

Comparing Reinforcement Strategies for Epoxy Networks Using Reactive and Non-Reactive Fortifiers

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ABSTRACT: Improvements in physical, mechanical, and thermal properties of an epoxy network are made with the use of a unique class of molecules that reinforce the network at the molecular scale. These molecules are commonly referred to as antiplasticizers or fortifiers. In this contribution, two types of fortifiers are incorporated into the model epoxy network. One, dimethyl methylphosphonate, is a simple additive while the other, diethyl phosphoramidate, contains a reactive amine and is cured as part of the network. The two approaches provide some unique differences

in the physical and mechanical properties of the networks. Several mechanisms of fortification are discussed and correlated to the observed properties. In addition, it is shown that the fortifiers improve the rheological characteristics of the epoxy resin and act as fire-retardants in the cured network. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4606–4615, 2006

Key words: thermosets; structure-property relations; additives; mechanical properties

INTRODUCTION

Properties in polymeric materials can be tailored relatively easily through the use of additives and modifiers. It is often desirable to be able to adjust the physical and mechanical properties of a polymer by simple additions of small molecules instead of synthesizing an entirely new polymer. A unique class of additives, known as antiplasticizers or fortifiers, has been shown to improve mechanical properties in glassy networks. These small-molecule compounds were first identified by Jackson and Caldwell in the late 1960s and used to enhance the properties of polycarbonates.¹ They were labeled antiplasticizers because they increase the modulus and yield stress of the polymer and decrease the elongation at break. This is opposite of what is expected with more traditional plasticizers that decrease modulus and strength and increase the elongation at break. Similarly though, both antiplasticizers and plasticizers are known to decrease the glass transition temperature, T_g , of the polymer.

Antiplasticizers similar to the ones first identified have been utilized in several other polymers such as polyesters,² cellulose acetates,² polyphenylene-ethers,^{3,4} polysulfones,⁵ and epoxies.^{6–12} Each of these polymers modified with an antiplasticizer show similar improvements in modulus and yield stress. Also, all of the mole-

cules used as antiplasticizers are low molecular weight compounds. Some work has been done with larger, oligomeric compounds, but the lower molecular weight compounds provide the greatest improvements in properties.^{3,10} It is believed that antiplasticizer compounds interact with the polymer through specific bonding interactions. Since these interactions occur at the molecular length scale, the compounds are said to provide molecular scale reinforcement. Thus, antiplasticizers have more recently been referred to as molecular fortifiers.

All of the molecular fortifiers that have been identified possess similar chemical architectures that are essential to provide the observed benefits in properties. One of these characteristics is the need for polar functional groups such as C=O, P=O, or S=O. The polar component is thought to contribute to the specific physical bonding interactions with the polymer chain. It was first believed that the fortifier molecule required two polar groups to act as a physically bonded crosslinker between adjacent polymer chains. It was later shown that similar improvements in properties could be obtained with molecules possessing only a single polar P=O group.³ Another characteristic initially thought to be required of a molecular fortifier was that there had to be some aromaticity associated with the molecule. It was believed the aromatic groups provided some inherent stiffness to the molecule aiding in the overall reinforcement of the polymer. However, later work showed nonaromatic fortifiers actually provide greater benefits in properties.⁸

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Earlier work conducted in this research group on molecular fortifiers investigated the effects of molecular architecture utilizing several phosphorus-based compounds in amine and anhydride cured epoxies.^{7,8} Phosphates containing various length aliphatic chains or aromatic rings were incorporated into an epoxy network as simple additives. The mechanisms of reinforcement were suggested to arise from a filling of free volume as well as hydrogen bonding between the phosphate and hydroxyl groups present along the epoxy network. The density of the networks increased upon the addition of fortifiers and it was concluded that the fortifiers filled free volume, effectively stiffening the network. This agreed with conclusions drawn by other groups studying fortifiers in epoxy networks.^{9,13}

It was also discovered that a methyl-substituted phosphate, trimethyl phosphate (TMP), provided the greatest improvement in modulus and strength with the least detrimental effect on the glass transition temperature (T_g). This agrees with other work showing low molecular weight fortifiers provide the greatest improvement in mechanical properties. This result also showed fortifiers need not be aromatic compounds.

The contribution of this research compares a covalently bound molecular fortifier to one that is simply added to the network. In all of the work discussed previously, the fortifiers were introduced as simple additives. By covalently bonding the fortifier to the network, the mechanism of reinforcement is anticipated to be different. The two types of fortifiers selected for this study are dimethyl methylphosphonate (DMMP), which is a simple additive, and diethyl phosphoramidate (PA), which contains a reactive amine group and will be shown to covalently bind to the network. Both compounds possess a polar P=O group and short alkoxy side chains. DMMP was selected over TMP, which was used in earlier fortifier studies and improved the mechanical properties of epoxy networks, because of its greater similarity in molecular structure to PA. Herein, it is shown that both the DMMP and PA act as effective molecular fortifiers by strengthening and stiffening the network. In addition it is shown that they also decrease the viscosity of the epoxy resin prior to cure and increase the T_g of the cured glass.

EXPERIMENTAL METHODS





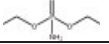
A crosslinked epoxy network composed of a diglycidyl ether of bisphenol-A (Epon 825), supplied by Resource Resins Inc. (Houston, TX), is cured with two aliphatic amines and chosen as the model network. The epoxy resin is degassed overnight at 80°C prior to use and kept at 50°C thereafter. Dimethyl ethylenedia-

mine (DMEDA) acts as the chain extender and ethylene diamine (EDA) is the crosslinking agent. The amines are purchased from Aldrich (St. Louis, MO) and used without further purification. Structures of all reagents are shown in Table I. The ratio of these two amines is adjusted to achieve a range of molecular weights between crosslinks, (M_c), within the network including 380, 818, and 1452 g/mol. A network with a M_c of 818 g/mol is selected as a control for molecular fortifier additions and will be referred to as the base, unmodified network. Dimethyl methyl phosphonate (DMMP) and diethyl phosphoramidate (PA) are purchased from Aldrich and used as received. Their structures are shown in Table I. The DMMP is incorporated as an additive and is mixed into the epoxy along with the amines. Diethyl phosphoramidate contains a reactive amine and acts as a chain extender in the epoxy network, therefore, the ratio of PA to DMEDA is calculated to maintain a constant crosslink density or M_c of 818 g/mol. PA is a solid and is melted at 80°C before blending into the epoxy resin along with the two other amine curatives. The relative amount of fortifier within the network is reported as a mole percentage of the total monomers used. This percentage includes the fortifier, amine curatives, and epoxy resin.

The blended mixture of all the reagents is placed at 50°C for 2 min for degassing before casting into plaques or cylinders. Glass plates pretreated with a silicon mold release, Surfasil (Pierce Chemical, Woburn, MA), are separated with a Teflon spacer and clamped together to form a mold and cast 3-mm thick plaques. Cylinders are cast in 8 mm diameter test tubes and are also pretreated with the mold release. The base and fortified networks with a M_c of 818 g/mol are cured at 50°C for 3 h while gelation occurred, followed by a postcure at 110°C for 6 h to ensure complete conversion. Networks of other crosslink densities are cured at 50°C for 3 h followed by a post cure at 20°C above their respective T_g 's for 6 h.

Tensile tests are conducted on a Model 4411 Instron using ASTM D638 Type IV tensile bars. Tests are performed at 22°C and an axial strain rate of 0.1 min⁻¹. An extensometer is used during each test to measure strain and calculate elastic modulus. The region in the

TABLE I
Structures and Molecular Weights of Starting Reagents

Monomer	Molecular weight (g/mol)
Epon 825 	352
<i>N,N'</i> dimethylethylenediamine 	88.15
ethylenediamine 	60.1
dimethyl methylphosphonate 	124.08
diethyl phosphoramidate 	153.12

nominal stress versus strain curve where the slope reaches zero is defined as the yield stress.

Room temperature compression testing is performed on an Instron 5800 at a true strain rate of 0.1 min^{-1} . These tests are taken beyond the yield stress of the material and to ultimate failure. The crosshead speed had to be slowed during the test to maintain a true strain rate of 0.1 min^{-1} . Samples are cut from the cured 8-mm cylinders with a 1:1 height to diameter ratio. The ends of each sample are covered with an adhesive coated Teflon tape. In addition, a drop of soapy water (SoftSoap brand hand soap in water) is also placed between the compression platens and teflon tape during testing to create a near frictionless surface. These special considerations allowed for gross yielding throughout the height of the sample and essentially eliminate any buckling or barreling response. This sample geometry and preparation have been successfully used by other groups to study the postyield deformation of thermoplastics.^{14,15} The strain hardening modulus is calculated from the slope of the final 25% strain before failure in a plot of true stress versus a function of the extension ratio.

The glass transition temperature is measured on a TA Instruments DSC 2910 using a ramp rate of $10^\circ\text{C}/\text{min}$ for all measurements. Thermal decomposition data is collected on a TA Instruments TGA 2050 in an air atmosphere at a ramp rate of $10^\circ\text{C}/\text{min}$. Pyrolysis combustion flow calorimetry (PCFC) is performed following the methods developed by Lyon and Walters.¹⁶ The sample is pyrolyzed in a nitrogen atmosphere and then combusted in an oxygenated atmosphere. The amount of heat released and oxygen consumed are measured and burn characteristics are assessed. The physical density of the cured net-

works is measured using the water buoyancy method described in ASTM D792. Square samples measuring $25 \text{ mm} \times 25 \text{ mm}$ and 3 mm in thickness are used for the measurement. Rheological data are collected on an AR-2000 rheometer using a 2° aluminum cone and plate geometry. A constant shear rate scan is made at 25°C from 0.001 inverse seconds to 1000 inverse seconds.

RESULTS AND DISCUSSION

Incorporation of fortifiers

The liquid DMMP molecular fortifier is relatively easily mixed into the epoxy resin along with the amine curatives. The PA fortifier however, is a solid with a melting point of 53°C and had to be melted at 80°C prior to mixing with the epoxy resin. Once the compound was liquified it was easily solvated by the resin. To check whether the amines on the PA are reacting with the epoxy resin during cure, Raman spectroscopy is used. Figure 1 shows a select region of the Raman spectra and the peak at 1260 cm^{-1} corresponds to breathing of the epoxide ring.¹⁷ The DMEDA and EDA amine curatives are known to react with the epoxy resin and form a network. When these compounds are mixed with the resin alone, the peak at 1260 cm^{-1} decreases in intensity suggesting the epoxide is being ring opened leading to network formation. The top trace in Figure 1 shows the epoxy resin cured with PA and a similar disappearance of the epoxide peak has occurred. This suggests that the PA is indeed reacting with the epoxy resin and covalently bonding as part of the network.

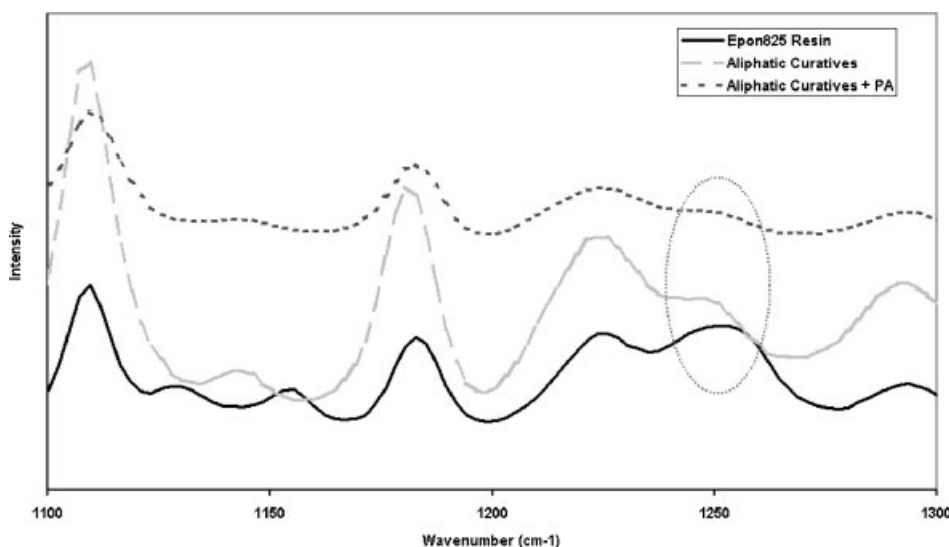


Figure 1 Raman spectroscopy shows the weakening of the epoxide peak at 1260 cm^{-1} with the addition of amine curatives and PA.

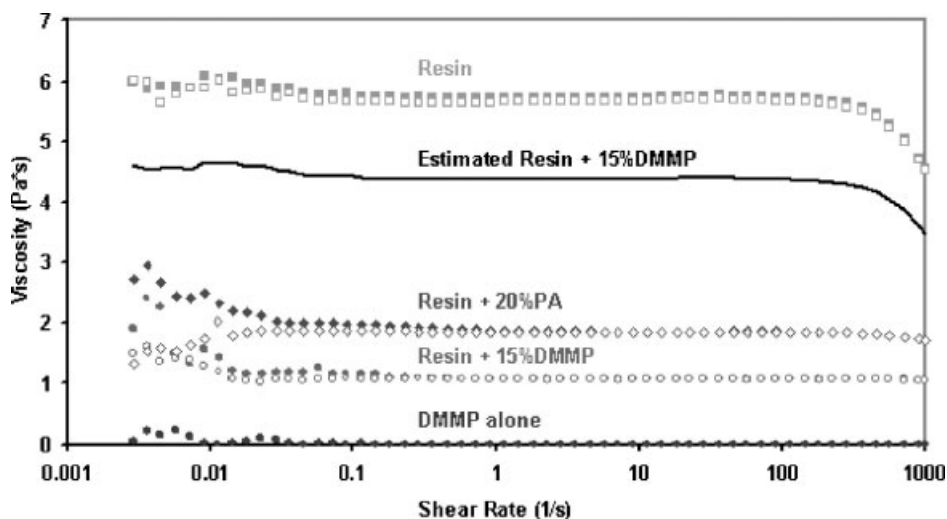


Figure 2 Both the DMMP and PA fortifiers lower the viscosity of the epoxy resin more than what is estimated. Solid symbols denote the first scan while hollow symbols denote a second scan on the same sample.

Rheological properties

Molecular fortifiers were originally labeled antiplasticizers because of their ability to increase the modulus and yield stress of polymers. This is opposite of what would be expected with a traditional plasticizer. However, it is found the DMMP and PA fortifiers decrease the viscosity of the epoxy resin too and possess this characteristic of a plasticizer. Figure 2 shows the viscosity of the epoxy resin with the two fortifiers prior to cure. The epoxy resin alone has a relatively high viscosity of 6 Pa*s while the neat DMMP has minimal viscosity. A model proposed by Hind,¹⁸ and shown in eq. (1), was used to estimate the viscosity of a mixture of 15 mol % DMMP in epoxy resin and is indicated by the solid line in Figure 2.

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + x_1x_2\eta' \quad (1)$$

where η is the estimated viscosity of the mixture, x_i and η_i are the mole fractions and viscosities of each independent component and η' is a viscosity cross coefficient approximately equal to the sum of the viscosities of each component. The actual measured viscosity of the epoxy resin and 15 mol % DMMP mixture is depicted by the circles and is significantly less than what is estimated. This shows a synergistic response in viscosity in that it cannot be predicted (and is much lower), suggesting interesting interactions between fortifier and epoxy occur in the liquid state. A similar drop in viscosity is measured when PA molecular fortifier is added to the epoxy resin. To our knowledge, there has been no previously published rheological data with molecular fortifiers showing they decrease the viscosity of binary liquid greater than what is predicted by

theory. The mechanisms associated for this reduction are not the immediate goal of this research but are presented for their significant industrial importance.

Physical properties

A rule of mixtures would predict that a low density compound (such as DMMP or PA) added to a polymer possessing a higher physical density would produce a compound with an intermediate density depending on the concentrations of the two components. However, the opposite is found when density measurements are made on the fortified networks presented here. Note that the physical density of the glass actually increases with fortifier concentration as shown in Figure 3. This agrees with earlier stud-

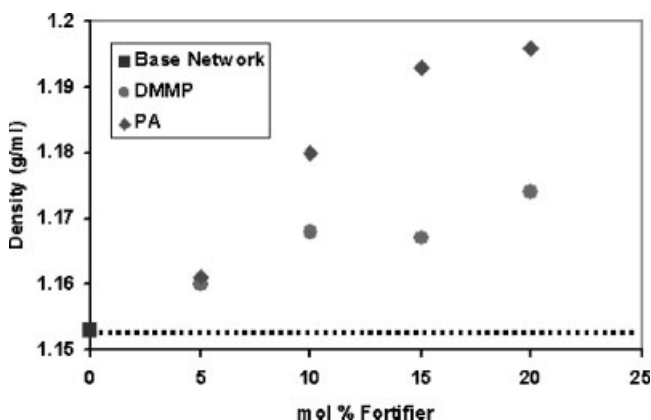


Figure 3 Density increases with fortifier addition in contrast to what a rule of mixtures (dotted line) would predict.

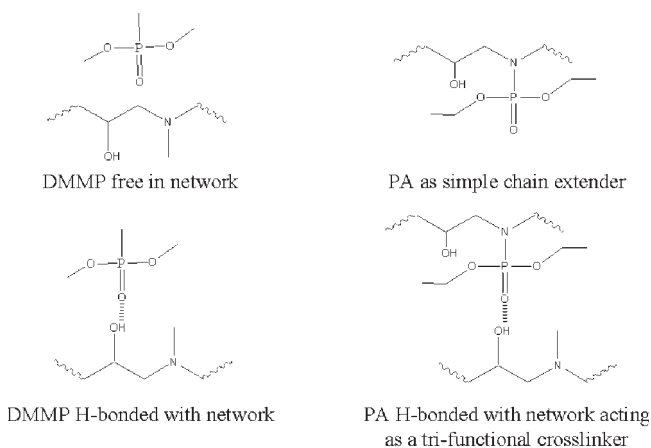


Figure 4 Several possible interactions can occur between the epoxy network and molecular fortifiers. The PA fortifier could act as a trifunctional crosslinker when it forms a hydrogen bond with adjacent network chains.

ies and suggests that free volume is being filled within the network.^{7-9,13} Also note the measured density of the network containing PA is greater than that of one containing DMMP at a given concentration. It is believed that the phosphate group of the fortifiers hydrogen bonds with the hydroxyl groups created upon ring opening of the epoxide. The DMMP fortifier could be physically bound and sit adjacent to the polymer chain as shown in Figure 4. If the PA fortifier hydrogen bonds with the hydroxyl group, it could effectively create an additional point of crosslinking in the network as depicted also in Figure 4. From previous work it is known the physical density of a network increases with increasing crosslink density¹⁹ as shown in Figure 5. If one takes the measured density (1.19 g/mL) of the 20 mol %

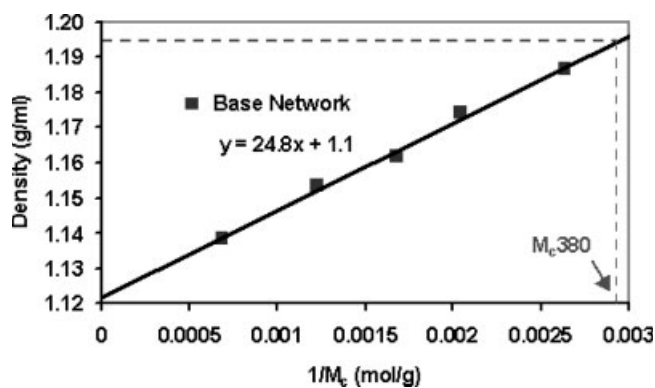


Figure 5 As the crosslink density of the unmodified, base network increases the physical density of the network increases. The effective crosslink density of the PA fortified network can be extrapolated from its measured density to a value of 380 g/mol.

PA network from Figure 3 and extrapolates this density onto Figure 5, it is possible to estimate the effective crosslink density of the PA fortified network assuming it is acting as a hydrogen bonded crosslinker. If one follows this, the effective molecular weight between crosslinks of the 20 mol % PA fortified network is 380 g/mol. This is a significantly higher crosslink density than the 818 g/mol calculated from the stoichiometric ratio of the amine curatives. This suggests that the additional increase in density of the PA fortified networks might be attributed to hydrogen bonding of the fortifier and epoxy network effectively increasing the crosslink density.

The glass transition temperature of the fortified networks is shown in Figure 6. As the fortifier concentration increases, the T_g of both the DMMP and PA fortified networks increases. The density measurements suggest the fortifiers are filling free volume, which would limit chain mobility. This decrease in mobility should increase T_g and this is indeed observed. Unexpectedly, the increase in T_g with the PA fortified network is less than with the DMMP networks. It is believed the PA forms additional crosslinks within the network as supported by physical and mechanical measurements to be presented. As the crosslink density of an epoxy network increases, the T_g increases also. Density measurements suggest the PA fortified network has an effective M_c of 380 g/mol, so it would be expected its T_g would be comparable to an unmodified network with a M_c of 380 g/mol. However, this is not measured. This is attributed to the additional crosslinks being formed by hydrogen bonds and at higher temperatures, they are most likely not present. So the difference in T_g between the DMMP and PA fortified networks arises from the two methods of incorporation. Having the PA covalently bound to the network, and being a pendant group at

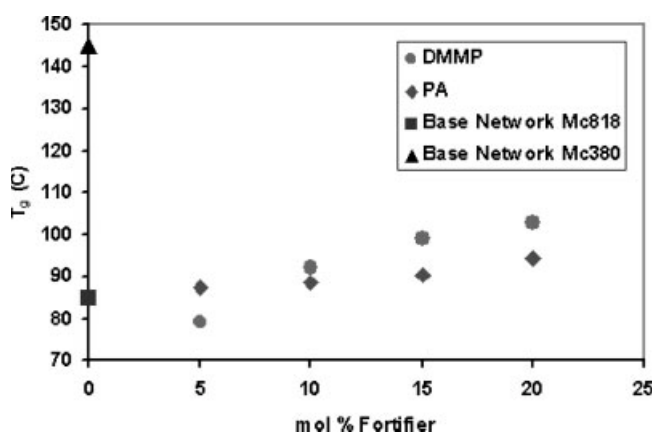


Figure 6 The glass transition temperature increases with fortifier concentration as would be expected when free volume is filled in a polymer.

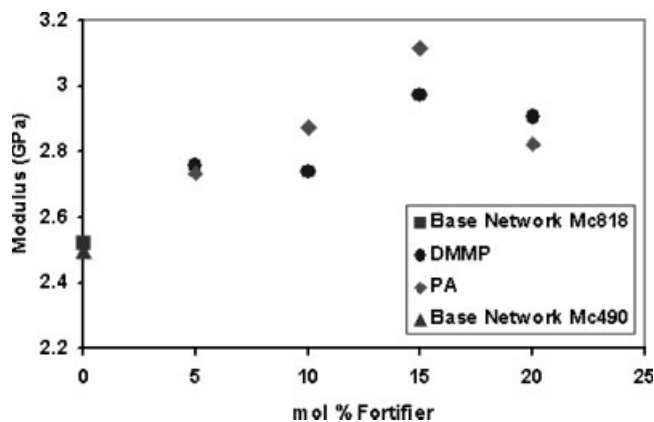


Figure 7 The fortifiers stiffen the network increasing the elastic modulus. Note changing the crosslink density of the unmodified base network does not increase the modulus.

higher temperatures, is not as effective at improving the T_g as incorporating the DMMP as a free additive.

A final note on the T_g is that prior studies with molecular fortifiers often showed a decrease in T_g with increasing fortifier concentration.^{1-3,7,8} The improvements in T_g with the DMMP and PA fortifiers could be attributed to the specific crosslink density and amine curatives chosen for this network. It is possible the T_g could be affected differently in a separate epoxy network. These are considerations that must be made for a scientist trying to optimize any fortifier/polymer system.

Mechanical properties

The tensile modulus of the fortified networks is shown in Figure 7. A greater than 20% improvement in modulus is observed with the addition of fortifiers when compared to an unmodified, base network of identical crosslink density. When the crosslink density of the unmodified, base network is increased from 818 g/mol to 490 g/mol, the modulus does not change. Earlier work has shown the elastic modulus is not affected by the crosslink density of the network and is more dependent upon the stiffness of the backbone between crosslinks.^{20,21} The fortifiers clearly stiffen the network in a unique manner.

The yield stress of the networks improves with increasing fortifier concentration as shown in Figure 8 (In Fig. 8, tensile strength is plotted because some samples failed in a brittle manner and a true yield stress is not measured). There are well-established relationships between yielding and the T_g of epoxy networks^{19,22} and both the DMMP and PA fortifiers increase T_g . So it should be expected that they also improve the yield stress of the network. Increasing the crosslink density or decreasing M_c can increase

the T_g of the unmodified, base network. The yield stress of a network with a M_c of 490 g/mol is also plotted on Figure 8. The strength of the fortified networks is comparable to this unmodified network with a greater crosslink density.

Differences in the mechanism of reinforcement by the two fortifiers are also apparent when looking at their tensile behavior. All of the DMMP fortified networks show a strong yield point and fail in a ductile manner. While at concentrations greater than 10 mol % PA, a ductile yielding response is no longer observed and the network fails in a brittle fashion. This change in failure mode is not observed with the DMMP fortified networks and is attributed to the additional hydrogen bonded crosslinks formed by PA. It is well known that as the crosslink density of a network increases, the ductility decreases.^{21,22} This observation of the mechanical behavior supports conclusions drawn from the physical properties made above.

When looking at the improvements in mechanical and physical properties, one would imagine there is some optimum concentration of fortifier to give the best overall properties. The modulus appears to reach a maximum at a fortifier concentration of 15 mol % for both DMMP and PA. The yield stress of the DMMP fortified networks improves steadily up to 20 mol %, the highest loading level investigated here, whereas the PA fortifier embrittles the network at concentrations greater than 10 mol %. The T_g of both the fortified networks also steadily increases up to 20 mol %. The intent of this paper is not to optimize the properties, but to present a range of improvements these fortifiers can impart in an epoxy network. That said, it appears that fortifier concentrations near 15 mol % give a good balance of

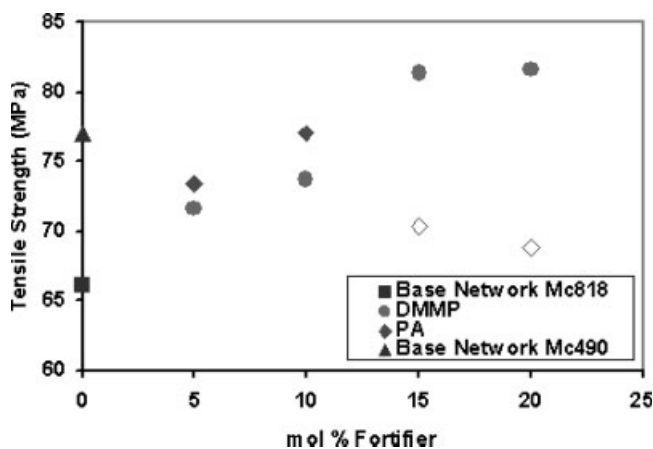


Figure 8 The yield stress increases with fortifier concentration comparable to increasing the crosslink density of the base network. The hollow symbols denote brittle fracture in the PA fortified networks at higher concentrations.

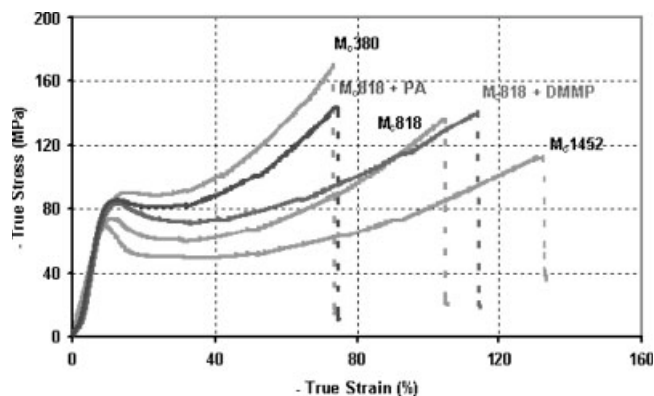


Figure 9 Plots of true stress and true strain for compression tests at 22°C and 0.1 min⁻¹. The compressive yield stress of the DMMP and PA fortified networks increase comparable to an unmodified network with a greater crosslink density.

improvements in stiffness, strength, and physical properties. This concentration most likely will change depending upon the exact desired characteristics and the chemistry of the specific network.

To more closely study the effects of additional hydrogen bonded crosslinks in the PA fortified network, compression tests are performed. By testing the networks in compression, brittle fracture is suppressed and the samples can be deformed to large strains allowing one to measure the mechanical behavior well past the yield point of the material. When measuring large strains, it is no longer accurate to work in terms of engineering stress and strain and one must now report true stress and strain values. As a reminder, the definitions of true stress, true

strain, and the extension ratio are summarized in eqs. (2)–(4).

$$\sigma_T = \frac{F}{A_i} \quad (2)$$

$$\varepsilon_T = \ln \frac{l_i}{l_0} \quad (3)$$

$$\lambda = \frac{l_i}{l_0} \quad (4)$$

where σ_T is the true stress, F is the applied force, A_i is the instantaneous cross-sectional area, ε_T is the true strain, l_i is the instantaneous length, l_0 is the initial length, and λ is the extension ratio.

Compression bullets are cut from cylinders as described in the *Experimental section* and the samples are tested until ultimate failure. Figure 9 shows the true stress versus true strain behavior for the DMMP and PA fortified networks as well as three unmodified, base networks with various crosslink densities. The fortified networks have a M_c of 818 g/mol as calculated from stoichiometry. The compressive yield stress of an unmodified, base network with a M_c of 818 g/mol is 77 MPa. The compressive yield stress of the fortified networks with an identical M_c from stoichiometry is 86 MPa. These improvements are comparable to the yield stress of an unmodified, base network with a M_c of 380 g/mol. Similar improvements in yield stress are measured when testing the networks in tension.

Careful evaluation of the post yield, plastic deformation of the fortified networks can give more insight into the different interactions occurring within the DMMP and PA networks. It has been published by other research groups studying ther-

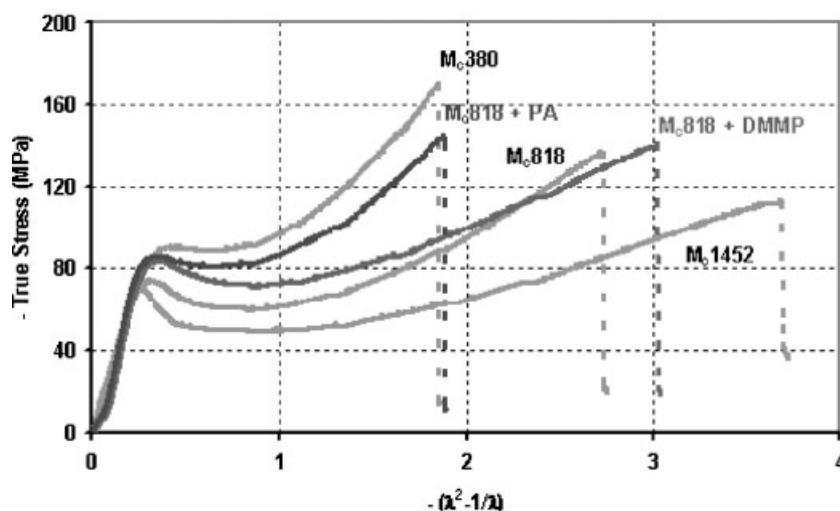


Figure 10 Compression tests at 22°C and 0.1 min⁻¹. The postyield response of the PA fortified network is similar to an unmodified, base network with a M_c of 380 g/mol. The slope of the strain hardening region of the PA fortified network is also noticeably greater than that of the DMMP fortified network suggesting additional crosslinking.

TABLE II
Summary of Room Temperature
Compression Tests (0.1 min^{-1})

Sample	σ true yield (MPa)	σ true failure (MPa)	G (MPa)	ϵ true failure
M_c 818 15 mol % DMMP	86	142	42	113
M_c 818 20 mol % PA	86	142	77	76
M_c 380	90	165	98	72
M_c 818	77	131	57	100
M_c 1452	73	106	31	125

moplastics that the slope of the strain hardening region is analogous to the shear modulus of a rubbery material.²³ From the theory of rubber elasticity, a relationship can be derived to relate the strain hardening modulus, G , to the true stress and extension ratio.^{24,25} This is shown in eq. (5).

$$\sigma_T = G \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (5)$$

If the strain hardening modulus is thought of as being analogous to the shear modulus of a material in its rubbery state, G can also be related to the molecular weight between crosslinks, M_c ,^{24,25} as shown by eq. (6).

$$G = \frac{\rho RT}{M_c} \quad (6)$$

where ρ is the physical density of the polymer, R is the gas constant, and T is the test temperature. Stud-

ies with physically entangled and crosslinked thermoplastics have shown the slope of the strain hardening region increases with increasing entanglement or crosslink density.^{26,27} It is reasonable then to correlate the strain hardening response of a thermoset, in this case an epoxy network, to its molecular weight between crosslinks.

Figure 10 is a plot of true stress versus $\lambda^2 - 1/\lambda$ at room temperature for the DMMP and PA fortified networks as well as unmodified, base networks with three crosslink densities. Qualitatively, the slope of the strain hardening region of the DMMP fortified network is less than that of the PA fortified network and more similar to that of the base network with a M_c of 818 g/mol. Table II summarizes the measured strain hardening moduli for the networks. Remember from stoichiometry the DMMP and PA fortified networks have an identical M_c of 818 g/mol also. In contrast, the PA fortified network has a strain hardening response closer to that of an unmodified network with a M_c of 380 g/mol. For comparison an unmodified, base network with a M_c of 1452 g/mol was also tested and as expected the slope of its strain hardening region is less than that of the networks with greater crosslink densities. Density measurements indicate the PA network has an effective crosslink density similar to that of an unmodified network with a M_c of 380 g/mol. When tested in tension, the PA network was brittle at higher loading concentrations suggesting the presence of additional crosslinks. Now, once again a mechanical measurement suggests additional crosslinking in the PA fortified network. The fact that the strain hardening modulus is approaching that of an unmodified M_c 380 g/mol network agrees reasonably well with measurements discussed previously.

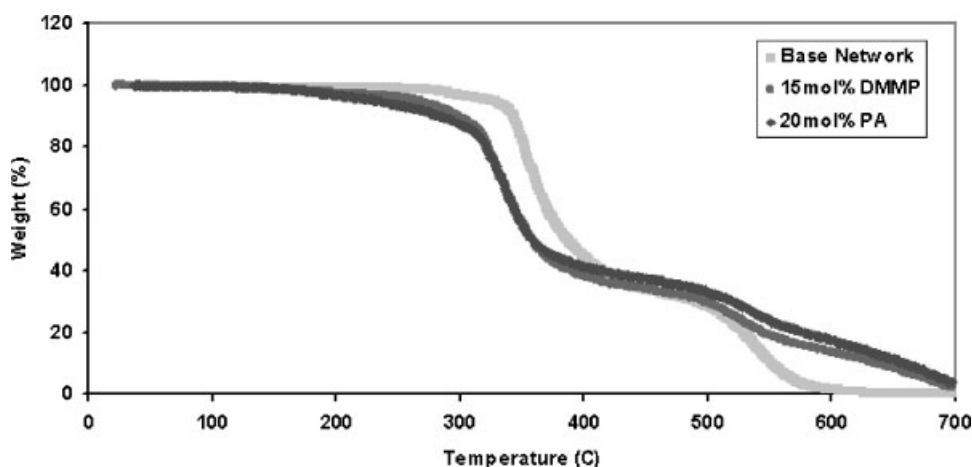


Figure 11 Thermal decomposition of the unmodified base network and PA and DMMP fortified networks. Decomposed in an air atmosphere at $10^\circ\text{C}/\text{min}$.

Flammability characteristics

Phosphorus-containing compounds have recently gained interest as fire resistant additives in polymers.^{28,29} Previously, halogenated compounds or halogenation of the polymer itself were common methods to improve fire resistance. Because of environmental concerns and the fact that halogenated compounds produce toxic and corrosive gases during combustion, phosphorus containing additives are a favorable alternative. Phosphorus additives often operate as char formers during combustion, thereby decreasing the burn rate of the polymer. The two molecular fortifiers, DMMP and PA, are no exception to this as shown by the thermal decomposition of the fortified networks shown in Figure 11 and Table III. Though the onset of thermal decomposition comes at a lower temperature, the rate of decomposition is slowed by roughly 30%.

Pyrolysis combustion flow calorimetry (PCFC) is a unique technique that allows one to test realistic burn characteristics of research sample sizes. The data collected from PCFC is similar to that gained from a cone calorimetry test.¹⁶ Table IV shows the results of PCFC tests performed on the fortified networks. The heat release rate of the networks containing molecular fortifier is decreased by 40% and 20% for the DMMP and PA fortified networks, respectively. The overall heat released is also decreased in the fortified networks. Though the DMMP fortified networks burn slower, they release a greater amount of overall heat when compared with the PA fortified networks. Since more heat is released in the end, more material is actually burned and char formation is decreased. The data in Table IV supports this. In addition to the two fortifiers presented here, the effects of various functional groups on the phosphorus compound could be explored to possibly improve fire resistance further.

CONCLUSIONS

Molecular-scale reinforcement in epoxy networks is achieved through the use of two fortifiers, dimethyl methyl phosphonate (DMMP) and diethyl phosphor-

TABLE III
TGA Results of Unmodified, Base Networks and Fortified Networks

Sample	Temp (°C)	Wt loss	
	at 2% Wt loss	Char at 650 °C (%)	rate (%/min)
Base Network M_c 818	284	0.5	14.3
M_c 818 + 15 mol % DMMP	175	8.2	10.9
M_c 818 + 20 mol % PA	177	11.2	9.7

TABLE IV
Burn Characteristics as Determined by PCFC

Sample	Heat release	Total heat	Char yield (%)
	capacity (J/g K)	released (kJ/g)	
Base Network M_c 818	539	25.5	8.1
M_c 818 15 mol % DMMP	319	22.8	9.8
M_c 818 20 mol % PA	413	19.7	14.8

amidate (PA). DMMP is incorporated as a conventional additive while PA is covalently bound as part of the network. The DMMP and PA fortifiers decrease the viscosity of the epoxy resin more than what is predicted by a hydrodynamic volume model. Both fortifiers provide improvements in elastic modulus and tensile and compressive yield stress. An increase in T_g is also observed with increasing fortifier concentration. The mechanism of reinforcement is suggested to be due to the filling of free volume, supported by measured increases in density, and specific hydrogen bonds formed between the fortifier and network. It is suggested that the PA fortifier acts as a trifunctional crosslinker and forms a physical crosslink within the network through hydrogen bonding. The unique interactions of the PA fortifier give the network characteristics of an unmodified network with greater crosslink density as supported by density, tensile strength, and strain hardening measurements. The P=O component of the fortifiers also aids in decreasing flammability and slows thermal decomposition of the networks.

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