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Interacting blends of styrenated unsaturated Poly(ester-amide)s with commercial unsaturated polyester resin (Iso-phthalic acid based)

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Abstract

Unsaturated poly(ester-amide)s resins (UPEAs) were prepared by the reaction between an epoxy resin (DGEBA) and unsaturated bisamic acids (B1-6) using a base catalyst. These UPEAs were then diluted by styrene and blended with commercial unsaturated polyester resin (Iso-phthalic acid based) to produce a homogeneous resin. The curing of these blends was carried out using Benzoyl peroxide (BPO) as a catalyst and N,N'-Dimethyl aniline (DMA) as a promoter. The glass fiber reinforced composites (*i.e.* laminates) of these Styrenated UPEAs-UPR (Iso-phthalic acid based) blends were fabricated. The mechanical and chemical properties of the glass fiber composites have also been evaluated. The unreinforced cured samples of the SUPEAs-UPR (Iso-phthalic acid based) blends were also analyzed by thermogravimetry (TGA).

Keywords: Styrenated unsaturated poly(ester-amide)s, unsaturated polyester resin, Glass fiber-reinforced composites, Mechanical property, Thermogravimetric analysis.

1. Introduction

Polyester and polyamide resins are manufactured industrially for a number of applications [1-5]. By blending or copolymerizing somewhat hydrophilic polyamide and hydrophobic polyesters products can be made that could find a variety of applications. The so-called poly(ester-amide)s resins are almost saturated [6-9]. Poly(ester-amide)s resins with unsaturated segments have received very little attention academically and industrially. The three polymer candidates, namely epoxy, unsaturated polyester and polyamides are most widely versatile industrial materials and have a broad spectrum of characteristics for wide applications ranging from aerospace to microelectronics. They are also important as laminating resins, molding composites, fibers, films, surface coating resins, fiber cushion [10-12]. Particularly polyamides material used in the form of fibers as especially thermoplastics of particular used in engineering applications. The glass fiber reinforced nylon plastics are now of substantial importance due to the rigidity and creep resistance. Polyamides are also used in fiber application, automotive industries, valve covers, coatings [13, 14].

Amalgamation of all three segments (*i.e.* epoxy, ester and amide) into saturated and unsaturated polymer chain has been recently reported from our laboratory [15-19]. Certain properties of resins may also be improved via interact of with the other unsaturated resin is another possibility. In order to improve certain properties of such SUPEAs their blending with commercial UPR (Iso-phthalic acid based) is possible. While UPR (Iso-phthalic acid based) is a versatile industrial resin today, hence, the present paper comprises studies of interacting blending of SUPEAs resin from our laboratory with commercial UPR (Iso-phthalic acid based). The glass fiber reinforced composites of these blends have been fabricated and characterized by mechanical, chemical and thermal properties.

2. Experimental

2.1 Materials

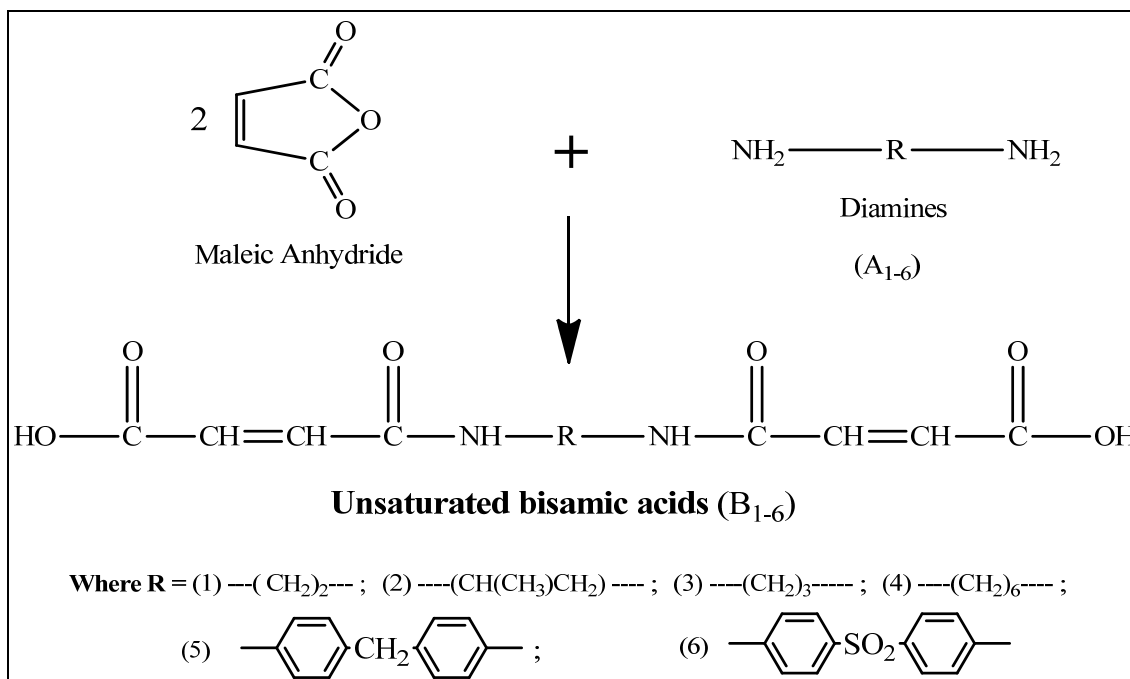
Epoxy resin (C) namely, Diglycidyl ether of bisphenol-A containing epoxy equivalent weight is 188.6, epoxy value 5.3, according to ASTM D 1652. Commercial unsaturated polyester resin (UPR)(Iso-phthalic acid based) containing an acid value 22mgKOH/gm, Benzoyl peroxide (BPO), The CSM continuous Glass fibers mate used for composites fabrication was obtained from Kemrock Industries & exports Ltd. Halol.

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The diamines used for the synthesis of unsaturated bisamic acids (A_1): 1,2-Ethylenediamine; (A_2): 1,2-Propylenediamine; (A_3): 1,3-Propylenediamine; (A_4): 1,6-Hexamethylenediamine, (A_5): 4,4'-Diaminodiphenylmethane, (A_6): 4,4'-Diaminodiphenylsulfone, were obtained in pure form from Sigma-Aldrich Pvt. Ltd. All the other chemicals used were of laboratory grade.

2.2 Synthesis of Unsaturated Bisamic Acids

All the six unsaturated bisamic acids were prepared by a simple addition reaction between Maleic Anhydride and the different diamines, following the method reported in the literature [17]. Prepared unsaturated bisamic acids were characterized by melting point, acid value determination and FT-IR analysis in the Figure 1. All the six bisamic acids (designated as unsaturated bisamic acids) (B_{1-6}) were obtained in the form of free flowing powder and their structures are shown in the Scheme 1. The preliminary characterization data are furnished in the Table 1.



Scheme 1: Synthesis of Unsaturated bisamic Acids

Table 1: Preliminary characterization Unsaturated bisamic acids

Sample code	Bisamic Acids	Appearance	Mole. Formula [Formula wt.]	Acid value mgKOH/gm and [melting point °C]
B ₁	1,2-ethylenediamine bisamic acid	Off white powder	C ₁₀ H ₁₂ N ₂ O ₆ [256]	440[178 °C]
B ₂	1,2-propylenediamine bisamic acid	Off white powder	C ₁₁ H ₁₄ N ₂ O ₆ [270]	415[152 °C]
B ₃	1,3-propylenediamine bisamic acid	Off white powder	C ₁₁ H ₁₄ N ₂ O ₆ [270]	415[174 °C]
B ₄	1,6-hexamethylene diamines bisamic acid	Off white powder	C ₁₄ H ₂₀ N ₂ O ₆ [312]	360[171 °C]
B ₅	4,4'-diamino diphenyl methane bisamic acid	Light yellow powder	C ₂₁ H ₁₈ N ₂ O ₆ [394]	285[226 °C]
B ₆	4,4'-diamino diphenylsulfonebisamic acid	Light yellow powder	C ₂₀ H ₁₆ N ₂ O ₆ S [444]	253[223 °C]

^aThough the IUPAC names of all the Bisamic acids are too long, so only trivial names are given in whole text.

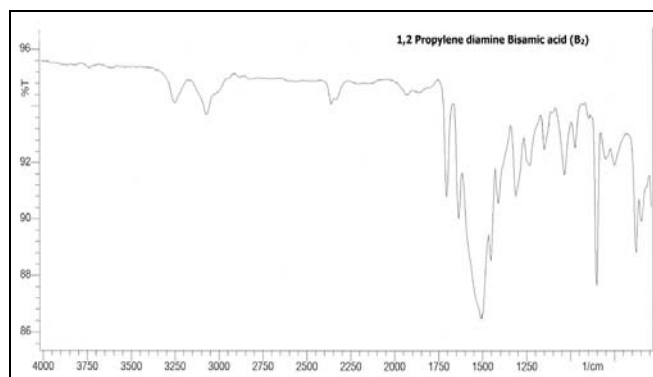


Fig 1: FT-IR Analysis spectra of Unsaturated Bisamic acid

2.3 Synthesis of Styrenated Unsaturated Poly(Ester-Amide)s

The unsaturated poly (ester–amide)s resins were prepared by the method reported in our earlier communication [17]. These UPEAs were designated as (D_{1-6}). Epoxy resin (C) *i.e.* DGEBA (1mole) and unsaturated bisamic acid (B_{1-6}) (1mole) were charged into a three necked flask equipped with a mechanical stirrer. To this, triethylamine (8.3%) of the total weight of the above was added as a catalyst. The mixture was heated to 85 °C with continuous stirring. Samples were taken at regular intervals to check the acid value. The reaction was carried out until the acid value found between 60 to 55mgKOH/gm and to give unsaturated poly(ester-amide)s resin(D_{1-6}). Into this, 0.01% of the total weight of resin, hydroquinone was added as an inhibitor and stirred well for a few minutes while maintaining the temperature at 85 °C. After

this, styrene monomer (40% w/w) was added. Then the temperature was lowered to 80 °C and the whole mixture was continuously stirred. This gave a viscous resinous blend of styrenated unsaturated poly(ester-amide)s resin designated as (E₁₋₆). All these resins (E₁₋₆) were obtained in the form of

reactive resin and light reddish brown in color. Their synthetic steps are shown in the Scheme 2. The preliminary characterization data are furnished in the Table 2.

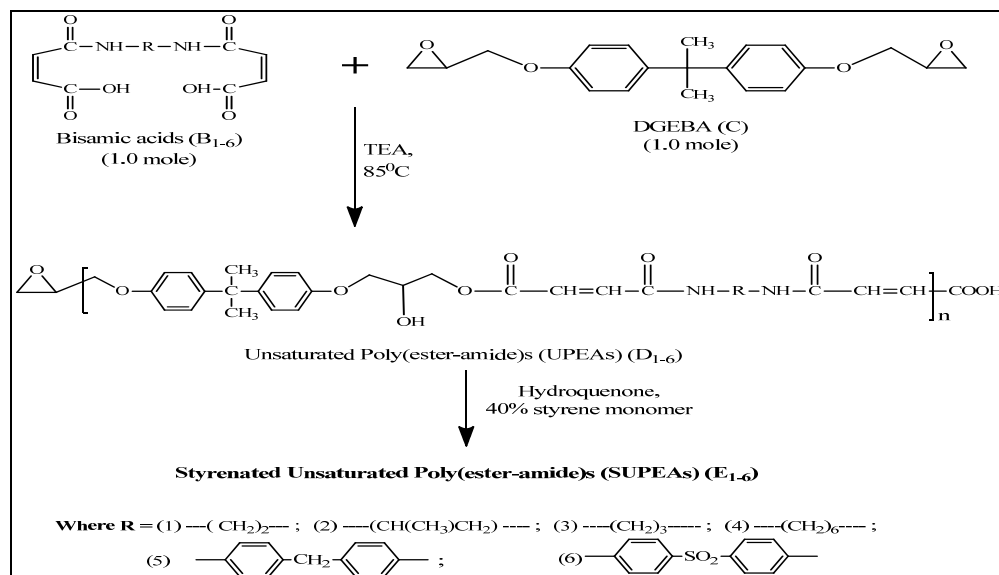


Table 2: Preliminary Characteristics of Styrenated Unsaturated Poly (Ester-Amide)s.

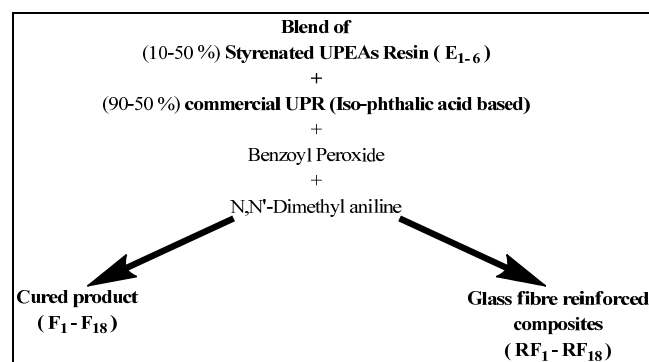
Sample ID	Appearance	Acid value
E ₁	Light Reddish brown liquid	30 ± 5
E ₂	Light Reddish brown liquid	30 ± 5
E ₃	Light Reddish brown liquid	30 ± 5
E ₄	Light Reddish brown liquid	30 ± 5
E ₅	Light Reddish yellow liquid	30 ± 5
E ₆	Light Reddish yellow liquid	30 ± 5

2.4 Blending and curing of Styrenated UPEAs with UPR (Iso-phthalic acid based)

The blending of Styrenated UPEAs resin (E₁₋₆) and commercial UPR (Iso-phthalic acid based) along with Benzoyl peroxide (BPO) as a catalyst and N,N'-Dimethyl aniline (DMA) as a promoter was carried out for room temperature curing. The blending proposition and Chart shows in the Table 3 and Scheme 3, respectively. The resulting solid hard materials (F₁₋₁₈) were designated as unreinforced material.

Table 3: Blended proportion of Styrenated UPEAs and UPR (Iso-phthalic acid based)

Sample Code	% SUPEAs (Bisamic acids based) w/w		Sample Code	% UPR w/w	
	% SUPEAs (Bisamic acids based) w/w	% UPR w/w		% SUPEAs (Bisamic acids based) w/w	% UPR w/w
B ₁	10%	90%	B ₄	10%	90%
	30%	70%		30%	70%
	50%	50%		50%	50%
B ₂	10%	90%	B ₅	10%	90%
	30%	70%		30%	70%
	50%	50%		50%	50%
B ₃	10%	90%	B ₆	10%	90%
	30%	70%		30%	70%
	50%	50%		50%	50%



3. Characterizations and thermal study

3.1. Characterizations of Bisamic acids and Styrenated-UPEAs

Prepared all unsaturated bisamic acids were characterized by melting point, acid value determination and FT-IR analysis spectra shown in the Figure: 1. Styrenated unsaturated poly (ester-amide)s were characterized by acid value determination.

3.2. Measurements

3.2.1 Curing

A curing study of all the Styrenated UPEAs-commercial UPR (Iso-phthalic acid based) blends (F₁₋₁₈) with and without continuous glass fiber was carried out using Benzoyl peroxide as a catalyst and N,N'-Dimethyl aniline (DMA) as a promoter at room temperature.

3.2.2 Thermogravimetric analysis

Unreinforced cured blend samples were subjected to thermogravimetric analysis (TGA) on NETZSCH STA449F3 thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10 °C min⁻¹ at GIRDA laboratory, Baroda. The

typical TG thermograms are shown in Figure 2, and data are furnished in Table 4.

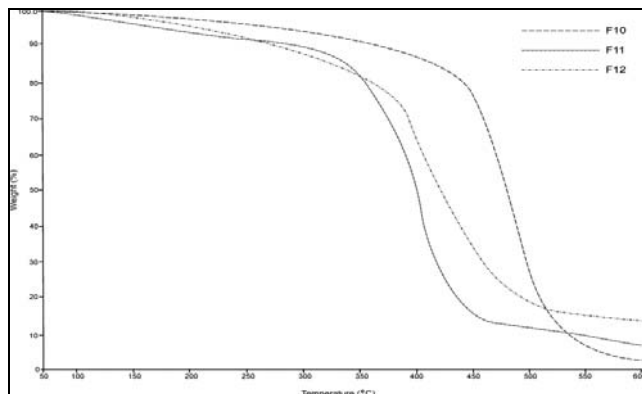


Fig 2: Typical TG thermograms of Blends samples F10-12

Table 4: Data obtained from TGA thermogram of samples (F1-18)

Sample code	% Weight loss at various Temp, °C From TGA					
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
F1	0.297	3.743	9.353	83.241	88.514	90.315
F2	1.547	6.536	13.550	90.204	99.182	-
F3	0.786	5.606	10.741	79.371	90.125	90.823
F4	0.630	4.823	12.075	82.304	74.970	88.085
F5	0.603	5.066	11.506	76.776	87.798	88.618
F6	0.209	3.988	10.298	74.356	85.840	86.719
F7	0.173	3.648	9.189	84.788	88.830	89.920
F8	0.245	4.387	11.031	76.817	86.681	87.403
F9	0.695	4.917	12.395	72.901	86.384	87.254
F10	0.028	2.061	7.195	20.055	81.381	86.418
F11	0.930	5.682	11.909	80.733	88.031	91.621
F12	0.958	6.621	15.297	61.059	83.662	85.915
F13	0.160	3.665	9.815	81.169	88.384	89.242
F14	0.281	5.040	12.831	70.369	80.393	83.430
F15	0.931	6.880	14.272	66.368	81.181	83.006
F16	0.677	4.443	11.194	83.614	89.870	90.628
F17	0.926	7.631	14.533	77.310	86.074	87.088
F18	0.862	7.909	15.042	70.280	81.892	83.258

4. Composite Fabrication

The composites were prepared using continuous glass fiber mat with a glass fiber to resin ratio of 40:60. 0.5% benzoyl peroxide as a catalyst based on the total weight of the Styrenated UPEAs-commercial UPR (Iso-phthalic acid based) blends with DMA as promoter for room temperature curing. This syrup was well stirred for about 5 min. The syrup was then applied on a 305 mm x 305 mm glass fiber ply. The prepregs plies were stacked on top of one another and pressed between mirror finished steel plates coated with a Miller film mold release sheet and compressed in a flat platen under 70 psi pressure and kept them at room temperature at their respective curing temperatures. The resulting laminates were designated as (RF₁ to RF₁₈) composites. The composites obtained were then machined to final dimensions.

4.1 Composite characterization

4.1.1 Mechanical Testing

All mechanical testing were performed using three test specimens and their average results are furnished in Table 5.

(1) The Tensile Strengths was measured on a UTM of Machine no. STS-165 at room temperature according to DIN EN 2747.

(2) The Flexural Strengths was measured on a UTM of Machine no. STS-165 at room temperature according to DIN EN 2746.

(3) The Inner Laminar shearing strengths were measured on a UTM of Machine no. STS-165 at room temperature according to ASTM D 3846.

Table 5: Mechanical properties of GFRC* of SUPEAs-UPR (Iso-phthalic acid based) Blends

Sample code	UNIT	TENSILE	FLEXURAL	ILSS
RF ₁	MPa	160.5	229.5	35.5
RF ₂	MPa	176.0	244.0	30.5
RF ₃	MPa	135.0	261.5	40.5
RF ₄	MPa	172.5	240.5	27.5
RF ₅	MPa	149.5	202.5	32.5
RF ₆	MPa	156.5	165.0	25.5
RF ₇	MPa	170.5	188.0	29.5
RF ₈	MPa	167.0	194.5	24.5
RF ₉	MPa	158.0	244.5	12.0
RF ₁₀	MPa	159.5	194.0	21.0
RF ₁₁	MPa	157.0	178.0	16.0
RF ₁₂	MPa	167.0	156.5	37.5
RF ₁₃	MPa	164.5	173.0	39.0
RF ₁₄	MPa	162.0	151.5	23.0
RF ₁₅	MPa	117.0	73.0	12.5
RF ₁₆	MPa	157.0	204.5	21.5
RF ₁₇	MPa	132.0	158.0	12.5
RF ₁₈	MPa	99.5	134.0	6.00

* Glass Fiber Reinforced Composite

4.1.2 Chemical resistance test

The resistance against chemicals of the composite was measured according to ASTM D 543. The specimen dimensions were 20mm x 20mm. The chemicals used for the study were H₂SO₄ (25% v/v), HCl (25% v/v), NaOH (25% w/v) ethanol, acetone, THF and DMF. The test was performed by dipping the composite sample in 100ml each of the above reagents for 7 days at room temperature. After 7 days the specimens were taken out from the reagents and after washing and drying they were examined.

5. Results and Discussion

In the Figure: 1 shown FT-IR Analysis Spectra of Typical Unsaturated Bisamic Acid. In spectra shown in Strong peak at 1705 cm⁻¹ is observed Carboxylic acid group. In peak at 1636 cm⁻¹ is indicated amide (C=O) group present. Unsaturation present in Bisamic acid peak at 849 cm⁻¹. These above peaks were observed to decide prepared completely Unsaturated Bisamic Acids.

Having unsaturation in both the unsaturated poly(ester-amide)s resins and unsaturated polyester resin, they were blended with Styrene monomer. As the structures of unsaturated poly(ester-amide)s and styrene are well established, the spectral study of the interacting blend of Styrenated UPEAs-UPR (Iso-phthalic acid based) has not been attempted.

These Styrenated UPEAs resins (E₁₋₆) are resinous form which can be cured by adding benzoyl peroxide as a catalyst and N,N'-Dimethyl aniline (DMA) as promoter at room temperature. The DSC study of all the blends did not give the proper thermogram. The thermograms show only steeper plot from the initial temperature. Thus may be due to fast curing reaction. Thus the DSC study has not been attempted. So all the blends were cured at room temperature for prolong time while the curing of all the blends exists rapidly in the temperature range of 70-120 °C. Thus, all the blends were

cured manually below 120 °C. This indicated that cross-linking took place rather than homo polymerization only as evidenced by high mechanical properties in Table 5.

Note that the polymerization condition of Styrenated UPEAs Resin blend is not of stereo regular type. Hence, if homo polymerization of styrene could have occurred in the present system, it could not be linear, but branched that might interact with the unsaturated segment of the UPR.

The unreinforced cured samples of Styrenated UPEAs-UPR blends (F₁₋₁₈) were analyzed by thermogravimetric analysis (TGA). Examination of the TGA data in Table 4 reveals that the cured samples started their degradation at about 150 °C and their initial weight loss was about 3%. This small weight loss might have been due to either insufficient curing of components used or due to the catalyst used. A weight loss of about average 20% was found range in between 350 °C to 400 °C. However, the rate of decomposition increased very rapidly in the range of 350 °C to 450 °C and the products were lost completely beyond 690 °C. It is interesting to note that the thermal stability increases with rise of SUPEAs in the blend irrespective of bisamic acids. The rise in UPR content in the blend deteriorates the thermal stability. This is very clearly indicated in the case of sample F₁₀ in Table 4 and also in Fig 2. Thus, the addition of SUPEAs into UPR to form useful resin blends by reducing ester groups, as done in vinyl ester resins, justifies present studies in order to improve the properties of resin blends.

The glass fiber reinforced composites of all Styrenated UPEAs-commercial UPR (Iso-phthalic acid based) blends (RF₁₋₁₈) were also prepared curing at the room temperature. These composites were also analyzed for their mechanical properties and their results are furnished in Table 5. Examination of the results reveals that the composites have good mechanical strength. The tensile strength remains around 160-176MPa for almost all composites while the flexural strength decreases with the size of the bisamic acid involved in the composite as expected.

The glass fiber reinforced composites of all Styrenated UPEAs-commercial UPR blends (RF₁₋₁₈) were also prepared curing at the room temperature. These composites were also analyzed for their chemical resistance. Results reveals that the composites have good resistance to common solvents like ethanol, acetone. The resistance of composites is found to decrease in the order:

Ethanol > Acetone > THF > HCl > NaOH > H₂SO₄

6. Conclusion

The present study is a novel approach to amalgamate three important resin classes: epoxy, polyamide and unsaturated polyester. Gradual reduction of ester links by adding mechanically strong epoxy links adds to the desired mechanical strength and resistance to aggressive environments. The addition of amide links adds to the polarity to the resin matrix, which the vinyl ester resins lack, necessary in some industrial applications. The polyester systems classified in to two main groups, those designed for high performance and those for the lowest cost. In reality, there is a continuum of system that merge in to each other, cheaper style of polyester being blended with the higher performance ones to increase processing tolerance or to improved properties. Thus it is simple process to tailor make the resin with desired properties.

7. Acknowledgement

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