

Polyphenylene Ether Macromonomer – Cyanate Ester Laminates

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ABSTRACT

The electronics industry is driven by constant technological changes, which have brought improved innovative products to the marketplace. [1,2] These advances have placed high demands on material performance, such as low dielectric constants (Dk), low loss tangent (Df), low moisture uptake and good thermal stability. Epoxy resins are an essential material of the electronic industry. [3] Significant enhancements of epoxy resins have been obtained through the use of PPE macromonomers. However, there is a limit on the performance that can be delivered from epoxy-based resins. Therefore, non-epoxy based dielectric materials are used to fulfill the need for higher capability. The focus of this paper is on the use of PPE macromonomers to enhance the performance of cyanate esters laminates.

INTRODUCTION

Cyanate esters (CE) are a family of monomers and oligomers, which contain the reactive ring-forming cyanate functional groups. [4] Cyanate ester resin systems have lower dielectric constant than both epoxy and polyimide. Cured cyanate esters give highly crosslinked networks that exhibit very high T_gs. These highly crosslinked structures tend to have very low toughness. However, moisture absorption is a serious problem both in secondary operations and in end use. In addition, CE resins undergo cyclotrimerization slowly and needs to be cured at very high temperatures.

Polyphenylene ether (PPE) is an amorphous polymer, which is used extensively in blends and alloys of engineering thermoplastics. This highly aromatic polymer has a fairly stiff backbone and contains no hydrolysable bonds. These structural features result in a polymer with outstanding hydrolytic stability, very low moisture absorption, extremely high T_g, low density and outstanding dielectric properties over a wide temperature range. [5-9]. This unique performance profile suggests that PPE would be an ideal material for electronic applications. However, its high molecular weight can lead to solubility and viscosity limitations when used in thermoset resin. Therefore, PPE macromonomers (PPE-M) were developed for use in thermoset resins. These macromonomers have high solubility in common solvents and monomers with tailored functionality to co-polymerize with thermoset resins. [10-16] Indeed, PPE macromonomers have been heralded as a breakthrough in the search for materials that broadly enhance the performance of epoxy resin. [10-12] Clearly, it is of prime importance to evaluate PPE-M with cyanate esters.

MATERIALS

The PPE-M macromonomer was company resin from the company's plastics business. The structure of PPE-M appears in Figure 1. The bisphenol A cyanate ester (BPA-CE) and the phenol novolac cyanate esters (PN-CE) were from Company A. Their structures are depicted in Figure 2. Aluminum acetylacetonate (Al acac) was used as a catalyst.

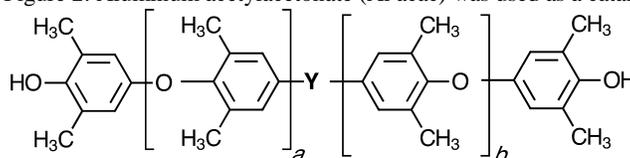


Figure 1. Structure of PPE-M

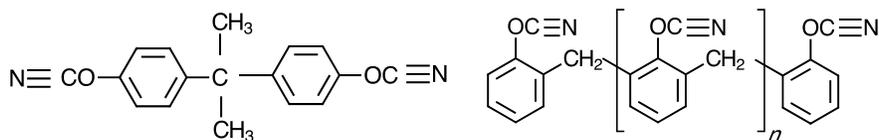


Figure 2. Structures of BPA-CE and PN-CE

EXPERIMENTAL

The effect of PPE-M on the onset of curing was determined by DSC (differential scanning calorimetry) 30-300°C at 20°/min. A comparison was done between BPA-CE and BPA-CE/PPE-M 1/1 ratio both with 0.05% Al acac.

The reaction of the PPE-M with BPA-CE was studied by real-time transmission FTIR (1 spectrum/sec) using a programmable, heated sample cell. The cell was ramped from room temperature to 225°C at a rate of 40°C/min and then held at temperature. FTIR absorption peaks at 2273 cm⁻¹ (cyanate), 3490 cm⁻¹ (PPE hydroxyl groups), 1670 cm⁻¹ (imidocarbonate), and 1565 cm⁻¹ (triazine ring) were ratioed to the baseline-corrected 1500 cm⁻¹ band, assigned to the C-H and C-C stretching of the phenyl groups of the cyanate ester. [17, 18]

CE castings were prepared with 0, 10, 20, 30, 40, 50 and 60wt% PPE-M. The PPE-M was dissolved in the cyanate ester with warming. After the addition of 0.05 parts Al acac, the solutions were transferred into molds and cured. The cure cycle for preparing castings was 150°C/30 min., 175°C/30 min., 200°C/30 min, and then 220°C/90 min. Test parts were cut from the casting.

DISCUSSION

The DSC thermo-gram in Figure 3 shows that the cyclotrimerization of BPA-CE proceeds slowly and needs to be cured at very high temperatures. However, PPE-M significantly lowers the onset of the heat of reaction to around 150°C.

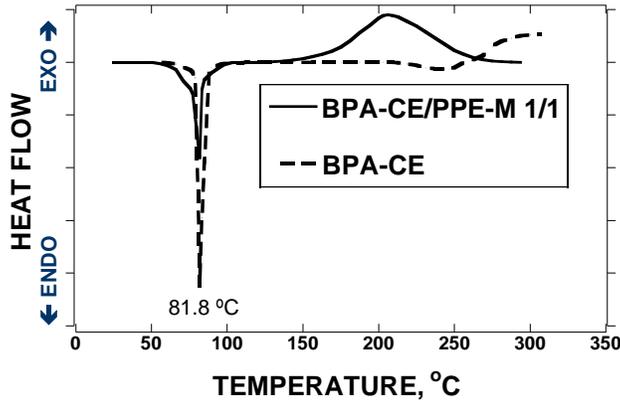


Figure 3. DSC curves of BPA-CE and BPA-CE/PPE-M

The curing behavior of cyanate esters have been studied by FTIR through the monitoring of cyanate ester group absorption and the triazine absorption peak. [19, 20] For the reaction of BPA-CE with PPE-M, the PPE-hydroxyl was monitored in addition to the appearance of an imidocarbonate absorbance. FTIR results are summarized in Figure 4. Upon heating the hydroxyl and cyanate absorbances decrease with time. Initially the absorbance of the imidocarbonate increases and then it decreases. The absorbance of the triazine ring increases with time. These results suggest that the PPE-M is reacting with a cyanate ester group to form an imidocarbonate intermediate, which reacts further to form a triazine. This reaction mechanism is depicted by the chemical structures in Figure 5.

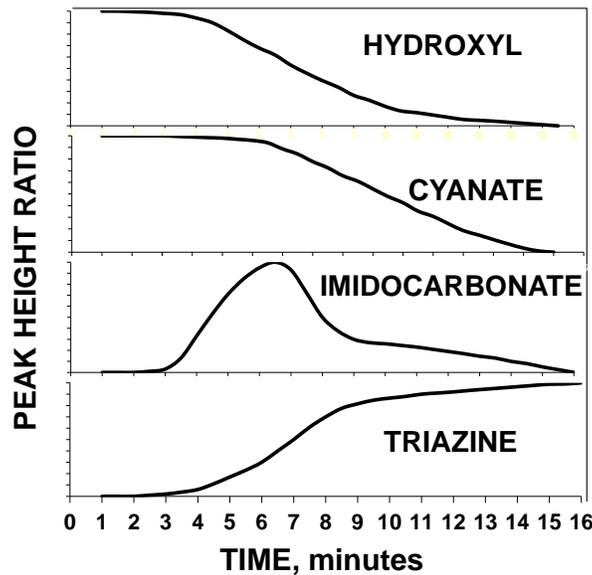


Figure 4. FTIR of Reaction Dynamics

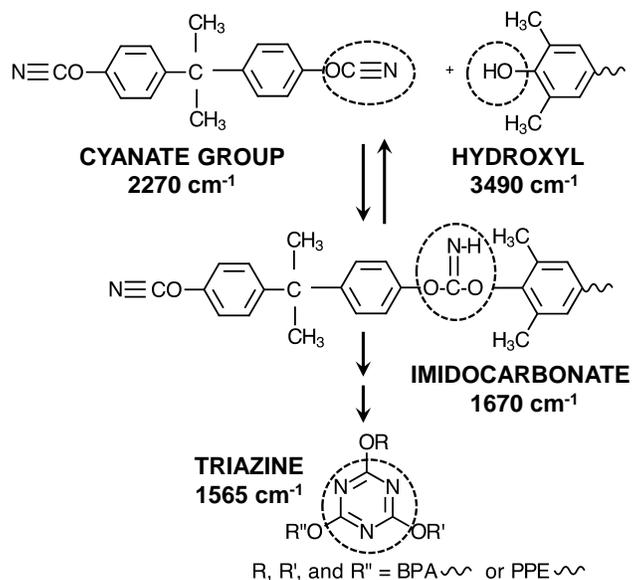


Figure 5. Reaction of PPE-M with BPA-CE

All castings were transparent and exhibited a single glass transition temperature (T_g) over the composition range studied. Both cured BPA-CE and PN-CE gave a material with very high T_g s of 285 and 320°C, respectively. These cured resins have very high crosslink densities. The use of PPE-M to CEs results in a lowering of T_g s as shown in Figure 6. This would be anticipated since the PPE has a lower T_g and with its much higher molecular weight, the crosslink density would be decreased. However, over the compositional range studied, all the T_g s of the CE/PPE-M networks remained above 210°C.

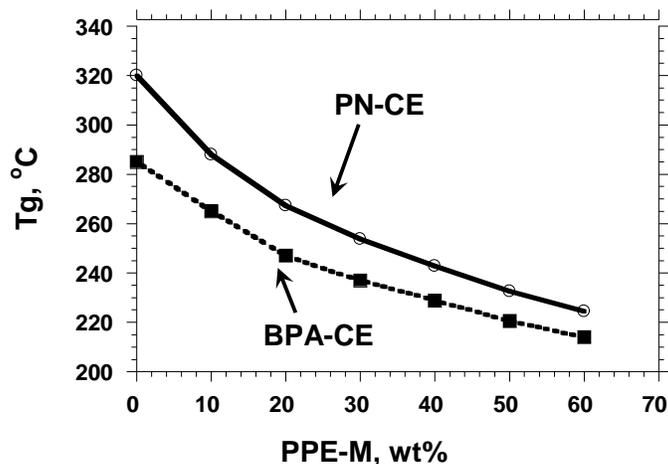


Figure 6. T_g BPA-CE/PPE-M and PN-CE/PPE-M

In general, T_g s increase with increasing crosslink density. [21-24] However, in highly crosslinked resins there can be a significant decrease in toughness. [25] The very high crosslink densities in CE based networks introduce significant restrictions on the molecular motions of the groups between crosslink sites, which can result in decreased toughness. The effect of PPE-M on the toughness of CE networks was studied by fracture toughness (K_{1C}). The data in Figures 7 and 8 show significant increases in fracture toughness as the PPE-M levels increased.

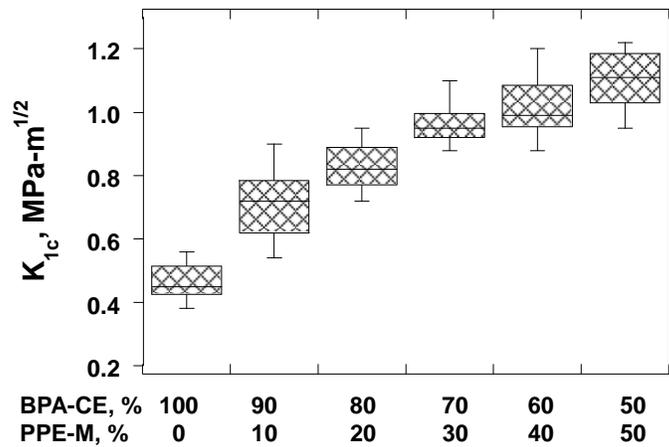


Figure 7. Fracture Toughness of BPA-CE/PPE-M

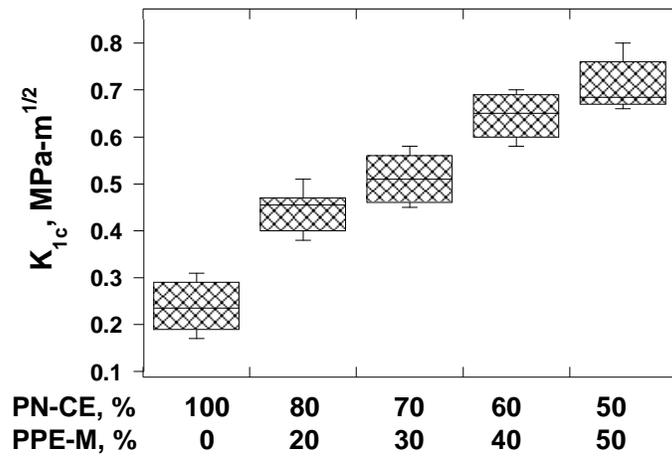


Figure 8. Fracture Toughness of PN-CE/PPE-M

The effect of PPE-M on the density of BPA-CE and PN-CE based castings appears in Figure 9. There are significant decreases in density as the PPE-M levels increase. Indeed, at 50wt% PPE-M there is a 6-8% decrease in density. These density reductions suggest that less resin would be needed to make molded parts or laminates.

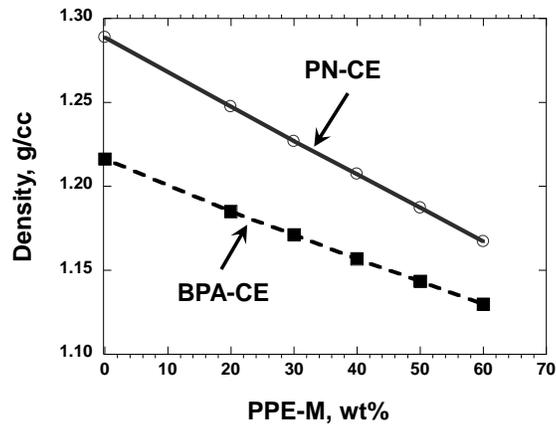


Figure 9. Density for BPA-CE/PPE-M and PN-CE/PPE-M

The effect of PPE-M on dielectric properties of BPA-CE based networks was measured at 1 GHz. The dielectric constants (Dk) and loss tangents (dissipation factor, Df) are compared to BPA Epoxy and appear in Figures 10 and 11, respectively. Over the composition range studied, all networks exhibited very low dielectric properties. The dielectric properties were similar over the range studied. For the loss tangent (dissipation factor, Df), there is a slight increase with increasing levels of PPE-M.

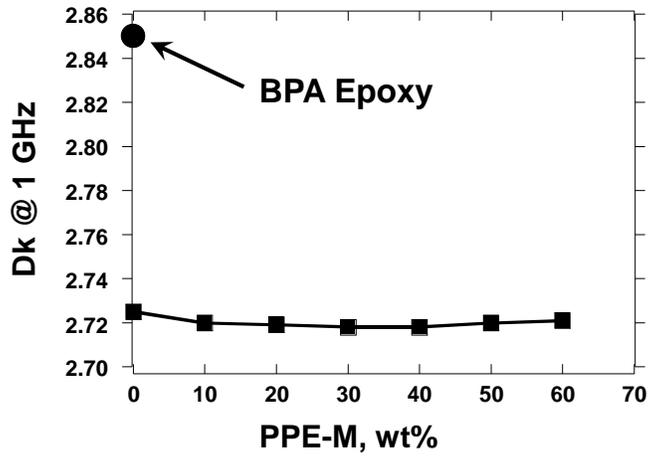


Figure 10. Dielectric Constant for BPA-CE/PPE-M

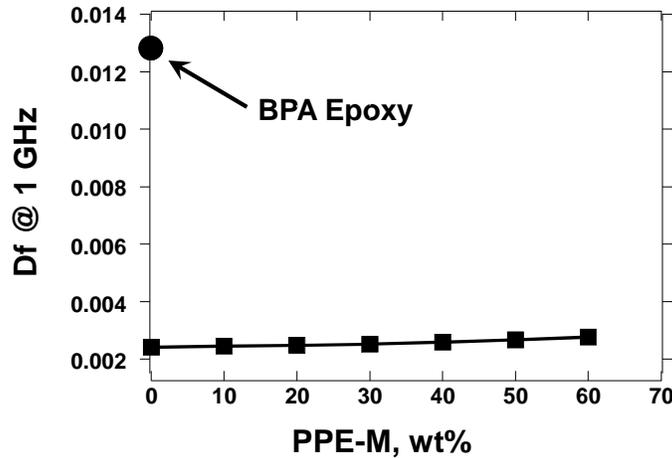


Figure 11. Loss Tangent for BPA-CE/PPE-M

Triazine rings will hydrogen bond with water. Hence, the high levels of triazine ring structures in cured cyanate ester resins results in absorption of water. On the other hand, PPE is known for its very low water absorption. Figure 12 shows that moisture absorption after immersion in water at 80°C is significantly reduced by the incorporation of PPE-M into the thermoset matrix.

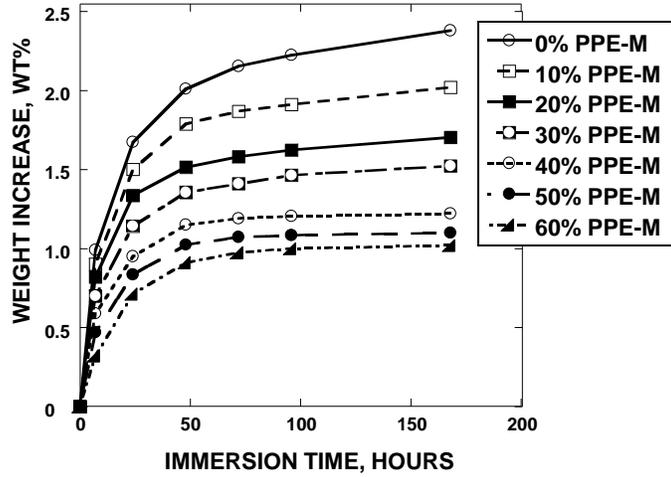


Figure 12. Moisture Uptake for BPA-CE/PPE-M

Water has high dielectric properties and absorbed water is known to have adverse effects on dielectric properties of polymers. The effect of water absorption on dielectric properties of BPA-CE and BPA-CE/PPE-M after immersion in water at 80°C is shown in Figures 13 and 14. As the moisture absorption increased, both Dk and Df increased. However, there was a significant reduction in the change in dielectric properties with the incorporation of PPE-M into the triazine matrix. Thus, the use of PPE-M should give more stable dielectric properties in humid environments.

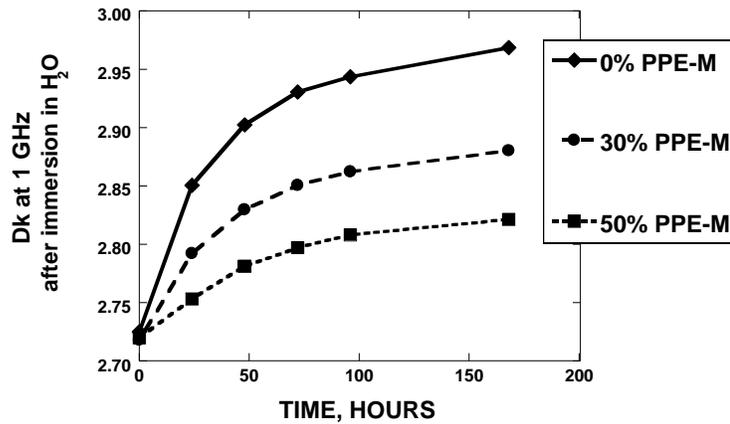


Figure 13. Dk after immersion in water

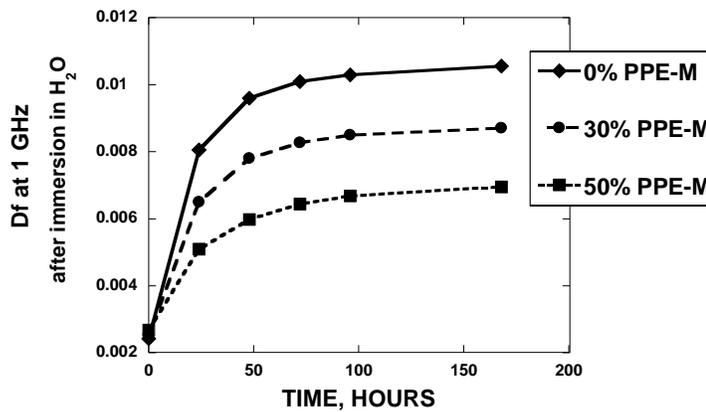


Figure 14. Df after immersion in water

Absorbed water effects dimensional stability. The increase in length due to absorbed water appears in Figure 15. This can introduce hygroscopic stresses through differential swelling. The growth through absorbed water is decreased with increasing levels of PPE-M. Clearly, the reduction in moisture absorption is related to better dimensional stability.

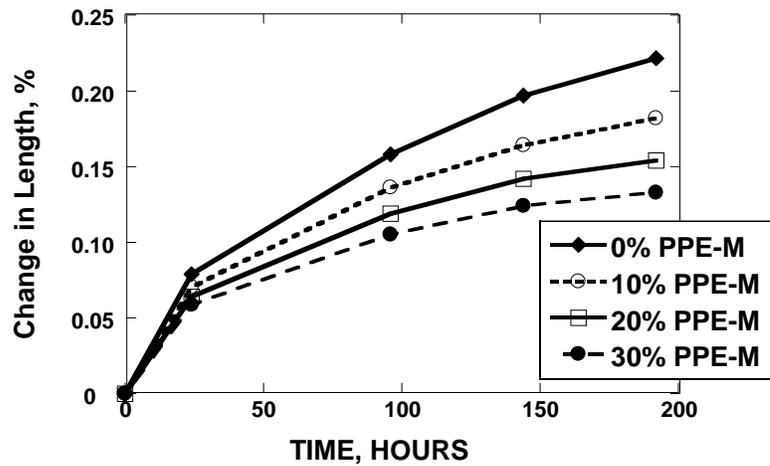


Figure 15. Growth after immersion in water

Absorbed water can act as a plasticizer and alter thermo-mechanical properties. This is exemplified by the decreases in flexural and tensile strengths after immersion in water shown in Figures 16 and 17. Over the range studied, BPA-CE by itself exhibited a 29 and 12 percent decrease in tensile and flexural strength, respectively. However, there is a significant improvement in the retention of properties with 30% PPE-M. Indeed, there was only a 17 and 2.6 percent decrease in tensile and flexural strength, respectively. Moreover, the samples with 30% PPE-M exhibited higher strengths after 200 hours of water immersion than the BPA-CE before immersion.

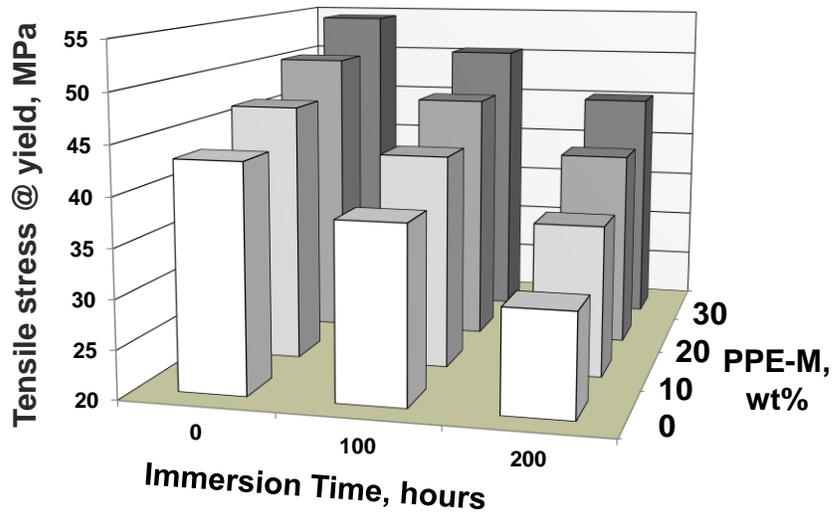


Figure 16. Tensile stress after immersion in water

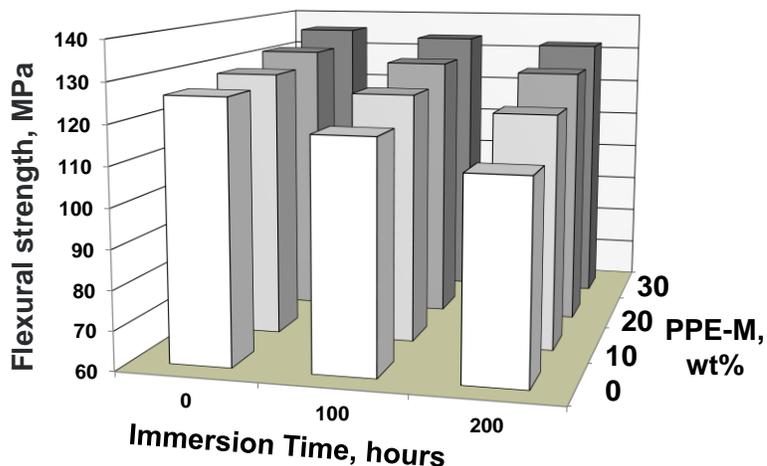


Figure 17. Flexural strength after immersion in water

An important part of the prepreps/CCL process is making the varnish, impregnating the glass cloth with the varnish and B-Staging. The varnish was prepared by dissolving the reactants in MEK. The glass cloth is impregnated with the varnish. B-Staging should give a prepreg which is flexible and non-tacky. In general, the resin should be homogeneous and the T_g of the resin should be above ambient temperatures.

Interestingly, in solution the PPE-M and CE react slowly at ambient temperatures to form imidocarbonate. The chemical reaction is depicted in Figure 18. This reaction was followed by changes in molecular weight and hydroxy ends groups of PPE-M and spindle viscosity. The rate of formation of imidocarbonate is much faster at 60 and 80°C. Figures 19 and 20 show increases in Mn and decreases in HO end groups, respectively. The reaction is relatively fast, the rate and molecular weight quickly plateaus, and forms a relatively stable solution. There was no significant change in solution viscosity.

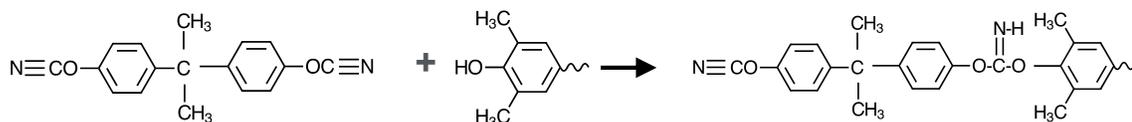


Figure 18. Formation of imidocarbonate

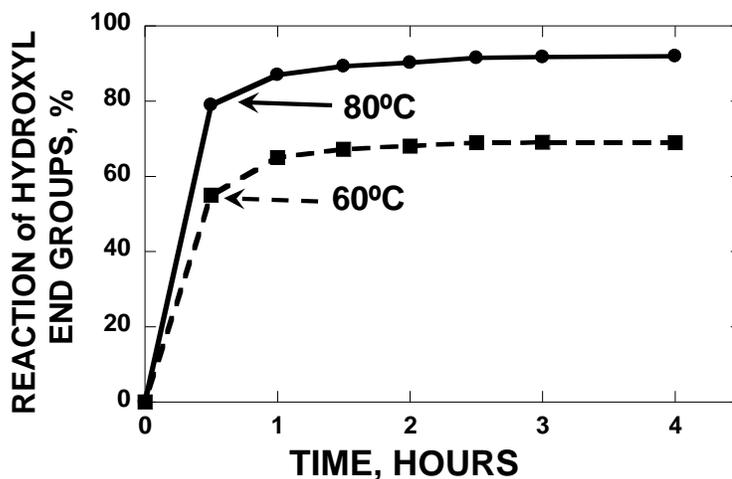


Figure 19. Reaction of hydroxyl groups

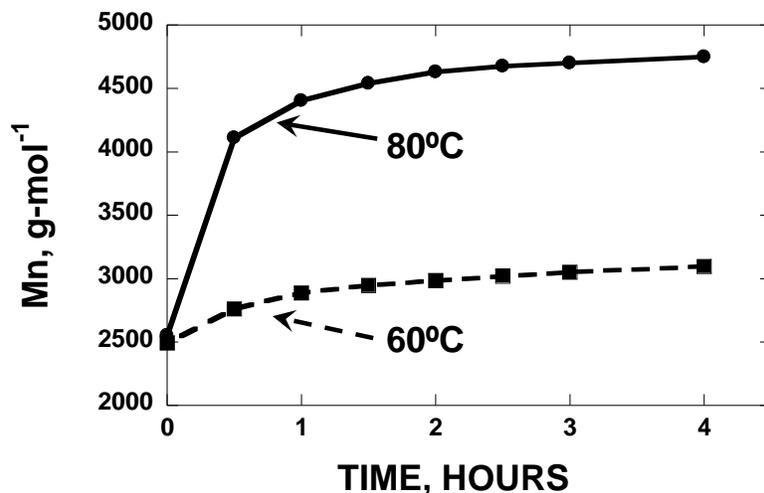


Figure 20. Change in Mn

BPA-CE is a crystalline monomer. Varnishes were prepared from BPA-CE and 40 to 55wt% PPE-M. To simulate B-Staging, the varnish was placed in an aluminum pan and the solvent was removed with heat. Visually the resultant film was not homogeneous and large crystalline domains noted. The crystallinity was corroborated by DSC. Clearly, there are potential homogeneity issues using BPA-CE/PPE-M. The film from the varnish prepared with 40wt% BPA-CE and 60wt% PPE-M was amorphous with a T_g of 69°C but was brittle. PN-CE resins are viscous, amorphous resins at ambient temperatures. Hence, varnishes were prepared with BPA-CE, PN-CE, and PPE-M. Simulating B-Staging, by heating and removal of the solvent resulted in amorphous resin mixtures which were flexible and exhibited T_gs above 45°C. These results are summarized in Table 1.

Table 1. Film quality of uncured resins

BPA-CE	PN-CE	PPE-M	Observations	Toughness	T _m , °C	T _g , °C
60	-	40	Crystalline domains	Brittle	65	
55	-	45	Crystalline domains	Brittle	64	
50	-	50	Crystalline domains	Brittle	58	
45	-	55	Clear	Brittle	55	
40	-	60	Clear	Brittle	-	69
25	25	50	Clear	Flexible	-	46
32.35	32.35	35.3	Clear	Flexible	-	48

For the preparation of laminates, the BPA-CE, PN-CE and PPE-M combinations were used. The flame retardant (FR) tris(2,4,6-tribromophenoxy)-1,3,5-triazine was used in the FR CE/PPE-M laminate. For comparison, two epoxy-based laminates (FR-4 Type and PPE-M modified FR-4) were prepared and included. The formulations and properties are summarized in Table 2.

The CE/PPE-M laminates had significantly better properties than the epoxy based laminates. Indeed, the CE/PPE-M laminates exhibited higher T_gs, lower D_k, D_f, and Z-axis coefficient of thermal expansion (CTE).

Table 2. Formulation and Properties of CE/PPE-M and Epoxy Laminates

	FR-4 Type	PPE Modified FR-4	Non-FR CE/PPE-M	FR CE/PPE-M
BPA Epoxy, wt%	50	25	-	-
Br Epoxy, wt%	50	25	-	-
PPE-M, wt%	0	50	-	-
2,4-EMI	2.0	1.5	-	-
BPA-CE, wt%	-	-	25	32.35
PN-CE, wt%	-	-	25	32.35
PPE-M, wt%	-	-	50	35.3
Brominated triazine, phr	-	-	-	15
Al acac, phr	-	-	0.05	0.05
Glass fiber content, %	52.4	51.1	52.5	48.3
T_g (DSC), °C	138	174	215	232
Delamination time at 288°C, min	<5	>30	>30	>30
Dielectric Constant at 1 GHz	4.4	3.78	3.425	3.515
Loss tangent at 1 GHz	0.02	0.012	0.0033	0.0033
Flammability, UL94	V-0	V-0	-	V-0
Z-axis CTE, ppm/°C	82.9	78.1	57.3	49.4

CONCLUSIONS

PPE macromonomers readily react with cyanate ester resins and lower the cure temperature. Incorporation of the macromers into the triazine matrix results in the broad enhancement of properties. Overall the combination of PPE macromers into cyanate ester resins results in networks with a single phase, high glass transition temperatures and low dielectric properties, enhanced fracture toughness and reduced moisture absorption.

Laminates prepared with cyanate esters and PPE-M exhibited broad enhancement of properties over BPA-epoxy based laminates. This includes T_gs greater than 210°C, very low Dk and Df and lower CTE.

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