Organotransition metal complexes as additives for epoxy resins: 2. Interaction with epoxy resins

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In our previous study, chromium acetylacetonate (Cr(acac)₃) was found to have a greater toughening effect on epoxy resin than Co(acac)₃. G.p.c. and n.m.r. results indicated that Cr(acac)₃ has a tendency to attach to the hydroxy groups of diglycidyl ether of bisphenol A (DGEBA) multimers during mixing. This is due to the fact that the (acac)⁻ ligands of Cr(acac)₃ are able to attract protons from hydroxy groups. As the DGEBA epoxy resin incorporating Cr(acac)₃ was cured with amine curing agents, each Cr(acac)₃ molecule was able to interact with more than one hydroxy group. This reinforced the cured epoxy network unless the amine curing agents exceeded the stoichiometric quantity of epoxy groups.

(Keywords: chrome acetylacetonate; epoxy resins; additives; interactions; toughness)

INTRODUCTION

Organotransition metal complexes have been used as accelerators for epoxy resins for several years ¹⁻⁵. Recently, several metal acetylacetonates have been reported to be able to enhance the mechanical properties of epoxy resins ⁶⁻¹⁰ and, in particular, their fracture toughness. Although Stoakley and St Clair ^{7,8} have attributed the toughening effects of cobalt acetylacetonate (Co(acac)₃) on the epoxy resins to the accelerated reaction it provided, others ^{5,9,10} have reported that the catalytic effects might not coincide with the toughening effects.

It is with this perception that a series of studies was undertaken to investigate the toughening mechanism of metal acetylacetonates. In our previous report¹⁰, we have pointed out that the incorporation of chromium acetylacetonate (Cr(acac)₃) in the diglycidyl ether of bisphenol A (DGEBA)/diethylene triamine (DETA) and tetraglycidyl diamino diphenyl methane (TGDDM)/diamino diphenyl sulfone (DDS) epoxy resins, respetively, provided much higher fracture toughness than Co(acac)₃. SEM and TEM also revealed that the structures of cured epoxy resins incorporating Cr(acac), were more cohesive. In this paper, we will focus our discussion on the interaction of Cr(acac)₃ and Co(acac)₃ with the epoxy resins during mixing and after crosslinking the epoxy resins. The interpretation for the reinforcement of the epoxy network by Cr(acac), incorporated at the molecular level is also provided.

EXPERIMENTAL

Materials

Most of the DGEBA difunctional epoxy resin used was Epon 826 (Shell) with epoxy equivalent weight

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0032-3861/93/102162-07

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Sample preparation

metal complex additives.

In the previous study, we employed MEK to facilitate the dissolution of Cr(acac)₃ and Co(acac)₃ in DGEBA and TGDDM epoxy resins¹⁰. In order to eliminate the solvent effects on their interactions with the epoxy resins, in this study we used direct mixing at 50, 70, 100 and 130°C, respectively, for various times. The changes in viscosity, the g.p.c. chromatograms and the i.r. and n.m.r. spectra were recorded.

(EEW) of 187 ± 4 g mol⁻¹. Epon 825 (EEW = 175 g mol⁻¹) and Epon 1001 (EEW = 605 g mol⁻¹) were also used

for comparison. However, unless otherwise specified,

the DGEBA resin was Epon 826. The TGDDM

tetrafunctional epoxy resin used was MY720 (Ciba-Geigy) with $EEW = 125 \pm 5 \text{ g mol}^{-1}$. The EEW values

were measured by the hydrochloric acid-methyl ethyl ketone (MEK) method¹¹. Aniline (reagent grade, BDH

Chemicals) was used as a monofunctional amine curing

agent for DGEBA resin. Cr(acac)₃ and Co(acac)₃ (Tokyo Kasei Chemical Industries) were used as organotransition

DGEBA resins were cured by aniline in 100 and 120% stoichiometric quantities with the epoxy groups, respectively, at 150°C for 10 h and some of them were additionally post-cured at 200°C for 2 h. The cured resins were still able to dissolve in MEK and they were then incorporated with 1 mol% Cr(acac)₃ using MEK. (The molar percentage was calculated by dividing the number of moles of Cr(acac)₃ by the total number of moles of DGEBA resin before curing.) The mixing procedure has been described in a previous study¹⁰. The g.p.c. chromatograms of cured epoxy resin with and without Cr(acac)₃ were recorded.

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Analytical technique

The viscosity of the DGEBA samples was measured by a Haake model RV-20 viscometer at 30°C, whereas that of the TGDDM samples was measured by a Brookfield model DV-11 viscometer at 80°C.

For g.p.c. samples (0.1 g) were dissolved in tetrahydrofuran (THF, 10 ml). Tests were run using a Shodex model RI SE-61 instrument with a mobile phase flow rate of 1 ml min^{-1}

I.r. spectra were recorded on a Hitachi 270-30 model IR.

300 MHz ¹H n.m.r. spectra of the DGEBA samples dissolved in deuterated chloroform were recorded on a Bruker model AM-300 WB NMR.

RESULTS AND DISCUSSION

DGEBA epoxy resin incorporating Cr(acac), was found to have higher viscosity than neat and Co(acac)3incorporated resins. As 1 mol% Cr(acac)₃ was mixed with DGEBA resin at 100°C, the viscosity measured at 30°C increased with mixing time as shown in Figure 1a, although the solution became clear within a few minutes of mixing. However, the viscosity of DGEBA resin was not apparently changed by mixing with 1 mol% Co(acac)₃. By choosing 24 h as a mixing time for DGEBA resin mixed with Cr(acac)₃ and changing the temperature, the viscosity was found to increase with temperature as shown in Figure 1b. In our previous study¹⁰, MEK was used as a solvent to facilitate the mixing of DGEBA resin and Cr(acac), at room temperature. Once mixing was completed, MEK was evaporated off in vacuum at 100°C for 24 h. Consequently, the viscosity of the MEK-free mixture was about the same as that prepared by directly mixing DGEBA resin and Cr(acac)₃ at 100°C for 24 h. The two different methods of mixing ultimately produced the same result.

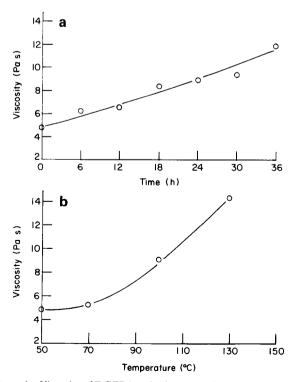


Figure 1 Viscosity of DGEBA resins incorporating 1 mol% Cr(acac)₃ measured at 30°C as functions of (a) mixing time at 100°C and (b) temperature at which it was mixed for 24 h

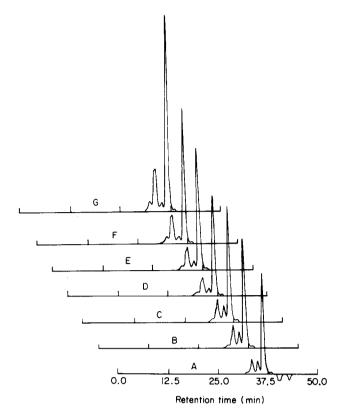


Figure 2 G.p.c. chromatograms of (A) DGEBA resin and its mixtures with 1 mol% Cr(acac)₃ after mixing at 100°C for various times: (B) 6 h; (C) 12 h; (D) 18 h; (E) 24 h; (F) 30 h; (G) 36 h

The increase in viscosity of the DGEBA resin by mixing with Cr(acac), indicated that an interaction had taken place between the components. Therefore, the molecular weight distribution of DGEBA resin incorporating 1 mol% Cr(acac)₃ prepared at various mixing conditions was measured by g.p.c. The g.p.c. chromatogram of the DGEBA resin shown in Figure 2 has three peaks and one shoulder, indicating that the resin contained four species with different molecular weights. A typical chemical structure of the resin is:

$$\begin{array}{c} O \\ CH_2 - CHCH - O \\ \hline \\ CH_3 \\ \hline \\ CH_3 \\ \hline \\ CH_2 \\ \hline \\ O \\ CH_2 \\ CHCH_2 \\ O \\ \\ O \\ CH_2 \\ CHCH_2 \\ O \\ \\ O \\ CH_2 \\ CHCH_2 \\ O \\ \\ O \\ CH_2 \\ CHCH_2 \\ O \\ CH_2 \\ O$$

We assumed that the largest (or first) peak at a retention time $t = 36.0 \,\mathrm{min}$ was due to DGEBA monomers with n = 0 ($M_w = 340$ g mol⁻¹), whereas the middle (or second) peak at $t = 34.9 \,\mathrm{min}$, the final (or third) peak at $t = 33.5 \,\mathrm{min}$ and the shoulder at $t = 32.2 \,\mathrm{min}$ were due to the dimer, trimer and tetramer with n=1 $(M_w = 624 \text{ g mol}^{-1}), n = 2 (M_w = 908 \text{ g mol}^{-1}) \text{ and } n = 3$ $(M_{\rm w} = 1192 \,{\rm g \, mol}^{-1})$, respectively. The volume fractions of DGEBA resins with n=0, 1, 2 and 3 estimated from the areas of the peaks were 90, 4.8, 5.1 and 0.1%, from which the average EEW value of the DGEBA resin was calculated to be $191 \,\mathrm{g}\,\mathrm{mol}^{-1}$, which is within the experimental error of the data measured by epoxy group titration¹¹. The above results confirmed our assumption that the first peak was due to DGEBA monomers, whereas the second and third peaks and the shoulder were due to the dimers, trimers and tetramers.

As DGEBA resins were mixed with 1 mol% Cr(acac)₃ at 100°C, the second peak gradually decreased in intensity and the third peak had an additional shoulder which appeared at t = 32.8 min as shown in Figure 2. Since the molecular weight of Cr(acac)₃ is 349 g mol⁻¹, as it

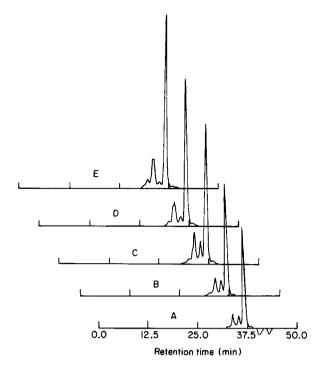


Figure 3 G.p.c. chromatograms of (A) DGEBA resin and its mixtures with 1 mol% Cr(acac), after mixing at various temperatures for 24 h: (B) 50°C; (C) 70°C; (D) 100°C; (E) 120°C

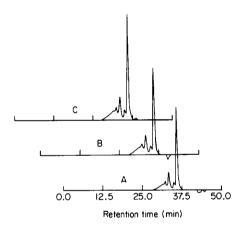


Figure 4 G.p.c. chromatograms of (A) TGDDM resin and its mixtures with (B) 1 mol% Cr(acac), and (C) 1 mol% Co(acac), respectively, after mixing at 100°C for 24 h

attached to DGEBA dimers, the molecular weight of the pair would be 973 g mol⁻¹, larger than that of the trimer but less than that of the tetramer $(M_w = 1076 \text{ g mol}^{-1})$. Therefore, it can be assumed that the additional shoulder at t = 32.8 min was due to Cr(acac)₃-attached DGEBA dimers. Moreover, the original shoulder at t = 32.2 minhad gradually grown to a small peak with the retention time decreased to 31.9 min. We believed that the growth of the small peak was due to the Cr(acac)₃-attached DGEBA trimers $(M_w = 1257 \text{ g mol}^{-1})$ formed during mixing. Similar results were obtained as the mixing temperature was increased but the mixing time was fixed at 24 h as shown in Figure 3, or as the amount of Cr(acac)₃ was increased as shown in Figure 22 of our previous report¹⁰.

However, it has been shown that the g.p.c. chromatogram of DGEBA resin was neither changed by incorporating Co(acac)₃ nor by incorporating Cr(acac)₃ if it did not contain multimers¹⁰. The viscosity of DGEBA resin

without multimers was also unaffected by incorporating Cr(acac)₃. Obviously, Cr(acac)₃ attaching to the hydroxy groups of DGEBA multimers caused the increase of viscosity during mixing since the difference between DGEBA molecules with n=0 and n>0 is that the latter possesses hydroxy groups. For the case of TGDDM epoxy resin, since it does not possess hydroxy groups, its g.p.c. chromatograms were not changed by incorporating Cr(acac)₃ or Co(acac)₃ as shown in Figure 4. Similarly, no change of viscosity was observed when adopting the same mixing conditions. Generally speaking, the change of viscosity was due to the fact that the molecular weight had been changed. It was then necessary to determine why Cr(acac), was able to attach to the hydroxy group of DGEBA multimers and how the interactions occurred.

Cr(acac)₃ and Co(acac)₃ have similar molecular structures:

where M = Cr or Co. The i.r. spectra of pure $Cr(acac)_3$ and Co(acac)₃ are shown in Figure 5. The notable difference between the two spectra is that the C-O bending peak¹² is at 600 cm⁻¹ for Cr(acac), but at 640 cm⁻¹ for Co(acac)₃. Both Cr and Co are in the first transition metal series. However, the radius of Co³⁺ is 0.53 Å whereas that of Cr³⁺ is 0.57 Å, as derived from the observed interatomic distances in the fluorides¹³.

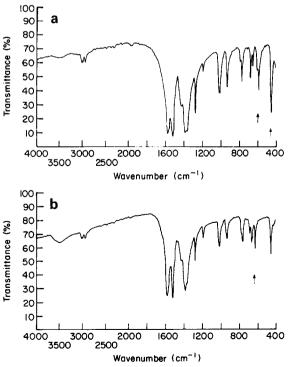


Figure 5 I.r. spectra of (a) Cr(acac)₃ and (b) Co(acac)₃

Thus, the positive charge density on the Co³⁺ ion is higher and so the ligands are drawn in more closely, as verified by the higher ligand field strength than the Cr³⁺ ion¹⁴. The higher bending frequency of the C-O bonds for Co(acac), compared to Cr(acac), resulted from the (acac) ligands being closer to the central ion and thus, required higher energy for bending.

Cr(acac), has been shown to be easily prepared by pH control with basic media in a solution of chromium(III) chloride and acetylacetone¹⁵. The reaction is:

The (acac) ligand exists in resonance forms which are best represented as:

In an acid environment, Cr(acac)₃ is easy to decompose by the reverse of the reaction of formation or by changes in the ligands. Therefore, we believed that the interaction between Cr(acac)₃ and DGEBA multimers was due to the latter possessing hydroxy groups which are able to donate protons for interacting with (acac) ligands. Because Co³⁺ withdrew electrons from the (acac) ligand more, so that the ligands were less active (or less negatively charged), it was not able to interact with DGEBA multimers.

The interaction of Cr(acac)₃ with DGEBA resin can be observed by ¹H n.m.r. in deuterated chloroform. The ¹H n.m.r. spectra of DGEBA resins with and without incorporating Cr(acac)₃, shown in Figure 6, revealed that the spin-spin splitting of the peaks at 2.72, 2.87, 3.33 and 3.92 ppm represented for the protons in the

segments of DGEBA resin¹⁶ has a tendency to coalesce as Cr(acac), was incorporated, although the chemical shift of the peaks was unchanged. A similar phenomenon has been reported in ethyl alcohol containing a trace of acid or base and was attributed to the exchange of protons in the hydroxy groups¹⁷. Therefore, we believe that the transfer of protons in the hydroxy groups of DGEBA resin to the (acac) ligand of Cr(acac)₃ is feasible.

So far we have only discussed the interaction of Cr(acac), with DGEBA resin containing a small percentage of multimers. The advantage of using such a resin is that we are able to distinguish each

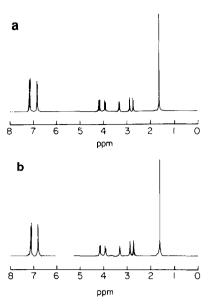
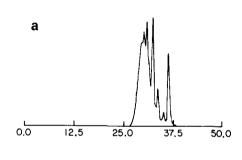


Figure 6 ¹H n.m.r. spectra of (a) DGEBA resin and (b) its mixture with 1 mol% Cr(acac), after mixing at 100°C for 24 h



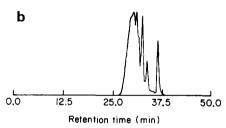


Figure 7 G.p.c. chromatograms of (a) DGEBA oligomer and (b) its mixture with 1 mol% Cr(acac)₃ after mixing at 100°C for 24 h

Cr(acac)₃-dimer or Cr(acac)₃-trimer pairs by g.p.c. However, each Cr(acac)₃ should be able to interact with more than one DGEBA multimer since it contains three (acac) ligands. In order to verify this, we employed a DGEBA oligomer (Epon 1001, $EEW = 605 \text{ g mol}^{-1}$) to mix with 1 mol% Cr(acac), and recorded the change in the g.p.c. chromatogram during mixing. DGEBA oligomer has a higher percentage of DGEBA multimers than monomers as shown in the g.p.c. chromatogram in Figure 7. As it was incorporated with Cr(acac), by mixing at 100°C for 24 h, the peak due to DGEBA dimers completely disappeared whereas the intensity of the peaks in the high molecular weight region increased substantially, as shown in Figure 7. Most of the new species created during mixing have molecular weights higher than the tetramer. Therefore, it can be assumed that more than one DGEBA molecule has attached to a single Cr(acac)₃ molecule.

The above results indicated that in the case of DGEBA resin incorporating Cr(acac)₃ and cured with DETA amine curing agent, each Cr(acac), molecule has the possibility of interacting with several hydroxy groups in the crosslinked epoxy network. Each reacted epoxy group produces a hydroxy group and thus, a large number of hydroxy groups are produced in the epoxy network. However, this statement is only true on the premise that Cr(acac)₃ does not decompose during the curing reaction and the reacted amine groups do not interfere with the interaction between Cr(acac)₃ and the evolving hydroxy groups. Cr(acac), has a strong and sharp characteristic peak in its i.r. spectrum at 470 cm⁻¹ due to the Cr-ring interaction as shown in Figure 5¹². Once it was mixed with DGEBA resin at 100°C for 24 h, the peak still possessed reasonable intensity as shown in Figure 8. As the incorporated epoxy resin had been cured with DETA amine curing agent at room temperature for 24 h and then post-cured at 128°C for 10 h, the position of the peak did not change but the peak broadened as shown in Figure 8. This indicated that most of the Cr(acac), still retained its chemical structure after curing the epoxy resin.

To verify that the reacted amine groups did not interfere with the interaction between Cr(acac), and the hydroxy groups, after the epoxy resin had been cured, g.p.c. was employed to investigate the change of molecular weight distribution of cured DGEBA/aniline epoxy resin by incorporating Cr(acac)₃. Initially, DGEBA resin was reacted with aniline monofunctional amine curing agent in a stoichiometric ratio at 150°C for 10 h and then a portion of cured resin was modified with 1 mol% Cr(acac)₃ using MEK solvent. Figure 9 shows the g.p.c. chromatograms of the cured DGEBA/aniline resins with and without Cr(acac)₃. As shown in the figure, the cured DGEBA/aniline resin was only an oligomer and some of the DGEBA monomers had not yet reacted with aniline. As Cr(acac), was incorporated in the DGEBA/aniline

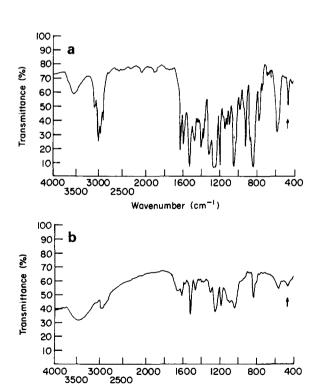


Figure 8 I.r. spectra of (a) the mixture of DGEBA resin and 5 mol% Cr(acac), after mixing at 100°C for 24 h and (b) the mixture of (a) cured with DETA in stoichiometric ratio

Wavenumber (cm⁻¹)

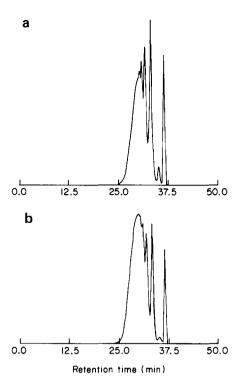


Figure 9 G.p.c. chromatograms of (a) DGEBA/aniline oligomer cured in stoichiometric ratio at 150°C for 10 h and (b) its mixture with 1 mol% Cr(acac)₃

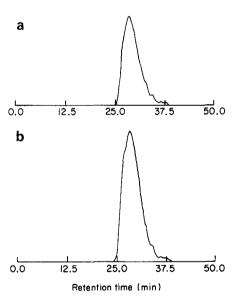


Figure 10 G.p.c. chromatograms of (a) DGEBA/aniline polymer cured in stoichiometric ratio at 150°C for 10 h and then post-cured at 200°C for 2 h and (b) its mixture with 1 mol% Cr(acac)₃

oligomer, the intensity of the peaks due to the low molecular weight species was reduced whereas that of the peaks in the high molecular weight regions was significantly increased. The change of total molecular weight distribution by incorporating Cr(acac)₃ was similar to that of the DGEBA oligomer shown in Figure 7. Apparently, Cr(acac)₃ had interacted with more than one hydroxy group in the DGEBA/aniline oligomer. As DGEBA/aniline oligomer was further reacted at 200°C for 2 h, the peaks in the low molecular weight regions in the g.p.c. chromatogram disappeared and those in the high molecular weight regions coalesced into a broad peak, as shown in Figure 10. As Cr(acac)₃ was incorporated in the post-cured DGEBA/aniline polymer,

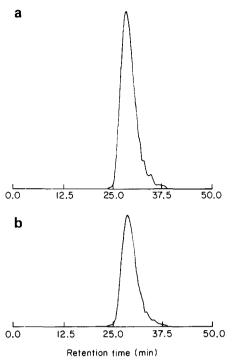


Figure 11 G.p.c. chromatograms of (a) DGEBA/aniline polymer cured in 120% stoichiometric ratio at 150°C for 10 h and then post-cured at 200°C for 2 h and (b) its mixture with 1 mol% Cr(acac)₃

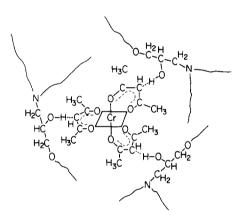


Figure 12 Schematic representation of Cr(acac)₃ interacting with three hydroxy groups in the cured epoxy network

the position of the peak was shifted from t = 28.5 to 27.9 min, indicating that the molecular weight had increased.

In order to make certain that Cr(acac)₃ had interacted with the hydroxy groups in the cured DGEBA/aniline polymer instead of interacting with reacted amine groups, an excess of aniline was employed to react with the DGEBA resin. Interestingly, the g.p.c. chromatogram of post-cured DGEBA/aniline polymer in 120% stoichiometric ratio was not changed by incorporating Cr(acac)₃, as shown in Figure 11. This is not surprising because the (acac)⁻ ligands of Cr(acac)₃ are stable in a basic environment. Once excess amine curing agent was employed to react with the epoxy resin, the unreacted amine will make the cured epoxy network more basic and thus, interfere with the interaction between (acac)⁻ and hydroxy groups. As a consequence, the molecular weight distribution of cured epoxy resin was not affected by incorporating Cr(acac)₃.

In brief, Cr(acac)₃ will interact with the hydroxy groups

in the DGEBA epoxy resin and also in the cured epoxy network, provided that the amount of amine curing agent employed does not exceed the stoichiometric quantity of the epoxy groups. The interaction was by way of proton transfer between hydroxy groups and (acac) ligands of Cr(acac)₃. Since each Cr(acac)₃ has three ligands, it should be able to interact with three hydroxy groups in the cured epoxy network. A schematic representation of the interactions is shown in Figure 12. However, it should be noted that the interactions are similar to acid-base interactions but quite different from covalent bonding. It is not appropriate to consider the interactions as equivalent to increasing crosslinking density, for the crosslinked chains by covalent bonds are more restricted in terms of bond angle and length. Nevertheless, the interactions were able to increase the cohesive strength of the cured epoxy resin. In our previous study¹⁰, the DGEBA/DETA epoxy resins incorporating Cr(acac)₃ were found to have a more cohesive structure and higher fracture toughness than neat resin and those incorporating Co(acac)3. This is believed to be due to the fact that Cr(acac)₃ interacted with hydroxy groups in the crosslinked network and hence, reinforced the structure.

CONCLUSIONS

Cr(acac)₃ has been found to have greater toughening effects on the cured DGEBA/DETA epoxy resins than Co(acac)₃. During the mixing of DGEBA resins with Cr(acac)₃, viscosity increased with mixing time and temperature. This has been verified as resulting from the interaction between the (acac)⁻ ligands of Cr(acac)₃ and the hydroxy groups of DGEBA multimers by the transfer of protons. Due to the higher positive charge density of Co³⁺ drawing the (acac)⁻ ligands in more closely, the (acac)⁻ of Co(acac)₃ is less active and does not interact with the hydroxy groups of DGEBA multimers. Consequently, the incorporation of Co(acac)₃ has no effect on the viscosity or the molecular weight distribution.

As DGEBA resin incorporating Cr(acac)₃ was cured with aniline, each Cr(acac)₃ was able to interact with more than one hydroxy group in the cured DGEBA/aniline polymers unless the amount of aniline employed exceeded the stoichiometric quantity of epoxy groups. Therefore, it is believed that a more cohesive structure and higher fracture toughness for the DGEBA/DETA epoxy resins incorporating Cr(acac)₃ compared to neat epoxy resin and those incorporating Co(acac)₃ are a result of the interaction of Cr(acac)₃ with hydroxy groups in the crosslinked epoxy network.

ACKNOWLEDGEMENTS

Financial support of this work by the National Science Council in Taiwan, Republic of China (grant NSC-79-0405-E-002-02) is gratefully acknowledged. We are also grateful to Ms Diana P. Lin, a pre-medical student at the Johns Hopkins University, for her assistance.

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