

Organophosphorous Additive for Fortification, Processibility, and Flame Retardance of Epoxy Resins

ADAM S. ZERDA, ALAN J. LESSER

Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received 18 June 2001; accepted 23 July 2001

ABSTRACT: Amine-cured epoxy resins are prepared containing an aliphatic phosphonate additive which aids in the processing of the epoxy by reducing the viscosity of the resin mixture. The additive also acts as an antiplasticizer in the cured epoxy by increasing the modulus and yield strength under uniaxial tension and compression. Additionally, phosphonates are known to behave as flame retardants and dimethyl methyl phosphonate (DMMP) demonstrates a reduction in the rate of thermal degradation and the heat-release rate upon pyrolysis. Addition of the antiplasticizer reduces the T_g and suppressed β -relaxations, while effectively increasing the density of the material. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 302–309, 2002; DOI 10.1002/app.10329

Key words: epoxy resin; antiplasticizer; additives; flame retardance; viscosity

INTRODUCTION

Additives and modifiers are a powerful tool for tailoring the physical and mechanical properties of polymers. Utilizing additives can allow a polymeric material to cover a broad range of applications that might otherwise be inaccessible. Increasingly, additives with selected structures are introduced to impart specific changes into the polymeric matrix. However, such modifications rarely occur without causing adverse effects on other properties. Employing a single additive to achieve a number of property enhancements may minimize the detrimental effects that occur when using a plethora of efficient modifiers. In the present study, dimethyl methyl phosphonate (DMMP) is considered for its ability to enhance the final mechanical and thermal properties of a crosslinked epoxy resin when used principally as a diluent during thermoset formulation.

Diluents are commonly used to reduce the resin viscosity in highly filled composites and laminates. However, removal of the diluent following processing is often difficult, if not impossible. The trapped diluent then acts to decrease the properties of the polymer matrix by depressing the glass transition temperature and lowering the mechanical strength and stiffness. These effects are inconsequential only if a plasticized polymer is the desired final product, as is the case in many PVC applications. For epoxy resins, the thermal stability and mechanical integrity are the desired characteristics and plasticizers should only be used if they do not significantly interfere with the final properties.

Thermosets are commonly used as matrix materials for filled composites. In such applications, filler material is introduced to impart enhanced properties. It has been well established, however, that the compressive strength of such composites is governed by the mechanical properties of the matrix material. For fiber-reinforced composites, failure occurs through a microbuckling mechanism dictated by the shear modulus of the matrix.^{1,2} In particulate-filled composites, compres-

Correspondence to: A. J. Lesser.

Contract grant sponsor: Federal Aviation Administration.

Journal of Applied Polymer Science, Vol. 84, 302–309 (2002)
© 2002 John Wiley & Sons, Inc.

sive failure is shear-dominated, suggesting that the yield strength of the matrix is of critical importance.³ In both cases, the interfacial adhesion between matrix and filler is also important. To enhance the compressive or flexural performance of filled composites, either or both of these limitations must be addressed.

One class of additives known to enhance the mechanical properties of thermosets, as well as the processibility of the resin, is known as antiplasticizers.^{4,5} These additives act to lower the glass transition of a polymer while increasing the modulus and yield strength properties. As already well known in thermoplastic polymers such as polycarbonate⁶ and PVC,⁷ antiplasticization has also been demonstrated in cured epoxy resins with a variety of additives.^{8,9} In the current investigation, a new, aliphatic antiplasticizer is considered as to its effects on the mechanical and physical properties, including the modulus and yield strength, in an epoxy thermoset. An amine-cured epoxy material is fully characterized, with particular emphasis on its processibility and flame-retardation characteristics.

EXPERIMENTAL

The crosslinked network investigated herein is a reactive product of a high-purity diglycidyl ether of bisphenol A (EPON 825 from Shell, Houston, TX) cured with an aliphatic diamine curing agent (Huntsman D230, Salt Lake City, UT). The network was modified with dimethyl methyl phosphonate (DMMP) obtained from Aldrich Chemical and used as received. The additive, DMMP, was mixed with the epoxy prepolymer resin at various concentrations and combined with a stoichiometric amount of the curing agent. This mixture was degassed under a vacuum for a period of 15 min and poured into appropriate molds to form 3-mm-thick plaques and 8-mm-diameter tubes. All samples were cured for 3 h at 75°C, followed by an additional 3 h at 125°C for postcure. At these conditions, the epoxide is fully reacted, as verified using Fourier transform infrared spectroscopy (FTIR).

Rheological measurements of the viscosity of the epoxy prepolymer were performed on an RSI ARES rheometer using a Couette geometry. Viscosity measurements were made at room temperature and 50°C to simulate typical processing temperatures. The thermal properties of the cured resins were investigated using both differ-

ential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The scanning rate was 10°C/min for DSC and 5°C/min for DMTA at 1 Hz while imposing a 0.05% dynamic strain. Densities were measured using a buoyancy method at room temperature in degassed, deionized water (ASTM D792).

Mechanical measurements of the modulus and strength were conducted both in tension and compression and samples were prepared according to ASTM D638 and ASTM D695, respectively. Compact tension specimens for fracture toughness were cut to ASTM D5045 and precracked by tapping a fresh razor blade. All samples were tested on an Instron 1123 machine. Tension and compression samples were loaded at a constant crosshead speed of 2 mm/min. Compact tension specimens were loaded at 10 mm/min to minimize plasticization in front of the crack tip. Extensometers were used where appropriate for measurements of the strain.

Thermal degradation measurements were made employing thermogravimetric analysis (TGA) on a TA 2050 at a heating rate of 40°C/min from ambient temperatures to 800°C. Samples were run under a nitrogen purge, although no significant differences were apparent in the char yield and degradation rate when the samples were run in air. Measurements of the heat-release capacity and total heat released upon degradation were made on a Federal Aviation Administration (FAA) pyrolysis-combustion flow calorimeter (PCFC) which was developed to monitor the flammability of polymers on milligram quantities.¹⁰ A sample is flashed (5°C/s) to 1200°C, and the pyrolysis gases are oxidized under an O₂/N₂ atmosphere. The rate of O₂ consumption under these conditions can be monitored and related to the heat-release rate. This technique has been shown to correlate well with larger-scale flammability tests such as the OSU fire calorimeter and cone calorimetry.¹¹

DISCUSSION

Viscosity

One goal of the current study is to determine the effectiveness of DMMP on the processibility of an epoxy resin. The EPON 825 used is a low molecular weight difunctional epoxy of moderate viscosity. Most commercial epoxies, however, are of varying degrees of viscosity, affecting their ease of

processibility. The viscosity of the modified resins was measured at room temperature as well as at an elevated (50°C) temperature as these temperatures are commonly used in commercial curing applications. Elevated temperatures are often used to achieve a significant reduction in the viscosity to aid in the ease of processing. As seen in Figure 1, the viscosity of the epoxy is greatly reduced upon addition of a small amount of the DMMP additive and follows in an exponential decay with an increasing concentration of the additive. At room temperature, with 20 phr DMMP, the viscosity of the epoxy is on the order of the undiluted epoxy at 50°C. The higher concentrations see an even more significant reduction at elevated temperatures. It is well known that such a reduction in viscosity is important to the processing of filled composite materials. The viscosity measurements were fitted using an additive viscosity equation:

$$\ln \eta = f \ln \eta_a + (1 - f) \ln \eta_e \quad (1)$$

where f is the weight fraction of the additive in epoxy; η_a , the viscosity of the additive; and η_e , the viscosity of the epoxy prepolymer under the test conditions.

The absence of a chemical bond between the additive and the polymer was determined

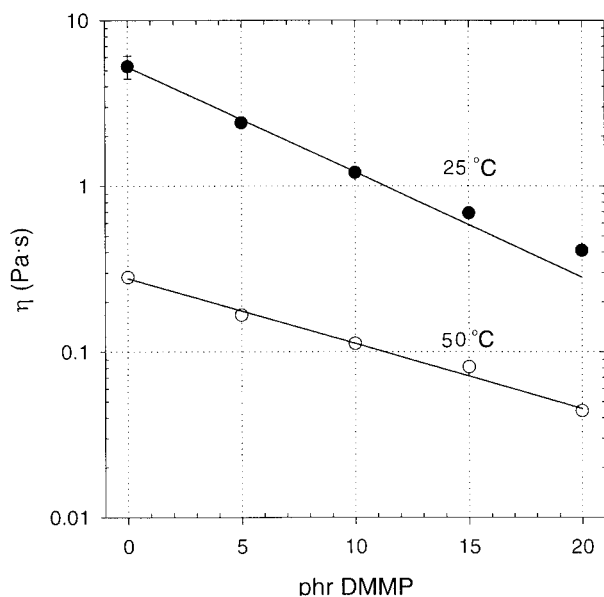


Figure 1 Viscosity of epoxy prepolymer is significantly decreased with the addition of the DMMP diluent. The points were fitted with an empirical additive viscosity equation.

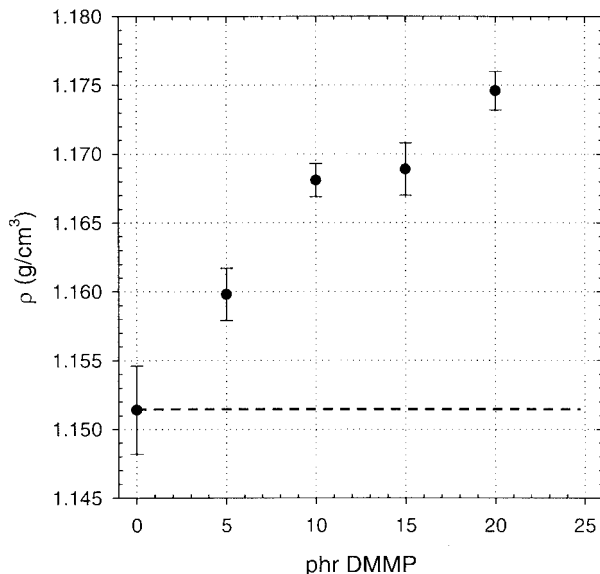


Figure 2 Apparent densification of the epoxy network with increasing DMMP concentration. Dashed line represents the rule of mixtures for the density.

through elemental analysis of phosphorus in the network following a high-vacuum, high-temperature (200°C) extraction. These conditions, which are above both the glass transition temperature of the polymer and the boiling point of the additive, result in a 50–100% reduction of the additive concentration within the polymer, depending on the extraction time. The absence of chemistry between the additive and the polymer network indicates that additional crosslinking is not occurring upon the addition of DMMP. Any physical and mechanical changes to the polymer, therefore, can be attributed to the physical interactions of the additive with the polymer backbone only.

Density

A common observation of antiplasticized polymers is the apparent negative volume of mixing between the polymer and the additive.^{12,13} This effect is manifested through densification, or a reduction of the free volume, of the polymer in a manner unrelated to the additive densities of the two constituents (Fig. 2).^{14,15} Since the additives are not reactive with the polymer matrix, the reduction in the free volume implies an interaction between the polymer and the additive which leads to a tight packing of the additive within the matrix.¹⁶

The reduction in the free volume is also accompanied by a suppression of the β -relaxation of the

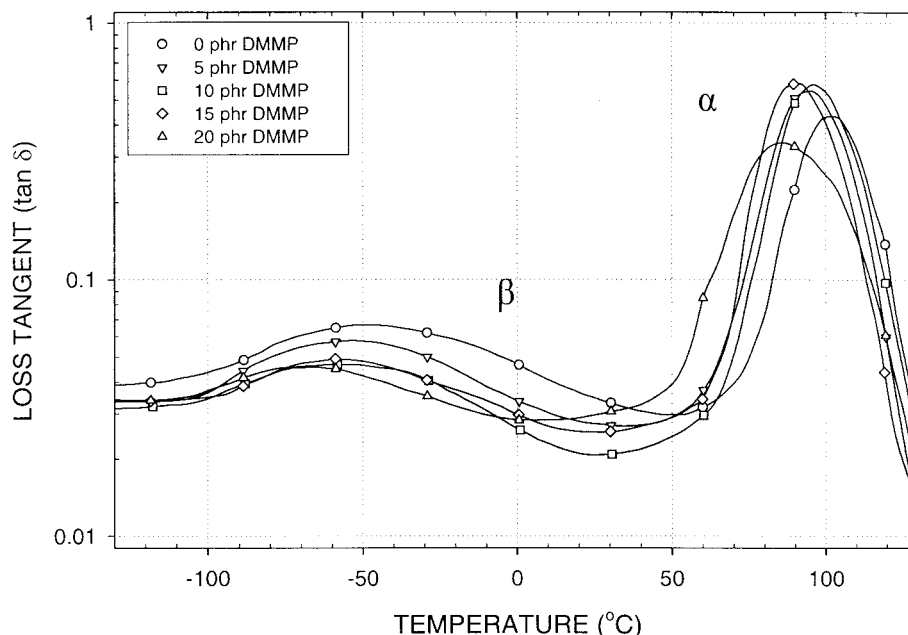


Figure 3 Loss tangent ($\tan \delta$) at 1 Hz versus temperature with DMMP concentration.

epoxy network. It has been shown that the β -relaxation consists of local motions at low temperatures and cooperative motions acting in the high-temperature portion of the relaxation.^{17,18} Antiplasticizers, including the DMMP investigated here, reduce or eliminate the high-temperature portion of this relaxation peak corresponding to cooperative mobility (Fig. 3). Dynamic mechanical investigations together with NMR studies of antiplasticized resins have demonstrated that the presence of an antiplasticizer decreases the mobility of hydroxypropyl ether groups.¹⁹ Phosphonates such as DMMP are hydrogen-bonding acceptors, and as the hydroxyl moieties are hydrogen-bond donors, it is likely that they provide the strong interaction previously reported necessary for antiplasticization.

The increase in the mechanical properties through antiplasticization is often accompanied by a decrease in the glass transition temperature of the matrix material. As seen in Table I, the

Table I T_g with DMMP

Measurement	DMMP (phr)				
	0	5	10	15	20
DSC (°C)	91	86	78	70	63
DMTA (°C)	101	96	97	90	82

glass transition of the epoxy is depressed upon addition of DMMP. Using DSC, only a single transition temperature is observed, indicating a homogeneous material. Dynamic testing of the DMMP antiplasticized networks, however, suggests an apparent phase separation at high concentrations of the additive via the evolution of a large shoulder in the α -relaxation of the 20 phr DMMP formulation (Fig. 3). It is important to note that the cured material did not at any point exhibit macroscopic evidence of phase separation. The observed phase separation, coupled with the decrease in the glass transition temperature, may explain the large decrease in the mechanical properties at DMMP concentrations greater than 10 phr.

Mechanical Properties

Mechanical properties of the antiplasticized amine-cured epoxy networks were characterized both under static uniaxial tension and compression (Figs. 4 and 5). Under optimal concentrations, those resulting in the greatest enhancement of material properties, both the tensile modulus and yield strength increase 12% over those of the unmodified epoxy. The compressive modulus improves 17%, while the compressive yield stress increases by 15% over the unmodified resin. Under both loading conditions, the greatest enhancements in the mechanical properties occur

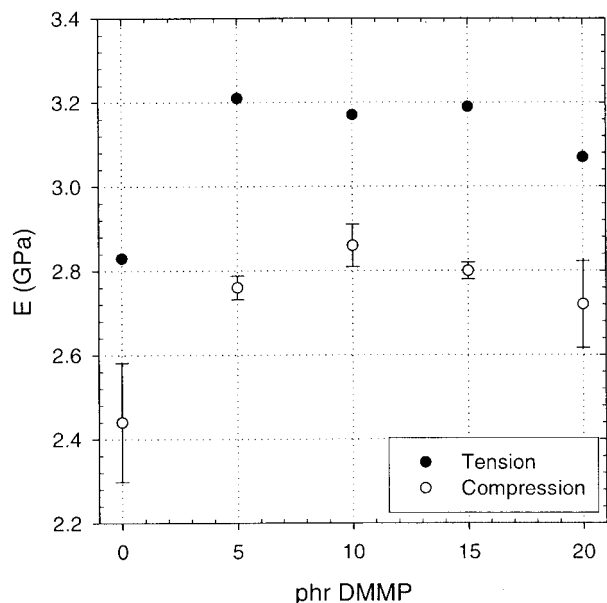


Figure 4 Static moduli with concentration of fortifier: (●) tensile modulus; (○) compressive modulus.

at a concentration of 10 phr DMMP within the resin. The yield strain is also affected by the presence of the antiplasticizer. At 10 phr DMMP, for example, the average strain at yield in tension and compression is reduced by 9.4 and 13.8%, respectively.

The effects of DMMP on the Young's modulus, E (Fig. 4), and yield strength, σ_y (Fig. 5), hint at the presence of a critical concentration of the additive above which the antiplasticizer ceases to fortify the network. Further addition of the antiplasticizer above 20 phr reduces the modulus and strength of the material until it can be said that the network is plasticized (its strength, stiffness, and T_g are all below that of the unmodified sample). This concentration threshold was previously reported for PVC and is a characteristic of small molecule antiplasticizers.²⁰

Previous discussions of antiplasticization in the literature have focused on the ability of the fortifier to reduce or eliminate cooperative motions (as evidenced in the β -relaxation) and therefore lead to an increase in the strength and stiffness characteristics. Previously in this discussion, it was demonstrated that DMMP exhibits this retardation effect. However, it is important to correlate the eventual reduction in mechanical properties with the dynamic mechanical measurements and reduction of the free volume, as well as the glass transition temperature. Both Figures 2 and 3 illustrate that the free volume

and the β -relaxation peak decrease with the fortifier concentration. The modulus and strength should therefore reflect this trend through a continuous increase in these properties. However, the glass transition temperature of the network is also systematically reduced with the fortifier concentration. It may be that the optimal additive concentration arises due to a balance between the detrimental decrease in T_g and an advantageous reduction in sub- T_g mobility.

The effect of DMMP on the fracture toughness was also investigated. An increase in the strength and stiffness of a material through the addition of an additive is often accompanied by a decrease in the fracture toughness. In other words, the material is effectively embrittled. It is, however, important to note that fortification of the network with DMMP was not accompanied by a transition from ductile to brittle failure under the applied test conditions. A yield point, defined through a zero-slope condition, is present in all materials tested in tension for all additive concentrations. Cohesive zone models that have been successfully used to describe the fracture behavior of thermosets show an increase in apparent toughness due to localized yielding at the crack tip.²¹ The size of the yielded zone at the tip, however, is inversely proportional to the modulus and yield stress:

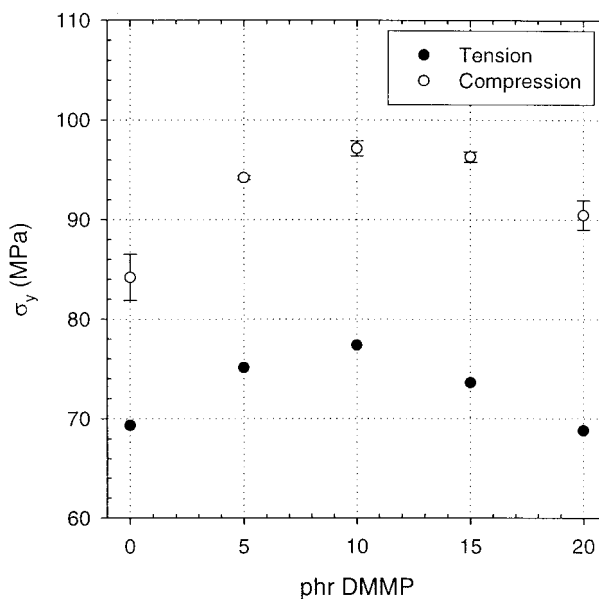


Figure 5 Yield strengths of epoxy with concentration of fortifier: (●) tensile yield strength; (○) compressive yield strength. Note that all samples failed in the negative slope regime after yielding.

$$\rho \propto \delta_t = \frac{K_{Ic}^2}{E\sigma_y} \quad (2)$$

where ρ is the crack tip radius. This radius can be approximated to be proportional to the crack opening displacement, δ_t . The crack blunting model predicts that with decreasing strength the material is allowed to yield in front of the crack tip, changing the radius of curvature and increasing the fracture toughness. This inverse relationship between strength and toughness is well known, especially in rubber-modified systems. As can be seen in Figure 6, the initial trend is as predicted by eq. (2). Both the stress intensity factor, K_{Ic} , and energy release rate, G_{Ic} , were reduced with increasing E and σ_y of the matrix. The energy release rate can be related to K_{Ic} through eq. (3):

$$G_{Ic} = \frac{K_{Ic}^2(1 - \nu^2)}{E} \quad (3)$$

where ν is the experimentally determined Poisson's ratio. The reduction in fracture toughness is, therefore, more pronounced in G_{Ic} , due to the corresponding increase in the modulus, E , upon addition of DMMP. The Poisson's ratio, ν , remains virtually unchanged with the DMMP concentration.

At higher fortifier concentrations, however, the fracture toughness remains depressed, even

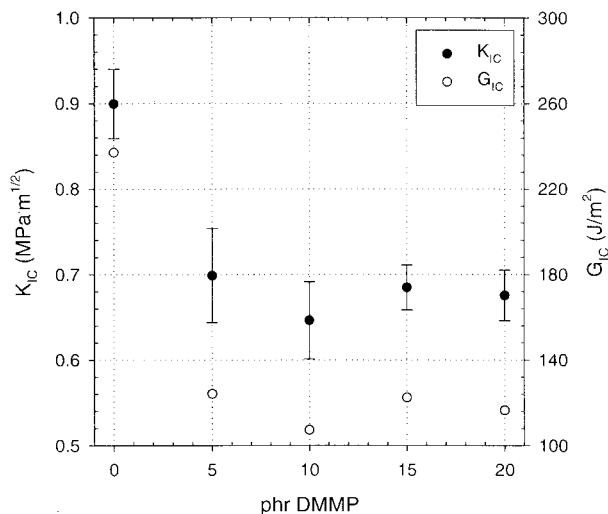


Figure 6 Changes in fracture toughness with increasing concentration of the additive. Reported are both the stress intensity factor (K_{Ic}) and energy release rate (G_{Ic}).

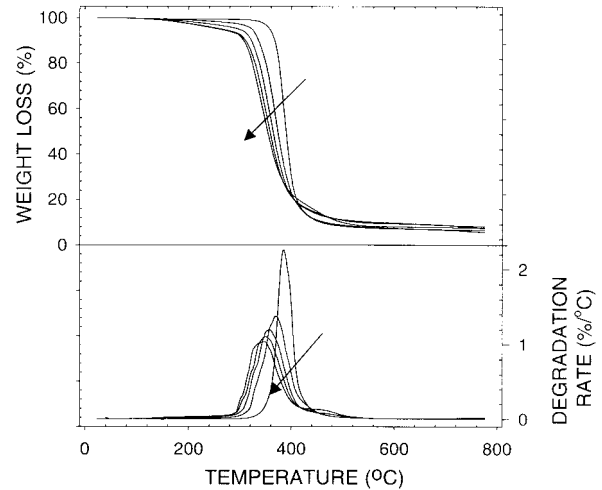


Figure 7 (Top) TGA decomposition curve and (bottom) rate of degradation plot versus temperature. Arrows indicate increasing concentration of the additive.

though the tensile yield strength has been reduced. This is contrary to the response predicted above. Upon closer inspection, it appears that only the initial introduction of the fortifier is necessary to reduce the fracture toughness. At 5 phr DMMP and above, the fracture toughness remains statistically equivalent, whereas the tensile properties change dramatically.

Flame Retardation

Organophosphorous materials, such as the DMMP currently being studied, are well known to act as flame retardants. Thus, it is interesting to investigate the potential of DMMP to also reduce the flammability of the epoxy network. Recently, organophosphorous additives and curing agents for epoxies were reported which reduce the flammability of epoxy resins.^{22,23} Presently, flame-retardant epoxy resins are based on brominated or chlorinated components which produce toxic gases and corrosive fumes upon degradation. Organophosphorous flame retardants, however, produce less toxic gas and smoke than do these halogenated products and are seen as possible replacements.

A good initial measure for the flame-retarding potential of an additive is the thermal degradation of the polymer as measured by TGA. These traces provide information on the thermal stability and degradability of the polymer with increasing temperature. In Figure 7, TGA curves of the epoxy network with increasing concentrations of

Table II Combustion Calorimetry of DMMP Flame Retarded Epoxy

DMMP (phr)	Rapid Weight Loss Temp. (°C)	Heat Release Capacity (J/g · K)	Total Heat Released (kJ/g)	Char Yield (%)
0	385	1063	27.2	3.1
5	370	469	25.4	4.6
10	357	371	23.8	4.5
15	350	365	23.7	6.0
20	347	382	23.7	5.2

the DMMP additive illustrate the changes in the flammability. Although the onset of degradation is decreased with the addition of the small molecular additive, the rate of degradation is likewise reduced. The degradation rate is a measure of how quickly the polymer pyrolyzes as the temperature is increased and is a good relative comparison of the flammability. By adding a small concentration of DMMP, this rate of degradation is significantly (up to 54%) diminished. The reduction in the onset of degradation is a result of the additive being unbound to the polymer backbone. DMMP has a boiling point of 181°C and evaporates as the temperature increases. Analysis of the volatiles produced below 300°C using a GC-mass spectrometer revealed that DMMP is the major component of the weight loss at this temperature. The reduction in the rate of degradation and the lack of considerable char formation indicates that DMMP acts as a gas-phase flame retardant, slowing the pyrolysis of the epoxy network.

The flammability of DMMP-containing epoxy was also investigated using a PCFC microcalorimeter. This method measures that amount of oxygen consumed during pyrolysis and provides a quantitative evaluation of the heat released upon incineration. The results of this evaluation are found in Table II. The total heat released is unchanged by the addition of the additive, indicating that the mechanism for degradation is unchanged through the addition of DMMP. The lack of additional char formation is also an indication of this. However, the heat-release capacity is reduced in a manner similar to the rate of degradation seen in the TGA, from a peak of 1063 to 365 J g⁻¹·K⁻¹ at 15 phr DMMP (65%).

It should be noted, however, that the formulation being investigated here is not ideal for flame-

retardant applications since the curing agent used is an aliphatic diamine with little inherent thermal stability. A stiffer curing agent with a higher aromatic content, such as 4,4'-diaminodiphenylmethane (DDM), would be better suited for exhibiting improved flammability characteristics.²⁴ Such formulations would yield significantly higher char upon degradation, further reducing the total heat released.

CONCLUSIONS

A new additive was investigated for implementation in amine-cured epoxies. The additive, a small, flexible phosphonate, provides a large decrease in the viscosity of the prepolymer during initial processing. The viscosity was found to decrease by an order of magnitude at 20 wt % additive concentrations both at room temperature and elevated temperatures.

In addition to the viscosity reduction, the additive was found to act as a molecular fortifier at low concentrations within the amine-cured epoxy network. Enhancements in the compressive and tensile modulus (17 and 12% respectively) and yield strength (15 and 12%) were found, with an additive concentration of 10 phr providing the greatest increases. These observations can be explained in terms of the antiplasticization behavior, including a decrease in free volume and suppression of sub-*T_g* cooperative motions within the polymer. However, this behavior was observed with a flexible additive, discounting the need for a highly rigid additive for antiplasticization.²⁵ Rather, it is the additive-polymer interactions which dictate the degree of fortification.²⁶

The flame retardancy of the additive within an epoxy network was also investigated. The additive demonstrated a reduction in the degradation rate and heat-release capacity of the polymer, although char formation and total heat released were not affected. These observations lead to the conclusion that DMMP is an effective molecular fortifier for amine-cured epoxy resins with the potential also as an additive for reducing the flammability of epoxy.

The authors would like to acknowledge the helpful suggestions of Dr. Richard Lyon and the financial support of the Federal Aviation Administration. The authors would also like to thank Huiqing Zhang for her help with the PCFC microcalorimeter data.

REFERENCES

1. Dudiansky, B.; Fleck, N. A. *J Mech Phys Solids* 1993, 41, 183.
2. Hahn, H. T.; Williams, J. G. In *Composite Materials: Testing and Design*; Whitney, J. M., Ed.; ASTM Spec Tech Publ 893; ASTM: Philadelphia, 1986; p 115.
3. Ahmed, S.; Jones, F. R. *J Mater Sci* 1990, 25, 4933.
4. Jackson, W. J.; Caldwell, J. R. *J Appl Polym Sci* 1967, 11, 227.
5. Jackson, W. J.; Caldwell, J. R. *J Appl Polym Sci* 1967, 11, 221.
6. Makaruk, L.; Polanska, H.; Mizerski, T. *J Appl Polym Sci* 1979, 23, 1935.
7. Mascia, L. *Polymer* 1978, 19, 325.
8. Daly, J.; Britten, A.; Garton, A. *J Appl Polym Sci* 1984, 29, 1403.
9. Khozin, V. G.; Farrakhov, A. G.; Voskresenskii, V. A. *Polym Sci USSR* 1979, 21, 1757.
10. Lyon, R. E.; Walters, R. N. U.S. Patent 5 981 290, 1999.
11. Westmoreland, P. R.; Inguilizian, T.; Rotem, K. *Therm Acta* 2001, 367, 401.
12. Maeda, Y.; Paul, D. R. *J Polym Sci Part B Polym Phys* 1987, 25, 981.
13. Maeda, Y.; Paul, D. R. *J Polym Sci Part B Polym Phys* 1987, 25, 957.
14. Ruiz-Trevino, F. A.; Paul, D. R. *J Polym Sci Part B Polym Phys* 1998, 36, 1037.
15. Ruiz-Trevino, F. A.; Paul, D. R. *J Polym Sci Part B Polym Phys* 1998, 36, 1037.
16. Merritt, M. E.; Goetz, J. M.; Whitney, D.; Chang, C. P. P.; Heux, L.; Halary, J. L.; Schaefer, J. *Macromolecules* 1996, 29, 605.
17. Shi, J. F.; Inglefield, P. T.; Jones, A. A.; Meadows, M. D. *Macromolecules* 1996, 29, 605.
18. Heux, L.; Halary, J. L.; Laupretre, F.; Monnerie, L. *Polymer* 1997, 38, 1767.
19. Heux, L.; Laupretre, F.; Halary, J. L.; Monnerie, L. *Polymer* 1998, 39, 1269.
20. Sears, J. K.; Darby, J. R. *The Technology of Plasticizers*; Wiley: New York, 1982.
21. Kinloch, A. J.; Williams, J. G. *J Mater Sci* 1980, 15, 987.
22. Wang, C. S.; Lin, C. H. *J Appl Polym Sci* 2000, 75, 429.
23. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S. *J Polym Sci Part A Polym Chem* 1997, 35, 565.
24. Derouet, D.; Morvan, F.; Brosse, J. C. *J Appl Polym Sci* 1996, 62, 1855.
25. Suvorova, A. I.; Hannanova, E. G. *Makromol Chem* 1990, 191, 993.
26. Gupa, M. K.; Ripmeester, B.; Carlsson, D. J.; Wiles, D. M. *J Polym Sci Polym Lett Ed* 1983, 21, 211.