-alumoxane, and (c) the solution $^{13}$C NMR spectrum of Dow DER 332 resin (in $C_6D_6$).

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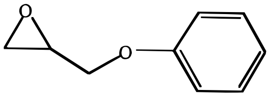
(16) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697.

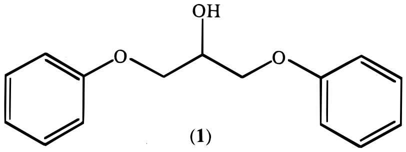
functional groups on the carboxylate-alumoxanes, i.e., the hydroxide and amines of the *p*-HB- and lysine-substituents, respectively? Additionally, in the case of the lysine-alumoxane, if the reactivity is indeed at the primary amines, which of the amines react, or do both amines react?

To further investigate these questions, we have studied the model reactions of a monoepoxide, 1,2-epoxy-3-phenoxypropane (**IV**), with phenol (as a model for the *p*-hydroxybenzoate functionality), propylamine (as a model for the functionality of the terminal amine in lysine), and isopropylamine (as a model for the β-amine in lysine). In addition, reactions of the same monoepoxide were carried out with boehmite (as a model for the alumoxane core), benzoic acid (as a model for the free acid portion of *p*-hydroxybenzoate), and butyric acid (as a model for the free acid portion of lysine). The latter experiments were designed to preclude the possibility that the cross-linking of DER 332 is due to impurities in the carboxylate-alumoxane samples. All the reactions were conducted in acetonitrile-$d_3$ which allowed them to be followed over time by $^1$H NMR spectroscopy, in addition, the reaction products were isolated and fully characterized.

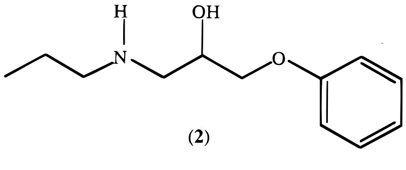


(**IV**)

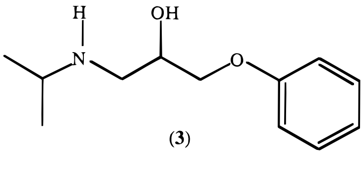
It was found that neither boehmite nor the free acids reacted with the monoepoxy; however, the phenol and amines did react via the expected epoxide ring opening. The reaction of 1,2-epoxy-3-phenoxypropane with phenol, propylamine, and isopropylamine yields $PhOCH_2CH(OH)CH_2OPh$ (**1**), $PhOCH_2CH(OH)CH_2NH^nPr$ (**2**), $PhOCH_2CH(OH)CH_2NH^iPr$ (**3**), respectively. Compounds **1**−**3** have been characterized by $^1$H and $^{13}$C NMR and $^{13}$C CP-MAS NMR spectroscopy and mass spectrometry (see Experimental Section). In addition, their molecular structures have been confirmed by X-ray crystallography.[17,18]



(**1**)



(**2**)



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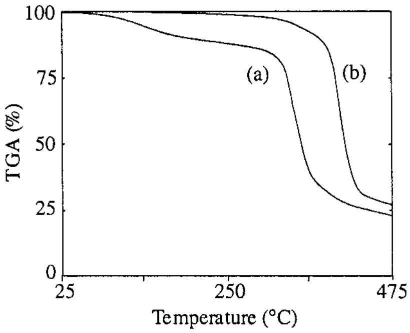

**Figure 6.** Thermogravimetric analysis (TGA) of (a) DER 332/ethylenediamine "blank" and (b) DER 332/*p*-hydroxybenzoate-alumoxane.

These reactions indicate that the functional groups (O−H and N−H) on the carboxylate-alumoxanes are the sole cross-linking centers. From the solution $^1$H NMR experiments, it was determined that both phenol and propylamine fully reacted in ~3 days; however, the reaction with isopropylamine, under identical conditions, took 5 days. The difference in rate of reaction of propylamine and isopropylamine suggests that for the case of lysine-alumoxane, it is the terminal amine, rather than the β-amine that is primarily responsible for the ring opening. It should also be noted that all the model reactions occur more slowly than in the actual resin samples due to the modifying nature of the solvent and the relatively low concentration of solutes.[19,20]

As a result of these model reactions, we can thus conclude that the functionalized carboxylate-alumoxanes do indeed cross-link with the epoxy resin and that they do so solely via their functional substituents.

**Synthesis and Characterization of Composite Epoxy-Alumoxane Resins.** In practical applications, it is unlikely that an epoxy resin system will utilize a functionalized carboxylate-alumoxane as its sole cross-linking agent. As a result, it is important to investigate the effect of the as synthesized alumoxanes on traditional two-part resin systems. To that end, lysine- and *p*-HB-alumoxanes were incorporated into a self-curing, commercially available epoxy resin system: Resin Services Resin HTR-212 with hardener no. 874. The epoxide base of the Resin Services Resin HTR-212 is the Dow DER 332 resin, making for a ready comparison with the hybrid materials.

The sequential addition of different ratios of the carboxylate-alumoxanes into the resin system (similar to the procedure performed for the hybrid system) yielded an optimal weight ratio of incorporation found to be 2:5:1 for the alumoxane/resin/hardener. For comparative purposes, unreacted boehmite was added in the same ratio to the resin system and a "blank" sample of the resin was also prepared without any additives (i.e., neat).

The neat resin and the resin/boehmite combination required full cure times of 4 h at 50 °C. The presence of either carboxylate-alumoxane in the same mass ratios significantly lowered both the cure time (30 min. at 50

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(17) Koide, Y.; Bott, S. G.; Barron, A. R. *J. Chem. Crystallogr.* **1999**, *29*, 247.

(18) Vogelson, C. T.; Bott, S. G.; Barron, A. R. Submitted for publication.

(19) Lu, M.; Kim, S. *J. Appl. Polym. Sci.* **1999**, *71*, 2401.

(20) Online monitoring of amine/epoxy cross-linking has been recently reported, see: Liu, T.; Elsby, S.; Fernando, G. F. *Proc. SPIE-Int. Soc. Opt. Eng.* **1999**, *3670*, 134.

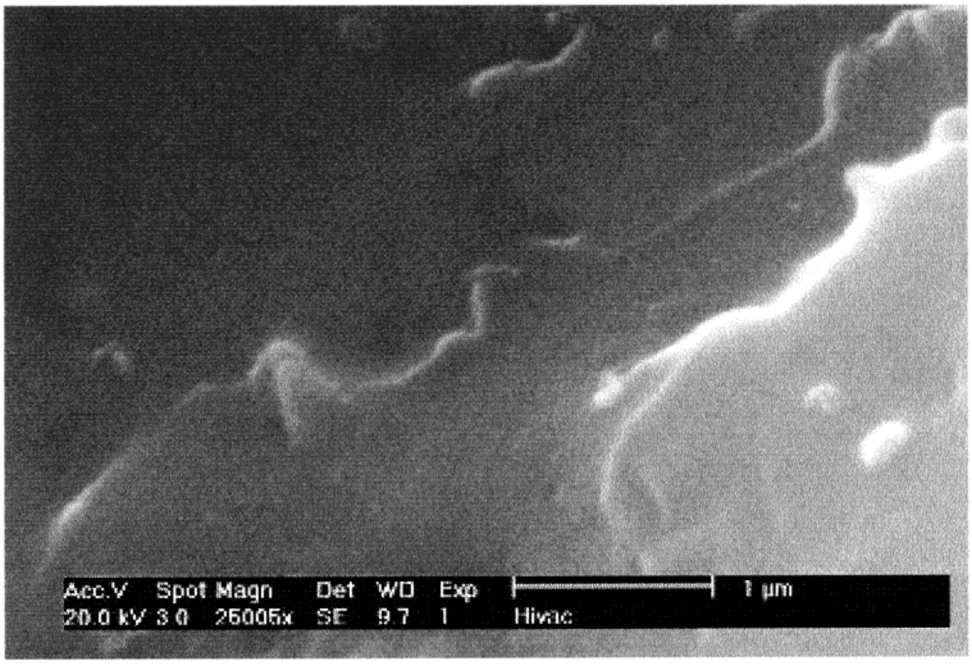

**Figure 7.** SEI micrograph of the surface of the lysine-alumoxane composite resin.

°C) and the required temperature (2 h at 35 °C).[21] The set times, however, as determined by differential thermal analysis of identical mass ratio formulations (see Experimental Section), were unaffected by the addition of either alumoxane (8 min at 25 °C). The hardness (scratch resistance) and strength of the resin composites are significantly increased by the presence of the carboxylate-alumoxanes, and these trends follow the order lysine-alumoxane resin > *p*-hydroxybenzoate-alumoxane resin ≫ neat resin > boehmite-impregnated resin. In addition, as may be seen from Table 4, the tensile strength of the alumoxane composite materials is significantly greater than the "blank" commercial resin. The peak load and peak stress are both increased by a factor of 5 and seven, respectively. Interestingly, contact angle measurements of the *p*-HB-alumoxane resin indicate a slight decrease in the material's hydrophillicity, rather than the increase seen for the same alumoxane in the hybrid system; see Table 3. However, as with the hybrid materials, the similarity between advancing and receding contact angles suggests a uniform material. The SEI micrograph of the lysine-alumoxane resin shows that the alumoxane particles are uniformly distributed throughout the composite (Figure 7). These results indicate that the carboxylate-alumoxanes are not simply acting as traditional ceramic fillers in the epoxy resin but are chemically bound to the organic backbone.

In addition to the Resin Services system, the alumoxanes were incorporated into other commercial materials, see Experimental Section. The ratios for incorporation into these materials were determined stoichiometrically, rather than experimentally. Thus, the amount of curing agent required by a specific quantity of resin mixed with a functionalized carboxylate-alumoxane can be determined. The ratio of alumoxane to resin is still qualitative; however, the ideal loading is one in which the alumoxane is well dispersed throughout the final mixture (often this is in the range of 5−10 wt %). The calculation to determine the optimal quantity of curative involves several parts:[22]

1. determination of the curing agent's active hydrogen equivalent weight, AHEW (eq 2), the carboxylate-alumoxane's active hydrogen equivalent weight, CAHE (eq 3), and the resin's epoxide equivalent weight (EEW, eq 4)

$$\mathrm{AHEW} = \frac{\text{mwt of curing agent}}{\text{no. of active hydrogens}} \tag{2}$$

$$\mathrm{CAHE} = \frac{\text{mwt of alumoxane}}{\text{no. of active hydrogens}} \tag{3}$$

$$\mathrm{EEW} = \frac{\text{mwt of the epoxy resin}}{\text{no. of active epoxy groups}} \tag{4}$$

2. determination of the EEW of the mixture (EEWM, eq 5) to adjust for the incorporation of the carboxylate-alumoxanes as well as any additional reactive and/or unreactive modifiers, fillers, etc.

$$\mathrm{EEWM} = \frac{\text{total mass}}{\left(\dfrac{\text{mass of resin}}{\mathrm{EEW}}\right) + \left(\dfrac{\text{mass of alumoxane}}{\mathrm{CAHE}}\right)} \tag{5}$$

3. determination of the proper stoichiometric ratio (psr) of epoxy resin to curing agent to carboxylate-alumoxane based on the parts by weight curative required per 100 parts epoxy resin (eq 6)

$$\mathrm{psr} = \frac{\mathrm{AHEW} \times 100}{\mathrm{EEWM}} \tag{6}$$

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(21) Note that for the Resin Services system, the epoxy was found to cure considerably faster when exposed to air than when placed within the confines of a sealed mold.

(22) Formulating with Dow Epoxy Resin, *Dow Plastics*, Form No. 296-346-1289.

**Table 5. Examples of Qualitative Properties of Various Composite Alumoxane Resin Formulations[a] by Weight**

| carboxylate-alumoxane | epoxy resin | additional hardener | additional catalyst[b] | comments |
|---|---|---|---|---|
| 1 part *p*-HB-alumoxane | 10 parts 332 | 1 part 201 | yes | strong, inflexible solid, deep red in color, with the alumoxane appearing to be well dispersed |
| 1 part *p*-HB-alumoxane | 10 parts 332 | 2 parts 2426 | no | brown solid, strong and inflexible; a significant amount of alumoxane settled to the bottom of the sample during cure |
| 1 part *p*-HB-alumoxane | 5 parts 332<br>+ 5 parts 732 | 1 part 201 | yes | red, rubbery material that is easily torn; alumoxane is well dispersed |
| 2 parts *p*-HB-alumoxane | 10 parts 4221 | 1 part 301 | yes | peanut colored solid, quite strong and hard, with evidence of the alumoxane having partially settled during cure |
| 1 part *p*-HB-alumoxane | 5 parts 332<br>+ 1 part 732 | n/a | yes | similar to the first material presented in this table, but with mild flexibility |
| 1 part lysine-alumoxane | 6 parts 828<br>+ 2 parts 732 | n/a | yes | contact transparent solid indicative of finely dispersed alumoxane particles; solid is mildly flexible and somewhat brittle |

[a] See Experimental Section for additional details. [b] If an additional catalyst was used, it was 1% (by weight) 1-methylimidazole.

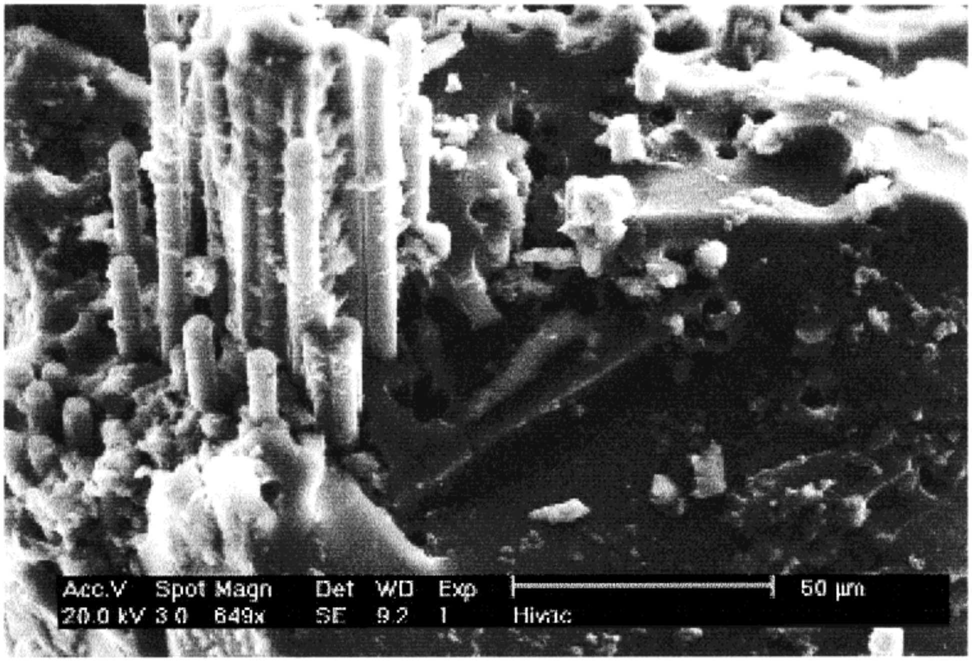

**Figure 8.** SEI micrograph of the surface of a purposefully failed *p*-hydroxybenzoate-alumoxane hybrid resin containing carbon fibers.

As with the hybrid systems, SEI micrographs of all the composite materials show that the alumoxanes are well dispersed throughout the resin systems and are similar to those discussed in detail above. A summary of the qualitative properties of various composite alumoxane resin formulations is given in Table 5, while the contact angle measurements are given in Table 3. In addition, in each case the composite resins with the carboxylate-alumoxanes all show improved physical properties as compared to a "blank", purely organic resin. It is thus apparent that the functionalized carboxylate-alumoxanes positively affect the physical properties of the commercial epoxy systems and are fully cross-linked into the organic matrix.

**Incorporation of Carbon Fibers and Carbon/Kevlar Mattings into a Hybrid Alumoxane Resin.** Fibers and mattings are commonly incorporated into epoxy materials due to their low mass and high tensile strength.[3,23] The advantages of fiber incorporation are most prominently seen in the automotive, nautical, and aeronautical industries where strong, lightweight epoxy-based materials serve numerous functions.[6] Both carbon fibers and carbon/Kevlar mattings were incorporated into a *p*-HB-alumoxane hybrid resin prior to curing.

SEI micrographs of a cleaved sample show that the fibers reside within the epoxy matrix; see Figure 8. Thus, the resin wets the fiber tow or matt, allowing for full infiltration of the resin (i.e., no void spaces are observed), showing that the presence of the alumoxanes does not alter the processability of the commercial resin systems. Unlike previously reported studies,[24] the morphology of the alumoxane-based resins is unaffected by the presence/absence and identity of the fibers. No large particles or agglomerates were observed. As may also be seen from Figure 8, some fibers have pulled out of the matrix, leaving holes, whereas other fibers are clearly visible, protruding from the epoxide. The opposing face of this purposefully failed material shows fiber

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pull-out holes where the exposed fibers exist on the original face. This demonstrates that the alumoxane cross-linking agents do not effect fiber pull-out in an appreciable manner while increasing the strength of the matrix.

## Conclusions

We have demonstrated that functionalized carboxylate-alumoxanes can readily be incorporated into both hybrid and composite epoxide resin systems in which the presence of the alumoxanes improves the overall cure times, temperatures, and physical properties of the organic resins. Unlike neat organic resins, the carboxylate-alumoxane composite resins do not undergo significant mold shrinkage, and the density of the resultant composites is uniform and comparable to, or higher than, that of the neat organic resin. Importantly, the tensile strength of these hybrid and composite resins (15−68 MPa) is significantly higher than organic resins. In fact, the alumoxane-based resins have values between concrete (2 MPa) and aluminum (90 MPa), but with a lower modulus than either. We are continuing our investigation into methods to further improve the tensile strength of the alumoxane-based resins with a view to producing materials comparable in properties to bone (200 MPa). The thermal stability of the hybrid and composite resins is significantly enhanced as compared to the purely "organic" resins.

Model reactions indicate that neither the aluminum-oxide core nor the nonfunctionalized carboxylic acids react with the epoxide and confirm that the active cross-linking centers are the functional groups on the carboxylate-alumoxanes. Furthermore, the reactions indicate that the terminal amine rather than the isoamine reacts preferentially in the case of the lysine-alumoxane.

We are presently using the compounds isolated from the model reactions to characterize the composite and hybrid resins. This will allow for a determination of the number of chemical linkages to the epoxide resin backbone formed per alumoxane nanoparticle which will then allow for full optimization of the alumoxane resins. Once optimization of the synthesis has been realized, we will further develop the molding process and investigate additional physical properties of the materials, including chemical resistance, coefficient of thermal expansion, corrosion resistance, and impact resistance.

## Experimental Section

AFM images of samples were obtained using a Nanoscope IIIa Scanning Probe microscope (Digital Instruments, Santa Barbara, CA) in tapping mode AFM. FESP tips were used with a pyramidal shape and end radius of 5−10 nm (also from Digital Instruments). SEM studies were performed on a JEOL JSM-5300 scanning microscope. Surface area measurements were obtained on a Coulter SA3100 BET Surface Analyzer. Particle size measurements were made on a Coulter N4 Plus Submicron Particle Sizer at scattering angles of 30° and 60°. The solvent used for these measurements was deionized water, and the solution concentrations were 2 g $L^{-1}$. Ceramic yields and set-time exotherms were obtained on a Seiko TGA instrument. Tensile strength measurements were obtained from an MTS 858 Mini-Bionix system. Microprobe analysis was conducted on a Cameca SX50 EDAX system. Solid state $^1H-^{13}C$ CP-MAS NMR spectra were obtained at 50.3 MHz $^{13}C$ on a Bruker Avance 200 spectrometer equipped with a VTN probe designed for use with a 7 mm OD rotor. Carboxylate-alumoxanes were studied via the standard software's cptppm pulse program with 5.0 kHz MAS, a 3.5 $\mu$s 90° $^1H$ pulse, 1 ms contact time[25] at the same power, TPPM decoupling[26] with 3 dB less power during the 33 ms FID, and a 5 s relaxation delay. The FID was processed with only 5 Hz of exponential line broadening. Dipolar dephasing spectra[21] were acquired under the same conditions via the standard software's cpnqs pulse program with a 40 $\mu$s delay before and after the 7.0 $\mu$s 180° $^{13}C$ pulse in the middle of the dephasing period preceding FID acquisition. The *n*-propylamine/epoxy and isopropylamine/epoxy products were studied under the same conditions but with 6.4 kHz MAS to optimize the separation of spinning sidebands from the centerbands. Solution-state NMR spectra were obtained on a Bruker AC-250 spectrometer using acetonitrile-$d_3$ solutions (unless otherwise specified).

**Synthesis of *p*-Hydroxybenzoate-Alumoxane.** A mixture of boehmite (10.0 g, 0.167 mol) and *p*-hydroxybenzoic acid (23.0 g, 0.167 mol) was refluxed overnight in 200 mL of water. The thick, white solid was removed by centrifugation, and then washed with water, ethanol, and ether prior to being air-dried. Yield: 26 g. Ceramic yield: 23%. Particle size (av) = 394 nm. Surface area = 71.98 $m^2$ $g^{-1}$. IR ($cm^{-1}$): 3610 (m), 3240 (b), 2980 (m), 1690 (s), 1613 (s), 1562 (s), 1434 (s), 1260 (s), 1178 (s), 1070 (s), 794 (s).

**Synthesis of Lysine-Alumoxane.** A mixture of lysine (24.4 g, 0.167 mol) and boehmite (10.0 g, 0.167 mol) was refluxed overnight in 200 mL of water. The mixture was then filtered to remove any unreacted boehmite. The solution was then pumped dry. The resulting white solid was air-dried. Yield: 19 g. Ceramic yield: 8%. Particle size (av) = 400 nm. Surface area = 1.84 $m^2g^{-1}$.

**Synthesis of $PhOCH_2CH(OH)CH_2OPh$.** An acetonitrile solution (5 mL) of phenol (1.0 mL, 11 mmol) and 1-methylimidazole (0.1 mL) was added to 1,2-epoxy-3-phenoxypropane (1.4 mL, 11 mmol) and refluxed under atmospheric conditions. After 5 days, the solution obtained a pale red tint and the reflux was discontinued. Upon cooling of the solution to −25 °C, a colorless crystalline material was obtained. MS (EI, %): *m*/*z* 244 ($M^+$, 100), 150 ($M^+ - OPh$, 38), 107 [$M^+ - CH(OH)CH_2OPh$, 72]. IR ($cm^{-1}$): 3550 (s), 3075 (m), 3050 (m), 2980 (s), 1244 (s), 1120 (s). $^1H$ NMR ($C_6D_6$): $\delta$ 7.10 [4H, m, *o*-C*H*], 6.82 [6H, *m*-, *p*-C*H*], 4.17 [1H, quin, *J*(H−H) = 5.4 Hz, C*H*(OH)], 3.84 [4H, d, *J*(H−H) = 5.4 Hz, C*H*$_2$], 2.74 [1H, s, O*H*]. $^{13}C$ NMR ($C_6D_6$): $\delta$ 159.4 (O$C_{Ph}$), 130.1 (*m*-*C*H), 121.7 (*p*-*C*H), 115.3 (*o*-*C*H), 69.6 (*C*H$_2$), 69.3 [*C*H(OH)].

**Synthesis of $PhOCH_2CH(OH)CH_2NH^nPr$.** An acetonitrile solution (10 mL) of propylamine (5.0 mL, 61 mmol) and 1-methylimidazole (0.1 mL) was added to 1,2-epoxy-3-phenoxypropane (8.2 mL, 61 mmol) and refluxed under atmospheric conditions. After 3 days, the solution obtained a pale red tint and the reflux was discontinued. Upon cooling of the solution to −25 °C, a colorless crystalline material was obtained. Mp: 74−75 °C. MS (EI, %): *m*/*z* 209 ($M^+$, 23), 165 [$M^+ - CH_3CH_2CH_2 - H$, 100]. IR ($cm^{-1}$): 3285 (s), 3100 (m), 2953 (s), 1262 (s), 1048 (s). $^1H$ NMR ($C_6D_6$): $\delta$ 7.31 [2H, m, *o*-C*H*], 6.95 [3H, *m*-, *p*-C*H*], 3.92 [3H, m, OC*H*$_2$C*H*OH], 2.61 [6H, m, O*H* + N*H* + C*H*$_2$NC*H*$_2$], 1.47 [2H, sex, *J*(H−H) = 7.2 Hz, CH$_3$C*H*$_2$], 0.90 [3H, t, *J*(H−H) = 7.3 Hz, C*H*$_3$]. $^{13}C$ NMR ($C_6D_6$): $\delta$ 159.2 (O$C_{Ph}$), 130.1 (*m*-*C*H), 121.5 (*p*-*C*H), 115.3 (*o*-*C*H), 71.4 (*C*OH), 68.9 (O*C*H$_2$), 52.8 (N*C*H$_2$), 52.3 (N*C*H$_2$), 23.9 (*C*H$_2$), 12.2 (*C*H$_3$). $^1H-^{13}C$ CP-MAS NMR: $\delta$ 154.4 (O*C*), 126.3 (*m*-*C*H), 116.3 (*p*-*C*H), 110.7 (*o*-*C*H), 67.2 and 64.2 (HO*C*H and O*C*H$_2$), 51.6 and 50.5 (N*C*H$_2$), 21.3 (CH$_2$*C*H$_2$CH$_3$ ), 10.7 (*C*H$_3$).

**Synthesis of $PhOCH_2CH(OH)CH_2NH^iPr$.** An acetonitrile solution (10 mL) of isopropylamine (5.0 mL, 61 mmol) and 1-methylimidazole (0.1 mL) was added to 1,2-epoxy-3-phenoxypropane (8.2 mL, 61 mmol) and refluxed under atmospheric conditions. After 5 days, the solution obtained a pale red tint and the reflux was discontinued. Upon cooling of the solution

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to −25 °C, a colorless crystalline material was obtained. Mp: 93−95 °C. MS (EI, %): *m*/*z* 209 ($M^+$, 8), 194 ($M^+ - CH_3$, 10), 165 [$M^+ - H - (CH_3)_2CH$, 18]. IR ($cm^{-1}$): 3320 (s), 3050 (m), 2983 (s), 1250 (s), 1090 (s). $^1H$ NMR ($C_6D_6$): $\delta$ 7.29 [2H, m, *o*-$C\mathit{H}$], 6.95 [3H, *m*-, *p*-$C\mathit{H}$], 3.95 [2H, m, $C\mathit{H}N\mathit{H}$], 2.71 [6H, m, $C\mathit{H}_2C\mathit{H}(O\mathit{H})C\mathit{H}_2$], 1.01 [6H, m, $(C\mathit{H}_3)_2CH_2$]. $^{13}C$ NMR ($C_6D_6$): $\delta$ 159.8 ($O\mathit{C}_{Ph}$), 130.1 (*m*-$\mathit{C}H$), 121.5 (*p*-$\mathit{C}H$), 115.3 (*o*-$\mathit{C}H$), 71.4 ($\mathit{C}OH$), 69.1 ($O\mathit{C}H_2$), 50.4 ($N\mathit{C}H$), 49.4 ($N\mathit{C}H_2$), 23.4 ($\mathit{C}H_3$). $^1H-^{13}C$ CP-MAS NMR: $\delta$ 156.5 ($O\mathit{C}$), 127.8 (*m*-$\mathit{C}H$), 117.3 (*p*-$\mathit{C}H$), 110.3 (*o*-$\mathit{C}H$), 71.3 and 66.0 ($HO\mathit{C}H$ and $O\mathit{C}H_2$), 47.0 and 46.0 ($N\mathit{C}H$ and $N\mathit{C}H_2$), 20.3 ($\mathit{C}H_3$), 17.6 ($\mathit{C}H_3$).

**Determination of Epoxy Resin Set Time.** A small sample (~10 mg) of resin, hardner, and/or alumoxane was placed in aluminum pan along with the appropriate catalyst. The mixture was then heated in the TGA to a controlled temperature and held constant at that temperature until a peak exotherm was observed. The time to the peak exotherm was defined as the set-time.

**Resin Molding Techniques.** *Method 1: Sheets.* The carboxylate-alumoxane modified resins were molded into uniform samples (6 in. × 6 in. and 1 mm thick) using a simple mold consisting of two moderately thick aluminum plates which were tapered on one edge of one side so that, when the two plates were placed together with the tapers adjoining, a sort of funnel cavity was formed. A single flat rubber gasket was fashioned to fit around the edges and corners of three of the four sides of the mold. The plates were coated with a mold release agent (e.g., Axel Products, F-57NC) prior to use. The alumoxane-resin system was degassed prior to its introduction into the mold. The mold was held with C-clamps and cured upright in a temperature controlled oven for 2 h at 150 °C (unless otherwise specified). For purposes of tensile strength testing, these sheets were cut using a diamond-blade saw to forms 25 mm × 45 mm × 1 mm in size.

*Method 2: Dog Bones.* Using a similar technique, “dog bones” for tensile strength measurements were fashioned using aluminum molds. The bottom mold had an inner bone shape, while the top mold consisted of a flat sheet. The preparation and use of these molds is analogous to that described in method 1.

**Hybrid Alumoxane Resins.** The carboxylate-alumoxane (2.8 g) was ground to a fine powder in a porcelain mortar and added to a glass vial of warm (40−45 °C) DOW DER 332 Epoxy Resin (5.6 g). The mixture was stirred for 30 min, and then 1-methylimidazole (0.1 mL) was added. The vial was placed into an oven (50 °C) and heated at the cure temperature for 10 h. Note that the “blank” Dow 332 resin mentioned in Tables 3 and 4 consisted of DER 332 mixed as stated above with ethylenediamine as a cross-linking agent in place of the alumoxane.

**Composite Alumoxane Resins.** Resin Services resin HTR-212 was used in combination with Resin Services hardener no. 874. The optimal ratio of epoxide:alumoxane:hardener was found to be 5:2:1 (by mass). (The “blank” Resin Services material mentioned in Tables 3 and 4 was formed with the given stoichiometric ratios of epoxide to hardener. No alumoxane was included in the formulation.) Additional composite materials were formulated using the relative amounts given in Table 5. In all cases the mixtures were poured into molds and cured for 2 h at 150 °C. 1-Methylimidazole was added (~1 wt %) to each sample to facilitate the cure unless otherwise noted. In all tables, the following abbreviations have been used: *p*-hydroxybenzoate-alumoxane (*p*-HB-alumoxane), Dow DER 332 (332), Dow DER 732 (732), Air Products Ancamide 2426 (2426), Union Carbide Tone Polyol 201 (201), Union Carbide Tone Polyol 301 (301), Union Carbide ERL-4221 (4221), Shell Epon 828 (828).

**Fiber-Reinforced Composite Resins.** Hybrid resins made from Dow 332 and *p*-HB-alumoxane were formulated as described above. For molding and fiber incorporation, the mold described above was used in a slightly different manner. The mold surfaces were first coated with a mold release agent, and then, one of the mold plates was placed flat on a countertop while ~15 g of the precured hybrid resin was poured onto the surface. The fibers or matting were then layered across the surface of the resin, with an additional 15 g of precured hybrid resin poured across the fibers/mattings. The top mold plate was placed on top of the “sandwich” materials and held in place with C-clamps. The mold was then placed upright in an oven at 150 °C for 2 h to allow for the resin to completely cure.

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**Supporting Information Available:** Schematics of aluminum molds used to prepare sheets of epoxy resin materials**.** This material is available free of charge via the Internet at http://pubs.acs.org.

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