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Polyphenylene Ether Macromonomers. XI.
Use in Non-Epoxy Printed Wiring Boards

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Abstract

The continuous progression toward portable, high frequency microelectronic systems has placed high demands on material performance, notably low dielectric constants (D_k), low loss tangent (D_f), low moisture uptake, and good thermal stability. Epoxy resins are the workhorses of the electronic industry. Significant performance enhancements have been obtained through the use of PPE telechelic macromonomers with epoxy resins. However, there is a ceiling on the performance obtainable from epoxy-based resins. Therefore, non-epoxy based dielectric materials are used to fulfill the need for higher performance. The focus of this paper is on vinyl monomers such as triallyl isocyanurate (TAIC) and t-butyl styrene/divinyl benzene (TBS/DVB) and their use with vinyl modified PPE macromers. When TAIC and TBS/DVB are cured by themselves, the resultant material was extremely brittle. However, the use in combination with vinyl modified PPE macromers, resulted in dielectric materials that exhibited major increases in toughness, very low dielectric properties, high glass transition temperatures (T_g), and very low moisture absorption. Printed wiring boards made from a combination of vinyl monomers and the PPE engineering macromonomer exhibited significant performance advantages over epoxy and modified-epoxy materials.

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Introduction

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, contains no hydrolysable bonds and no polarizable groups. 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. [1-4]. This unique performance profile suggests that PPE would be an ideal material for composites and electronic applications. However, its high molecular weight can lead to solubility and viscosity limitations, especially when considering thermoset systems.

PPE telechelic copolymers are unique low molecular weight materials 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. Previously we reported on an OH terminated macromonomer. The step-growth copolymerization of this macromer into epoxy and cyanate ester resins resulted in single-phase materials with enhanced performance - noticeably, higher T_g, increased toughness, lower dielectric properties, and a decrease in moisture absorption. [5-7]

Even with these performance enhancements it is increasingly difficulty for epoxy-based resin systems to fulfill the ever increasing performance requirements demanded by high frequency applications and correspondingly the importance of non-epoxy based dielectric materials is increasing. As part of our continuing studies on PPE macromonomers, methacrylate-terminated PPE macromonomer (M-PPE-M) have been prepared for use with free radical cured vinyl resins. [8] The structure of M-PPE-M is depicted in Figure 1. The focus of this paper is on vinyl monomers such as triallyl isocyanurate (TAIC) and t-butyl styrene/divinyl benzene (TBS/DVB) and their use with M-PPE-M in non-epoxy based dielectric materials. The chemical structures of TAIC and styrenic monomers appear in Figures 2 and 3.
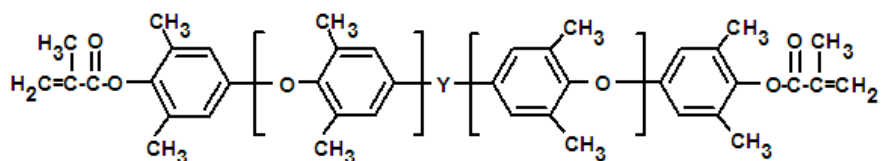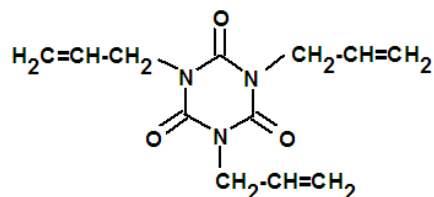

Figure 1. Structure of M-PPE-M
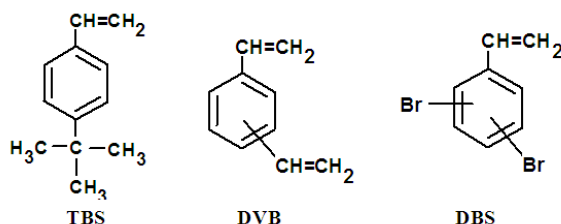
Figure 2. Structure of TAIC

Figure 3. Structures of TBS, DVB, and DBS

Vinyl monomers such as TAIC are important thermosetting resins used in the electronics, aerospace, and adhesive industries. [9, 10] However, TAIC by itself is an excessively brittle material. [11, 12] In general, attempts to improve the mechanical properties of TAIC resins have been unsatisfactory. [12]   Explanations for its brittleness include: The incomplete occurrence of intermolecular crosslinking reaction due to the rigidity of the polymer chains; steric crowding between polymer radical and pendant allyl groups; and short length of primary chains of networks with short chain lengths that provide many terminal polymer chain ends, which produce many defects in the resin. [13, 14]

Styrenic monomer based systems are of interest because of the absence of polarizable group. In addition, they are good solvent for PPE. Various styrene monomers include *p*-methylstyrene, dibromostyrene (DBS), and *p*-tertiary butylstyrene (TBS). Table 1 compares properties of these monomers and their corresponding polymers. Perusal of the data indicates that TBS and DBS have the best features of these styrenic monomers, such as, higher boiling points giving lower vapor pressure during fabrication, lower heat of polymerization minimizing exotherm during cure, lower shrinkage on polymerization, and higher T_g. In addition, polyTBS and polyDBS exhibited lower dielectric properties. Divinylbenzene was chosen as a crosslinking co-monomer because of the absence of polar groups and its demonstrated ability to increase the T_g and cross-linking density of styrene networks. [15, 16]

Materials
The methacrylate-terminated telechelic PPE copolymer is available from Sabic Innovative Plastics LLC under the SA9000 designation. In this paper this material is designated by the acronym M-PPE-M. The triallyl isocyanurate was from Sigma-Aldrich. The Deltech Corporation supplied TBS and DVB. The TBS was distilled prior to use. The DVB is composed primarily of 80% divinylbenzene and 20% ethylvinylbenzene isomers. Chemtura Inc supplied the dibromostyrene and poly dibromostyrene.

Experimental
Castings were prepared by dissolving the M-PPE-M in TAIC monomer. The catalyst, 1.5 parts 2,5-bis-(t-butyl peroxy)-2,5-dimethyl-3-hexane, was added, the solution degassed, transferred into a mold, and cured.

Discussion
In general, resins with high crosslink densities can have high T_gs. [8] Trifunctional TAIC-based resins would have very high crosslink densities. Unsuccessful attempts were made using differential scanning calorimetry (DSC) and dynamic mechanical analyses (DMA) to measure the T_g of TAIC and TAIC with 10wt% M-PPE-M. However, TAIC with 20% M-PPE-M exhibited a T_g around 290°C. The T_gs were lower with increasing levels of M-PPE-M as shown in Figure 4. The lower T_g may be due in part to the decreased crosslink density with the addition of M-PPE-M. At 50wt% M-PPE-M the T_g was 212°C and

levels off around 200°C with 70-80% macromer. Over the composition range studied for TAIC with M-PPE-M, all materials were transparent and exhibited a single glass transition temperature as determined by DSC.
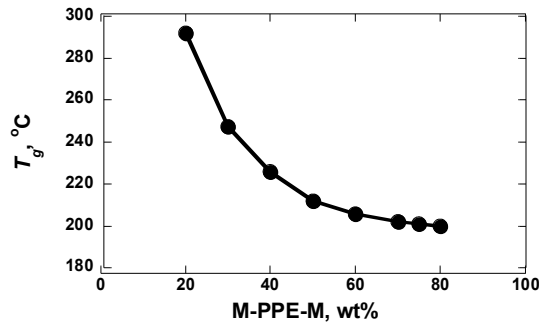

Figure 4. Glass Transition temperatures of TAIC/M-PPE-M castings

The effect of M-PPE-M on dielectric properties of TAIC based networks was measured at 100, 500, and 1000 MHz. Over the composition range studied, all networks exhibited very low dielectric properties. There is a slight increase in dielectric constant (Dk) and dissipation factor (Df, loss tangent) with increasing levels of M-PPE-M. Dielectric properties of DGEBPA (BPA epoxy resin cured with imidazole catalyst) are used as a reference. The dielectric properties of TAIC/M-PPE-M are much lower than that of DGEBPA as shown in Figures 5 and 6.
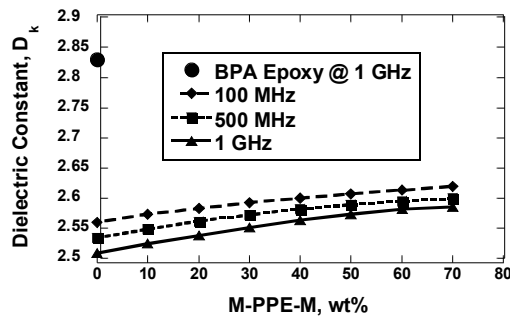

Figure 5. Dielectric constants of TAIC/M-PPE-M castings
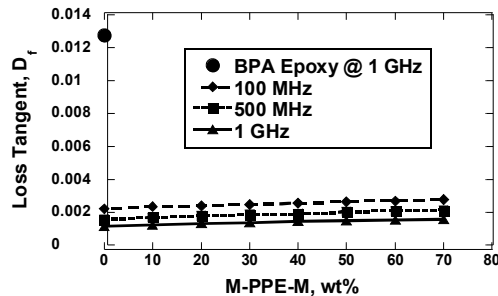

Figure 6. Loss tangent of TAIC/M-PPE-M castings

The very high crosslink densities in TAIC based networks introduce significant restrictions on the molecular motions of the groups between crosslink sites, which can result in decreased toughness. The effect of M-PPE-M on the toughness of TAIC networks was studied by pendulum impact. The toughness of TAIC and TAIC with 10 and 20% M-PPE-M was extremely low and difficult to quantify. However, the addition of 30-60wt% M-PPE-M resulted in significant increases in impact strength as shown in Figure 7.
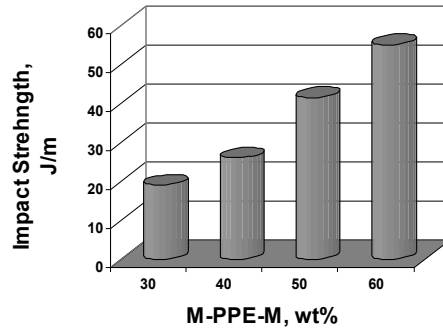
Figure 7. Impact Strength

Another way of quantifying toughness is tensile strength. Various attempts to improve the strength of TAIC only resulted in very brittle resins with very low tensile strength. [13] However, tensile strengths increased with the use of M-PPE-M as shown in Figure 8. Indeed, there is a significant increase in tensile strength with increasing levels of M-PPE-M.
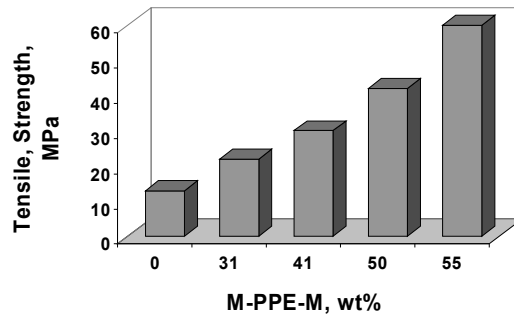

Figure 8. Tensile Strength

Water absorption in polymers is known to have adverse effects on dimensional stability, T_g, mechanical properties, and dielectric properties. Water will hydrogen bond to the triazine rings of TAIC. On the other hand, PPE is known for its very low water absorption. The results from immersion of test specimens in water at 80°C on moisture absorption and dielectric properties appear in Figures 9 and 10. As the moisture absorption increased, both Dk and Df increased. The incorporation of 50wt% M-PPE-M into the TAIC matrix resulted in a significant reduction in moisture absorption and much less change in dielectric properties.
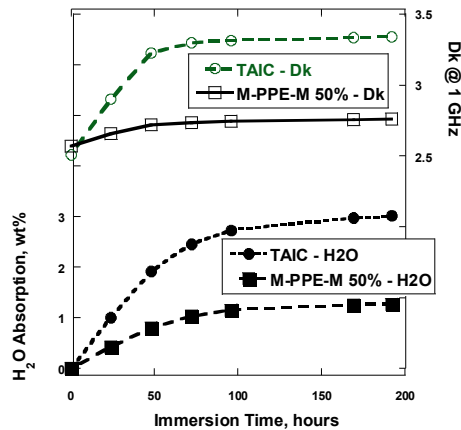

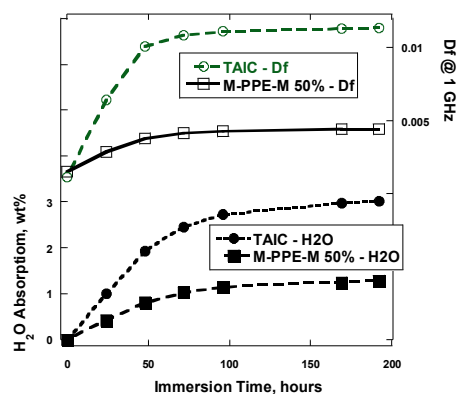**Figure 9. Moisture uptake and effect on dielectric constant**

Figure 10. Moisture uptake and effect on loss tangent

In an effort to assess the real world performance of the TAIC/M-PPE-M system, it was screened in printed circuit board laminates and the data is summarized in Table 1. Two epoxy-based laminates (Formulations A and B) were prepared for reference. Formulation A would be a typical FR-4 material. Formulation B was made with phenolic terminated PPE macromonomer (PPE-M). Two laminates (Formulations C and D) were prepared using a combination of TAIC and M-PPE-M. A brominated triazine, tris(2,4,6-tribromophenoxy)-1,3,5-triazine, was added as a flame retardant. The formulations and properties are summarized in Table 1. Clearly, the TAIC/M-PPE-M laminates had significantly better properties than the epoxy based laminates. Indeed, the TAIC/M-PPE-M laminates exhibited higher T_gs, lower Dk, Df, and Z-axis CTE.

Table 1. Formulation and Properties of TAIC/M-PPE-M and Epoxy Laminates

	A	B	C	D
DGEBPA, wt%	50	25	-	-
Br Epoxy, wt%	50	25	-	-
PPE-M, wt%	0	50	-	-
2,4-EMI, phr	2.0	1.5		
M-PPE-M, wt%	-	-	50	40
TAIC, wt%	-	-	50	60
Tris(2,4,6-tribromophenoxy)-1,3,5-triazine, phr	-	-	12	13
Peroxide, phr	-	-	1.5	1.5
Glass fiber content, %	52.3	51.2	50.3	51.2
Thickness, mm	1.22	1.21	1.43	1.44
T_g (DSC), °C	138	167	210	225
Delamination time @ 288°C, min	<5	>30	>30	>30
Dielectric Constant @ 1 GHz	4.2	3.78	3.475	3.495
Loss tangent @ 1 GHz	0.0112	0.0072	0.0031	0.0030
Flammability, UL94	V-0	V-0	V-0	V-0
Z-axis CTE, ppm/°C	82.76	78.17	59.27	51.08

Styrenic-based building blocks were another area of investigation. Styrenic monomers and polymers contain no hydrolysable bonds and no polarizable groups. These structural features translate into outstanding hydrolytic stability, very low moisture absorption, and outstanding dielectric properties. TBS and DVB were used to define structure properties relationships. Combinations of TBS, DBS, and DVB with M-PPE-M were studied in castings and laminates.

Both DVB, and M-PPE-M are bi-functional. DVB is much lower in molecular weight than M-PPE-M. Hence, the crosslinking efficiencies of DVB and M-PPE-M are significantly different. These differences manifest themselves in T_g and toughness.

The TBS/DVB resins saw a meteoric raise in T_gs with DVB levels. Indeed, 16wt% DVB increased the T_g about 50°C. On the other hand, the T_gs of TBS/M-PPE-M increased more slowly with increasing M-PPE-M levels. For example, 50wt% M-PPE-M is required to increase the T_g by 50°C. The results appear in Figure 11
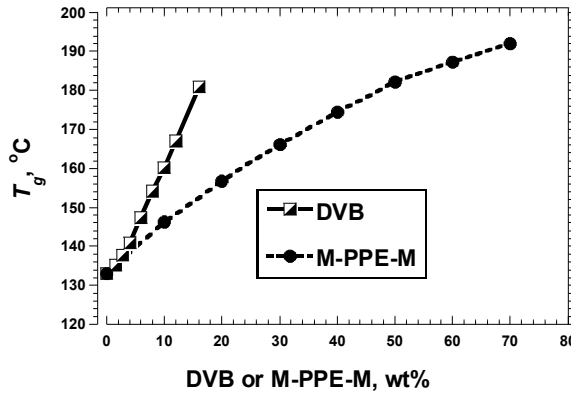

Figure 11. Effect of DVB and M-PPE-M on Glass Transition Temperature

Pendulum impact was used to study the toughness. The impact strength of TBS/M-PPE-M increases with increasing levels of M-PPE-M. However, for TBS/DVB there was a precipitous drop in impact strength with increasing levels of DVB. The very high crosslink densities in DVB/TBS based networks introduce significant restrictions on the molecular motions of the groups between crosslink sites, which can result in decreased toughness. The data are summarized in Figure 12
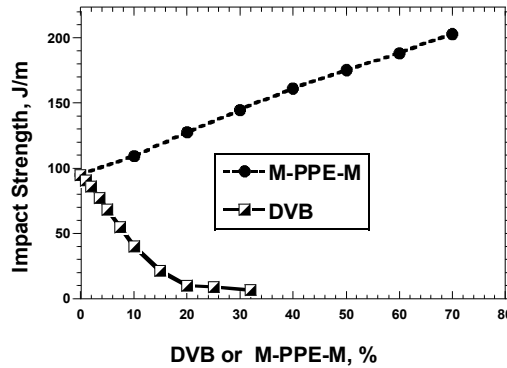

Figure 12. Effect of DVB and M-PPE-M on Impact Strength

Dielectric properties of TBS/M-PPE-M at 1.2, 5, and 10 GHz revealed very low Dk and Df over the range studied as seen in Figures 13 and 14. Dielectric properties of DGEBPA at 1 GHz is shown as a reference.
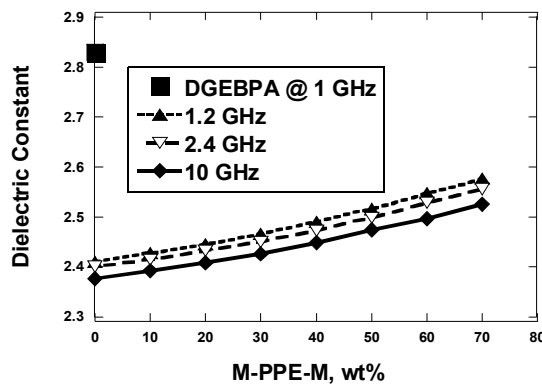
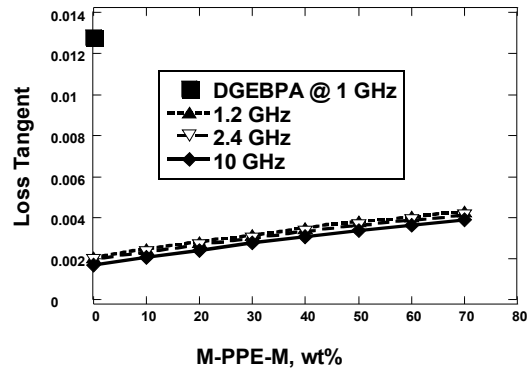**Figure 13. Effect of M-PPE-M on Dielectric Constant**

Figure 14. Effect of M-PPE-M on Loss Tangent

TBS is non-polar and hence has no sites to hydrogen bond with water. The moisture uptake of TBS/M-PPE-M (1/1) was compared with other thermoset resins, such as TAIC, TAIC/M-PPE-M (1/1), and DGEBPA. The results from moisture absorption after immersion in water at 80°C appear in Figure 15. Clearly, TBS/M-PPE-M (1/1) exhibits significantly lower H_2O absorption.
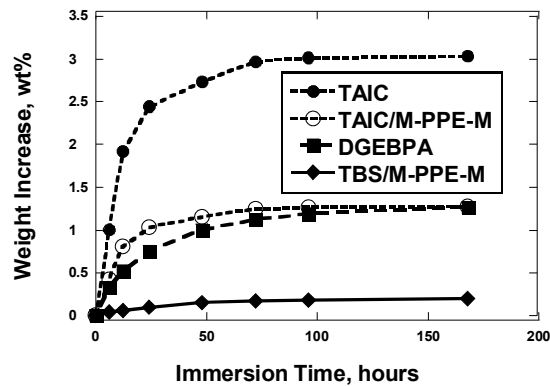

Figure 15. Comparative moisture uptake

Overall styrenic-based resins have very low Dk, Df, and moisture absorption. The use of a combination of DVB and M-PPE-M would give a balance between T_g, impact strength, and crosslink density (needed for chemical resistance). A styrenic-based laminate was prepared. In Table 2 Formulation E was prepared using a combination of M-PPE-M, DBS, and DVB. Formulations A and B are the two DGEBPA-based references. Clearly, the M-PPE-M/DBS/DVB laminate has significantly better properties than the epoxy based materials. Indeed, the DBS/DVB/M-PPE-M laminate exhibited higher T_g, lower D_k, D_f, and Z-axis CTE.

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

	A	B	E
DGEBPA, wt%	50	25	-
Br Epoxy, wt%	50	25	-
PPE-M, wt%	0	50	-
2,4-EMI	2.0	1.5	-
M-PPE-M, wt%	-	-	50
DBS, wt%	-	-	35
DVB, phr	-	-	15
Peroxide, phr	-	-	1.5
Glass fiber content, %	52.3	51.2	49.8
Thickness, mm	1.22	1.21	1.42
T_g (DSC), °C	138	167	199
Delamination time @ 288°C, min	<5	>30	>30
Dielectric constant @ 1 GHz	4.2	3.78	3.436
Loss tangent @ 1 GHz	0.0112	0.0072	0.0030
Flammability, UL94	V-0	V-0	V-0
Z-axis CTE, ppm/°C	82.76	78.17	62.13

Conclusion

Vinyl terminated PPE macromonomers were used in combination with TAIC and styrenic monomers to prepare non-epoxy laminates. These laminates exhibited enhanced performance over epoxy and modified epoxy based laminates. The performance features included much lower dielectric constants and loss tangent with lower CTE values.

The PPE engineering macromer reacted into the thermoset matrices and gave single-phase morphologies. The presence of the PPE macromonomer in TAIC and styrenic networks resulted in an increase in toughness while maintaining high T_gs and low dielectric properties. There was a significant decrease in moisture absorption in the TAIC-based materials. The styrenic-based material exhibited extremely low moisture absorption.

The distinct performance attributes of PPE modified non-epoxy resin systems suggest utility as dielectric materials for electrical and electronic components to address the increasing challenges of high frequency, digital components.

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