The Dynamic Mechanical Analysis of Epoxy–Copper Powder Composites Using Azole Compounds as Coupling Agents

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SYNOPSIS

The dynamic mechanical properties of cured epoxy resin have been studied in which copper powder treated or untreated with azole compounds was used as fillers. The untreated fillers do not shift the glass transition temperature of the matrix polymer of the composites, whereas the storage modulus rises with increasing content of fillers. The application of azole compounds as coupling agents, which could react with both copper and epoxy resin, extended the polymer–filler interactions. The composite filled with copper powder treated with benzotriazole shows a strong reinforcement effect and high resistance to moisture.

INTRODUCTION

Azole compounds, such as imidazole (IMH), benzimidazole (BIMH), benzotriazole (BTAH), and 2-mercapto-benzimidazole (MBIH), are of interest not only as corrosion inhibitors,[1-4] but also as curing agents for epoxy resins.[5-9] We found that azole compounds could react with copper and other transition metals at zero oxidation state to form metal (+1) or metal (+2) "inner" complexes,[10-12] which were usually insoluble in organic solvents and covered the metal surface in a form of polymeric layer.[13-16] This film could change the physical and chemical properties of a metal surface, and might provide active sites for coordination or covalent bonding by which strong adhesion for polymers to metals could be promoted.[10] By using FT-IR reflection absorption spectroscopy, Ishida observed that epoxy resin could be cured on the imidazole treated copper surface. With a suitable combination of chemical reactivities of the azole compounds towards metals and epoxy resins, it was thought that a new kind of coupling agent could be designed for epoxy resin to metals.[9] The report here involves the studies of dynamic mechanical properties, the temperature dependence of mechanical loss (tan δ), and storage modulus (E') for the composites of epoxy resin–copper powder using azoles as the coupling agents.

EXPERIMENTAL

IMH, BIMH, BTAH, and MBIH with high chemical purity were dissolved in ethanol (95%) to form saturated solutions. Two hundred mesh copper powder was etched with 3% HCl to remove surface oxides, and rinsed with distilled water. The chemically cleaned copper powder was then mixed with azole solutions. These mixtures were agitated gently for 6 h. The treated copper powder was isolated and washed with ethanol to remove the physisorbed materials, and dried under vacuum.

The epoxy-copper composites were prepared by mixing 100 parts by weight of epoxy resin (Epon 828), 28 parts 4,4′-diaminodiphenyl methane (DDM) and a designated amount of copper powder. Their compositions are listed in Table I. Both Epon 828 and DDM were separately heated to 373 K until DDM was completely melted, and then mechanically mixed for 5 min. After being weighed according to the sample compositions listed in Table I, the blended liquid and the copper powder were mechanically mixed and spread onto Teflon rubber plates to form films with about 0.5 mm thickness, and were cured at 363 K for 10 h, and then at 453 for 3 h, before they were cooled down to room temperature.

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Table I Sample Compositions

Sample No.	Content of Fillers (% by Weight)	Pretreatment for Fillers
1	0	No
2	10	No
3	15	No
4	20	No
5	15	BTAH
6	15	IMH
7	15	BIMH
8	15	MBIH

The dynamic mechanical properties in terms of storage modulus (E'), loss modulus (E''), and mechanical loss ($\tan \delta$) for each sample were measured using a dynamic viscoelastometer Rheovibron DDV-II-EA over a range of temperature at a constant frequency of 110 Hz. The reactions of azole treated copper with the epoxy group were studied by using a Perkin-Elmer DSC-2C thermal analysis meter.

RESULTS AND DISCUSSION

The Effect of Copper Fillers on Dynamic Mechanical Properties of Epoxy Matrix

Figure 1 shows the temperature dependence of the mechanical loss ($\tan \delta$) and storage modulus (E') of epoxy composites unfilled and filled with copper powder. In the curves of $\tan \delta$ versus temperature, two relaxation bands exist in the temperature region from 150 to 480 K, which are referred to as β and α peaks, respectively. The β-relaxation near 235 K is attributed primarily to localized motions of the polymer chain,[17,18] and the α relaxation at 438 K is due to the long-range motions corresponding to glass transition. Since the influence of phase structure on the behavior of β-relaxation is less significant, attention will be paid to the discussion of the behavior of α-relaxation of the composites filled with copper powder. In Figure 1, curves 1, 2, 3, and 4 correspond to samples 1, 2, 3, and 4 respectively, whose compositions are shown in Table I. All these four samples display similar patterns for the curves of mechanical loss against temperature. The temperature of the α-peak remains the same (438 K) as the filler content increased from 0 to 20% by volume. It is clear that fillers do not shift the glass transition temperature of the matrix polymer in these two-phase mixtures. Because copper powder is a kind of elastic filler, it does not dissipate energy, and the heights of the α-peaks decreased as the content of

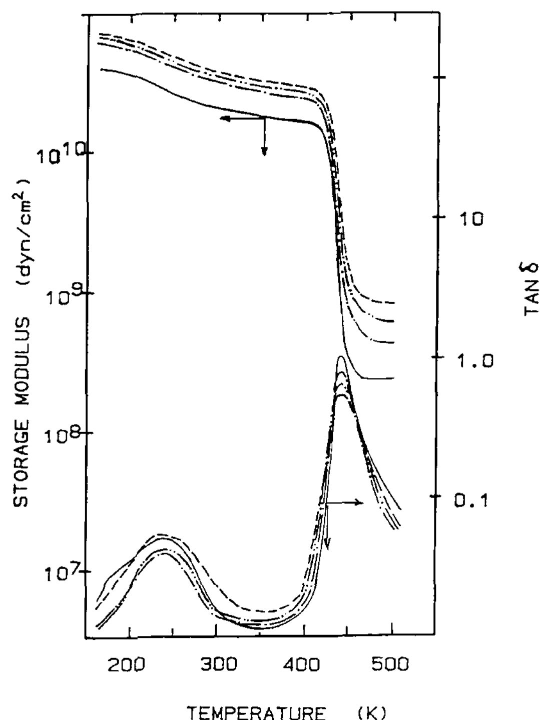

Figure 1 Storage modulus and mechanical loss vs. temperature for unfilled epoxy (——) and filled epoxy with 0.10 (—·—·—), 0.15 (—··—··—), and 0.20 (- - - -) volume fraction copper powder.

copper powder increased, from 1.05 for the sample 1 to 0.60 for the sample 4. The peaks width also increased slightly. This feature is similar to other polymer–filler composites.[19-24] Figure 1 also shows that the filled composites have higher storage modulus (E'_c) than the unfilled polymers (E'_0) in the range of experimental temperature. In Figure 2, the

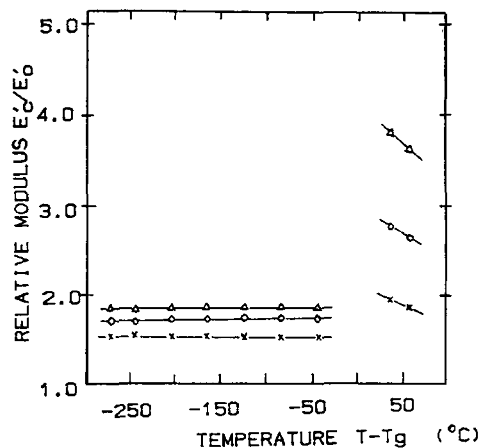

Figure 2 Relative modulus of filled epoxy to unfilled epoxy vs. temperature: (×) ϕ = 0.10; (○) ϕ = 0.15; (△) ϕ = 0.20.

relative moduli for the epoxy–copper systems are plotted as three volume fractions versus temperature differences between the measuring temperature and T_g. The values of E'_c/E'_0 above T_g are larger than those below T_g, and they decreased as temperature increased in the range above T_g, whereas those values in the temperature range below T_g kept almost constant as the temperature changed. This means that the filler has a larger effect on raising the storage modulus in the rubbery state than in the glass state.

The Coupling Effect of Azole Compounds

Figures 3 and 4 show the temperature dependence of the mechanical loss and storage modulus of epoxy resin filled with copper powder which was pretreated or untreated with azole compounds. The content of filler in each sample is 15% by volume. It is clear that their relaxation characteristics are different. Plot 3 is due to the sample in which the filler is untreated copper powder, whereas plots 5, 6, 7, and 8 correspond to samples 5, 6, 7, and 8 whose compositions are listed in Table I. In Figure 3, the shape of the α-peak of either sample 5 or 6 is similar to

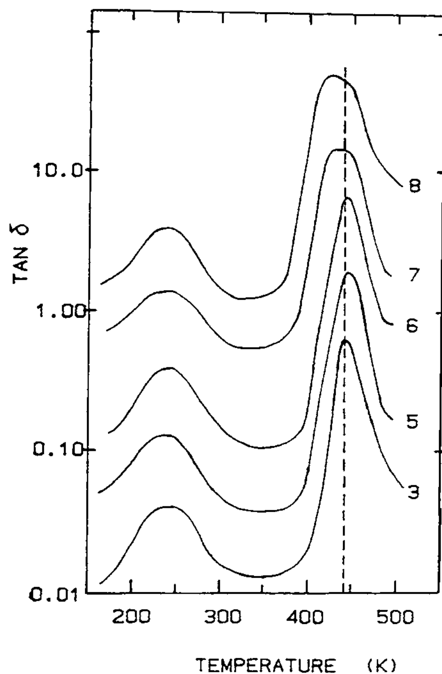

Figure 3 Mechanical loss vs. temperature for filled epoxy with 15% copper powder by volume. Plot 3 for untreated filler sample. Plots 5, 6, 7, and 8 for the samples in which the filler is treated with BTAH, IMIH, BIMH, and MBIH, respectively. Plots 5, 6, 7 and 8 are progressively shifted upwards by a half decade.

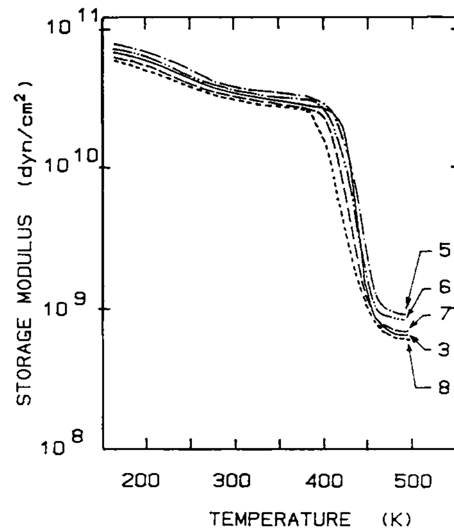

Figure 4 Storage modulus vs. temperature for filled epoxy with 15% copper powder by volume. Plot 3 for untreated filler sample. Plots 5, 6, 7, and 8 for the samples in which the filler is treated with BTAH, IMIH, BIMH, and MBIH, respectively.

that of sample 3. The temperatures of the α-peaks for samples 5 and 6 are 442 and 440 K, which are 4 and 2 K higher than for sample 3. Their storage moduli in the rubberlike region are higher than sample 3. The relative moduli for sample 5 and 6 to sample 3 are 1.4 and 1.3, respectively. In these three samples, the content of filler is the same, but the fillers used in samples 5 and 6 were pretreated with BTAH and IMH, respectively. So we suggest that the increase in T_g and storage modulus is caused by the increase of crosslinking density in the interfacial region between the azole-treated filler and resin matrix. The increase of crosslinking must be attributed to the chemical bonds formed in the interfacial region. This is referred to as the coupling effect of BTAH and IMH for the epoxy–copper composites.

Figures 3 and 4 also show that the temperatures of α-peaks for samples 7 and 8 are lower than that of sample 3, and their widths are much broader, whereas their storage moduli in the rubberlike region are similar to each other. This is probably due to the boundary layers of the composites having a different structure when copper filler was pretreated with BIMH or MBIH under the experimental conditions.

Our previous study indicated that azole compounds, such as IMH, BTAH, BIMH, and MBIH, could react with copper metal to form polymeric complex layers which deposited on the surface of metal.[10-16] By analyzing the increase in weight of copper powder after treatment with azoles, we could

estimate the thickness of the deposit layers formed on copper surface. When copper powder was treated with BTAH and IMH under these experimental conditions, the layers were very thin. The X-ray photoelectron spectroscopic analysis shows the thickness of these layers to be less than 100 Å,[25] while the thickness of the layer on the copper surface when treated with BIMH and MBIH is more than 1000 Å, with much looser structures.[15,16] The catalytic effect of these complexes on the ring-opening reaction of epoxy resin has been investigated by the use of DSC. Figure 5 shows that all these complexes could react with the model compound, phenyl glycidyl ether (PGE). The peak temperatures of the reactions in the DSC curves are 422, 453, 470, and 389 K, respectively, which are in the region of the curing temperature used in the experiment. This means that the deposit layers on the filler surface formed by treatment with azoles could take part in the ring-opening polymerization during the process of curing the epoxy resin. As a result, chemical bonds between the resin matrix and the filler were formed in the composites in which copper filler was treated with BTAH and IMH. This increases the crosslinking density of the network and causes the increase in T_g and the storage modulus in the rubbery state. But, for the composites in which the filler was treated with BIMH and MBIH, since the deposit layers formed on filler surface were thick and loose, when epoxy resin was mixed with the pretreated filler, it could penetrate into the loose layer, and an interpenetrating polymer network of epoxy and the polymeric complex was formed on the copper surface as a boundary layer after curing. This boundary layer broadens the α-peak.

Resistance to Moisture

In order to observe the influence of moisture on the dynamic mechanical properties, a newly cured strip of the epoxy–copper composite with the composition of sample 3 was measured. Then it was stored at room temperature and under the relative humidity of 70 to 90% for 5 months, and measured again. The dynamic mechanical properties were determined from 150 to 490 K. After measurement, the sample was cooled to room temperature, a third measurement was performed. In Figure 6, plot A corresponds to the newly cured sample, plot B is the stored sample, and plot C is from the third measurement for the stored sample which was heated to 490 K and cooled to 300 K. The width of the α-peak of plot B is much broader than plots A and C. This is mainly due to the absorption of moisture onto the interfacial region between copper and resin during the long period of storage under humid conditions. The α-peak could be returned to the plot A configuration by heating the stored sample to 490 K (plot C).

A similar experiment was performed on the composite in which BTAH was the coupling agent. In Figure 7, plots A and B are due to the fresh and stored samples respectively. They are similar to each other, which indicates the storage under humid environment for 5 months did not influence its mechanical properties. We concluded that using BTAH as a coupling agent for copper and epoxy resin com-

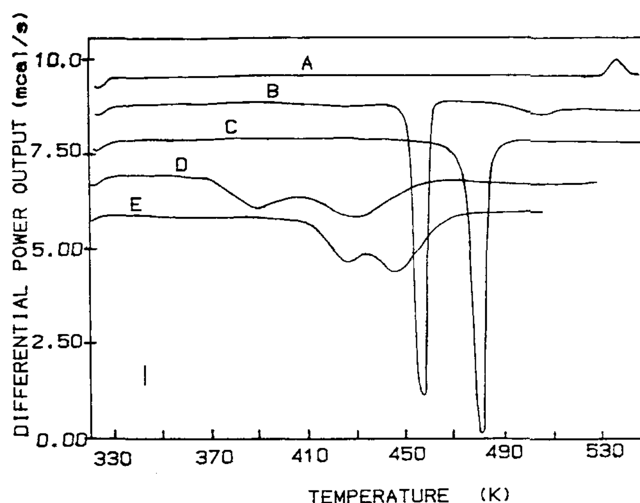

Figure 5 DSC measurement for the reaction of phenyl glycidyl ether with (A) copper powder, (B) IMH-treated copper, (C) BIMH-treated copper, (D) MBIH-treated copper, and (E) BTAH-treated copper.

posite provided good moisture resistance. This result coincides with the study on the breakage stress for a similar system by Park and Bell.[26]

CONCLUSION

The effect of copper powder on dynamic mechanical properties of the composites was evaluated by changing the concentration of copper powder. We found that T_g of the resin matrix was not influenced by the content of copper powder. The storage modulus of the sample increased with the increasing content of copper filler in the temperature range of these experiments.

The azole compounds which were used to treat copper powder acted as coupling agents in the epoxy-copper composites. We have elucidated that chemical bonds formed between filler particles and epoxy matrix caused the glass transition temperature and the storage modulus increases with the BTAH and IMH treated composites. When the copper powder was treated with BIMH and MBIH, the α-relaxation peaks became broadened and the temperatures of the peaks were decreased. Such behavior is a direct consequence of the existence of inhomogeneities in thermoset morphology. We believe that a boundary layer with a different structure exists between filler particles and epoxy matrix. This layer was formed by the catalytic effect of the deposit layer on the ring-opening reaction of epoxy resin in the curing process of the sample.

After storing in the laboratory for 5 months, the relaxation characteristics of the untreated composite shows a broadened α-peak. We believe that it is caused by the absorption of moisture onto the interfacial region between copper and resin. The effect of storage under humid environment for 5 months on BTAH treated composite is not significant. It indicates that pretreatment of copper filler with BTAH provided the composite with good moisture resistance.

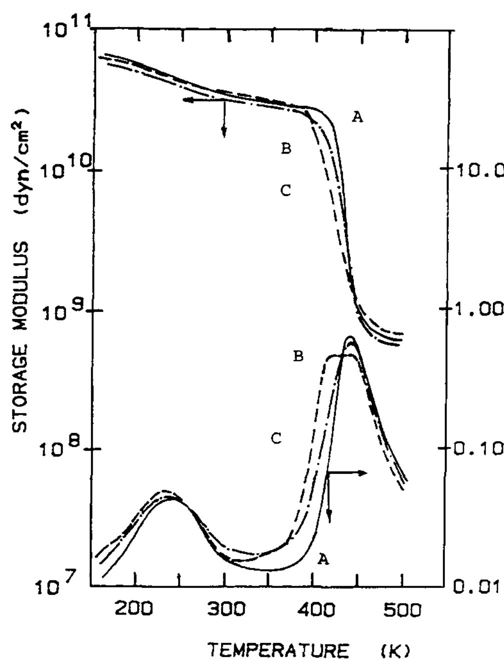

Figure 6 Storage modulus and mechanical loss versus temperature for sample 3: (——) the newly cured sample; (- - - -) the stored sample; (— · — · —) the third measurement.

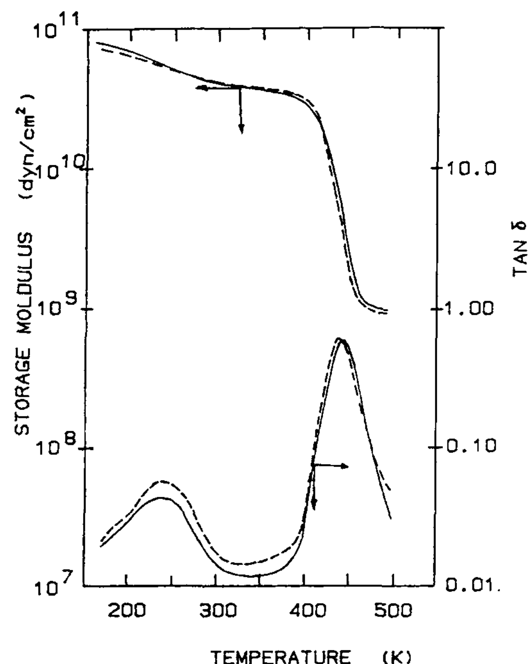

Figure 7 Storage modulus and mechanical loss versus temperature for sample 5: (——) the newly cured sample; (- - -) the stored sample.

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