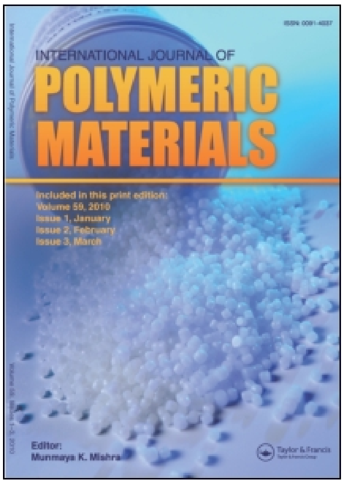

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Acetone – Formaldehyde – Phenol based IPNs for Glass Fibre Reinforced Composite Applications

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Three component IPNs Glass fibre reinforced composites (GRC) have been prepared from acetone-formaldehyde-phenol (AF-P) resin, Diglycedyl ether of bisphenol-A (DGEBA) (a commercial epoxy resin) and methyl methacrylate (MMA) (a vinyl monomer). The curing catalyst hexamethylene tetramine (HMTA) for AF-P, radical initiators 2,2'-azobisisobutyronitrile (AIBN) for MMA and curing catalyst 4,4'-diamino diphenyl methane (DDM) for epoxy resin were employed. All the IPN GRCs were characterized in terms of their resistance to chemical reagents, thermal behaviour (DSC, TGA) and mechanical properties.

Keywords: Composites; acetone-formaldehyde-phenol; IPNs; glass fibres

INTRODUCTION

IPNs (Interpenetrating polymer networks) are physical mixture of different homo or co-polymers. They are produced in order to improve certain final use of processing properties so that the property spectrum of bulk plastics can approach that of engineering plastics in an economical viable way. Such IPN may be from thermoplastics, thermosets or elastomers. Much of the work on IPNs based on different system have been reported [1-3]. Sperling *et al.*, have developed simply, effectively

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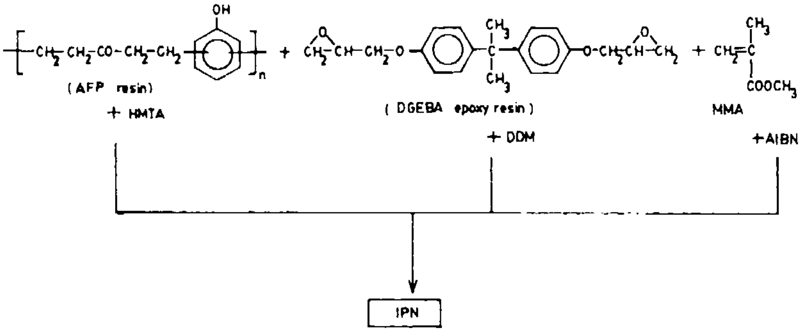
*Corresponding author.

and less expensively IPN based on castor oil [4] (an agriculture material). Many IPNs are also prepared from epoxy resin/thermoplastic resin [5, 6]. The area in which the IPN based on phenols has not been reported except one instance. Yamamoto *et al.*, developed IPN laminates using phenolic resin, epoxy and vinyl monomer [7] which have open the doors for broad industrial applications.

The present authors reported recently the glass reinforced composite based on acetone-formaldehyde-phenol [8]. Looking to the important properties of phenolic base IPNs [7] and individual properties of epoxy [9] and phenolics [10] it was thought interesting to explore the field of IPNs based on AF-P resin as shown in Scheme-I.



SCHEME I

EXPERIMENTAL

Materials

Commercial epoxy resin, diglycidyl ether of bisphanol-A (DGEBA) was obtained from synpol products Pvt. Ltd., Ahmedabad, India. The specification of DGEBA are as follows:

1. epoxy equivalent weight, 190;
2. viscosity, 40 – 100 poise at 25°C;
3. density at 25°C, 1.16 – 1.17 g·cm ^{3}.

Methylmethacrylate (MMA) was obtained from polymers unit, G. S. F. C. Ltd., Baroda, India. All other chemicals used were of laboratory grade.

Procedures

Preparation of Acetone-Formaldehyde-Phenol Resin

Acetone-Formaldehyde-phenol (AF-P) resin was prepared by the method reported in our earlier communication [8].

Preparation of Three Component IPNs Syrup

Three component syrups systems were prepared by dissolving AF-Phenol, DGEBA in methyl methacrylate (MMA) in different proportions. To this curing catalyst hexamethylene tetramine (HMTA) (0.5% of wt. of AF-P), initiator AIBN (0.2% of wt. of MMA) and 4,4′-diamino diphenyl methane (DDM) (0.2% of wt. of epoxy resin) were added under stirring and stirred well for 15 minutes to form a homogeneous syrup. Five such different syrup systems were prepared with different compositions and designated as I to V. In a similar manner three component syrups were also prepared by dissolving AF-PhOH, DGEBA and MAA containing 1 % ethylene-glycol dimethacrylate (EGDMA) a vinyl monomer crosslinker and designated as VI to VIII. The curing of all syrup systems has been followed by DSC. The data are shown in Table I. Based on their curing temperature all the syrups were subjected to bulk polymerization to form unreinforced IPNs and designated as IPN-I to IPN-VIII.

Preparation of IPNs Glass Fibre Reinforced Composites

A typical method for composites fabrication is given below.

TABLE I Curing characteristics of IPNs syrup system

Syrup	*Composition (% by weight)*				*Cure*	*Peak*	*Final*	*Activation*
System	*AFP*	*-DGEBA*	*-MMA*	*(EGDMA)*	*onset tempera-ture* T_i(°C)	*tempera-ture* T_p(°C)	*tempera-ture* T_f(°C)	*energy Ea* (KJ/mol)
I	40	20	40	(-)	127	187	212	110.1
II	30	40	30	(-)	125	178	212	125.0
III	20	60	20	(-)	125	175	205	130.6
IV	20	40	40	(-)	122	171	210	92.8
V	30	30	40	(-)	150	170	185	125.5
VI	30	30	40	(1%)	157	214	232	122.6
VII	20	60	20	(1%)	134	170	208	157.6
VIII	20	40	40	(1%)	143	174	205	235.0

A suspension of above syrup in acetone in ratio of 60:40 was prepared and stirred well for 5 minutes. The suspension mixture was applied with a brush to a 250 mm × 250 mm fibre glass cloth and the solvent was allowed to evaporate. The 10 dried prepregs prepared in this way were stacked one on top of another and pressed between steel plates coated with a Teflon film release sheet and compressed in a flat platen pressure under about 70 psi pressure. The prepreg stack were cured by keeping it in a preheated air-circulating oven maintained at 160 ± 5°C for 30 minutes and post cured for further 1 hrs at 175°C. The composite so obtained was cooled to 50°C before the pressure was released. Composite were designated as C-I to C-VIII as they were prepared from syrup system I to VIII. Test specimens were made by cutting the composites and machining them for final dimension.

MEASUREMENTS

Curing of syrup systems I to VIII was carried out by differential scanning calorimetry. A Du Pont 900 DSC was used for this study. The instrument was calibrated using standard indium metals with known heat of fusion ($\Delta H_f = 28.43$ J/g). Curing was carried out using a single heating rate (10 K min^{-1}) in nitrogen gas. The sample weight for this investigation was in the range of 4 to 5 mg, an empty cell was used as reference.

Cured samples were subjected to thermogravimetric analysis (TGA) on Du Pont 950 thermogravimetric analyzer in air at a heating rate of 10 K min^{-1}.

All chemical, mechanical and electrical tests of the prepared composites were conducted according to ASTM methods following the method reported [11].

RESULTS AND DISCUSSION

The cure reaction (IPN system) of AF-P:DGEBA: MMA and AF-P: DGEGA: MMA (1% EGDMA) was studied on DSC for the different proportions (Tab. I). The typical DSC thermogram data obtained from DSC scans are given in Table I. Examination of the DSC thermograms reveals that all the AF-P: DGEBA: MMA cured system gave a single exotherm peak in the range of 122°C to 222°C. This is indicating miscibility between three component i.e., extensive mixing between three components without any proof of molecular dispersion. Absence of T_g due to PMMA, may be due to formation of crosslinks through Michael addition reaction between diamine and MMA, i.e. part of PMMA crosslinks and losses it's T_g. The AF-P: DGEBA: MMA (1% EGDMA) cured system gave also a single exotherm peak in the range of 130°C to 232°C. Typical DSC thermograms are shown in Figure 1. The cure on set temperature (T_i), peak exotherm temperature (T_p) and temperature of completion of curing (T_f) were obtained and furnished in Table I. From the curing characteristic of varying syrup system it is observed that curing temperature increase, when % of AF-P is higher but at the same time activation energy is low. It may lead to faster rate of reaction. When % of AF-P and DGEBA is 30% and crosslinker of vinyl monomer EGDMA is added curing temperature is higher. It is also observed that activation energy (*Ea*)

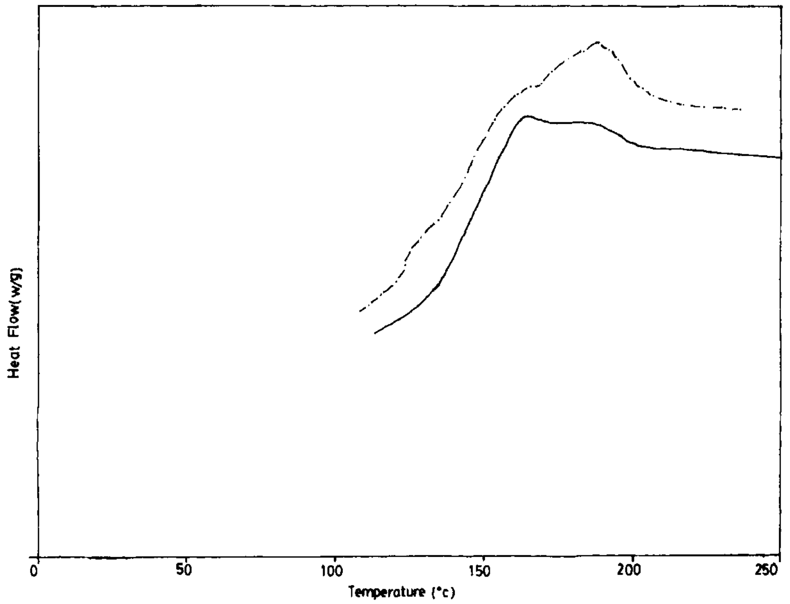


FIGURE 1 DSC thermogram of AFP-DGEBA-MMA(.-.-.-.-); AFP-DGEBA-MMA (1%EGDMA) (————).

increase with decrease in the % of AFP; indicating the lower reactivity of such systems. The kinetic parameters such as (*Ea*) (activation energy) were calculated by assuming that the curing reaction obeys Arrhenius type kinetics and that the peak maximum represents a point of constant conversion.

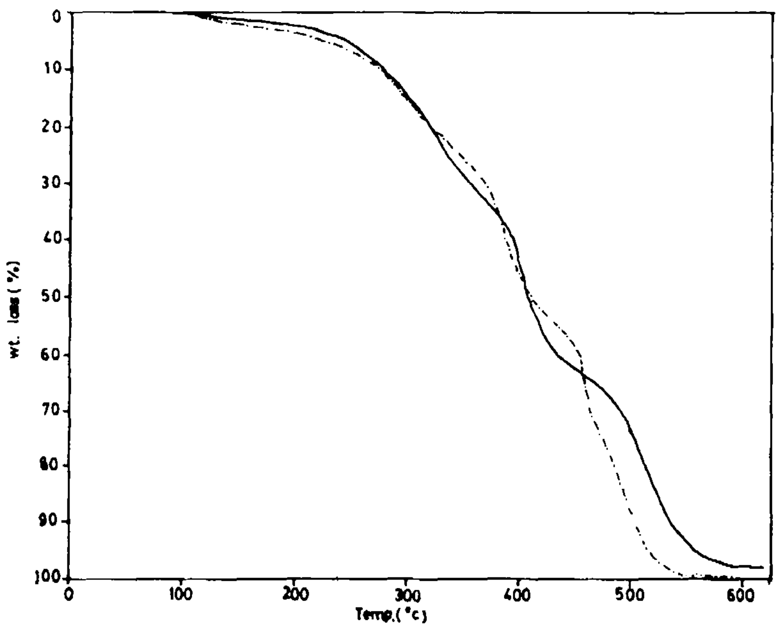


FIGURE 2 TG thermogram of AFP-DGEBA-MMA(--------); AFP-DGEBA-MMA (1%EGDMA) (———).

TABLE II TGA of unreinforced IPNs

	% Weight loss at °C from TGA				
IPNs	200	300	400	500	600
I	3.5	15.0	45.0	88.5	99.5
II	5.0	15.0	25.0	65.0	99.5
III	2.5	15.0	45.0	73.5	97.5
IV	5.0	12.5	45.0	70.0	96.5
V	2.0	13.5	22.5	64.5	87.0
VI	4.5	17.0	31.1	66.0	99.0
VII	3.0	16.0	45.0	74.0	98.5
VIII	4.5	13.5	50.0	76.0	99.5

TABLE III Chemical, mechanical and electrical properties of glass-reinforced IPNs composite based on AFP-DGEBA-MMA

Composite[a]	*% change on exposure to 25 % (W/V) NaOH*[b]		*Density (g/ml)*	*Flexural strength (MPa)(ASTM D-790)*	*Compressive strength (MPa) (ISO method)*	*Impact strength (MPa) (ASTM-D-256)*	*Rockwell hardness (R) (ASTM D-785)*	*Electrical strength (in air) (kv/mm)*
	Thickness	*Weight*						
C-I	1.2	1.1	1.44	118	179	220	111	18.7
C-II	1.2	1.2	1.48	113	188	217	108	18.4
C-III	1.0	1.1	1.58	112	194	215	104	19.1
C-IV	0.9	1.5	1.52	108	186	229	103	19.3
C-V	0.9	1.4	2.50	114	175	221	109	18.4
C-VI	1.1	1.2	1.54	116	189	232	112	20.6
C-VII	1.0	1.1	1.60	115	196	229	115	19.2
C-VIII	0.9	1.2	1.59	114	190	224	110	20.4

[a] Conditions. Reinforcement: E glass cloth; Plain Wave, 10 mm; 10 layers. Resin content, 60±2% curing temperature, 160±; 5°C, time 30 min; pressure, 60–70 psi, Composite size 250 mm × 250 mm, 3.0–3.5 thick.

[b] Unaffected by organic solvents and concentrated mineral acids (25% V/V).

All the unreinforced IPN are dark brown coloured and insoluble in almost all organic solvents.

The TGA (typical thermograms shown in Fig. 2) data of all unreinforced IPNs are given in Table II. The IPNs start their decomposition at around 300°C. The rate of decomposition increase between 350°C to 550°C and lose almost 99% of their mass at 600°C.

The produced IPN-glass reinforced composites are in the form of dark brown hard sheets. The density were in the range of 1.44 to 1.60. The higher density of above composite is attributed due to interpenetration and entanglement of polymeric chains [12, 13]. Chemical resistance studies at room temperature indicate that the IPNs glass reinforced composites were not affacted by immersion in organic solvents for 24 hours (alcohols, ketones, DMSO, 1, 4-dioxane, THF). It was also noted that concentrated hydrochloric acid (25% V/V) did not affacts the composites. However, exposures to concentrate alkali (25% W/V) results in slight change in thickness and weight (Tab. III). The chemical resistivity of all the composites indicates the high level of crosslinking of epoxy and vinyl monomer with AF-P resin. The mechanical properties of all composites are given in Table III.

The electrical strength of all the composites has been found in the range of 18.4–20.1 KV/mm.

CONCLUSION

The overall advantages of GRC base IPNs are as follows:

(i) All monomer/oligomer are easily and effectively mixed without any phase separation.
(ii) Void free composite could be prepared with good chemical resistance.
(iii) Ease of composite fabrication.

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