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RESEARCH ARTICLE

Interpenetrating Polymer Networks Based on Acetone-Formaldehyde-1,5-Dihydroxynaphthalene Resin and Their Glass Reinforcement

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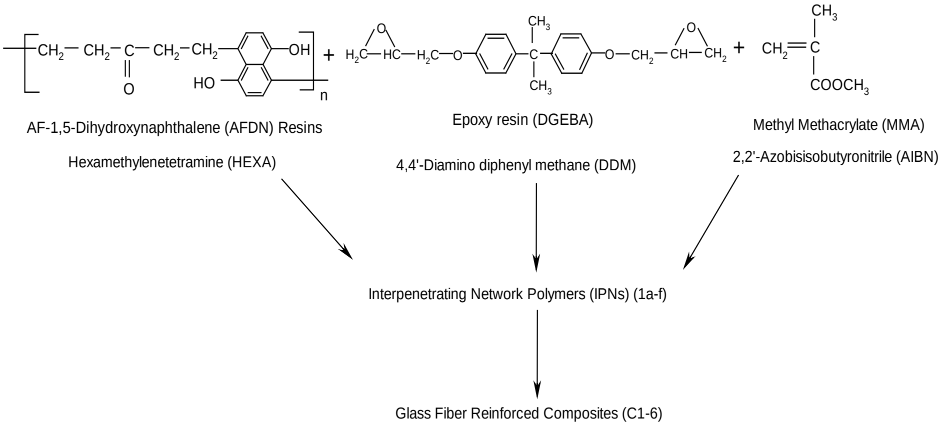
Abstract: Acetone-formaldehyde (AF) resin having dihydroxy functionality (-CH_2OH) was prepared and polycondensed with 1,5-dihydrxynaphthalene (DN) at equimolar. Three component interpenetrating polymer networks (IPNs) were prepared from actone-formaldehyde-1,5-dihydrxynaphthalene (AF-DN) resin, diglycidylether of bisphenol-A (DGEBA) and methyl methacrylate (MMA) monomer. Thermal behavior of IPNs was studied by a differential scanning calorimeter (DSC) and unreinforced cured samples of IPNs were subjected to thermogravimetric analysis (TGA). Glass fiber reinforced composites (GFRC) based on such IPNs have been prepared and characterized by chemical, mechanical and electrical properties.

Keywords: Interpenetrating polymer networks, Acetone-formaldehyde resin, Actone-formaldehyde-1,5-dihydrxynaphthalene resin, Glass fiber reinforced composites

Introduction

An interpenetrating polymer network system is simply known as any material that containing two or more polymers which are synthesized or cross linked together. These reactions may take place simultaneously. Interpenetrating polymer networks (IPNs) are getting increasing attention as materials with improved physical and mechanical properties that result from their multi component nature. IPNs are physical mixtures of different homo-or-co-polymers, in which they are cross linked[1]. Thermoplastic modification via blending or the addition to a thermoset is another possibility in order to improve certain properties has been extensively studied and reported[2-5]. Blending of two thermosets via IPNs has been extensively studied and reported[6-10]. Several studies on IPNs revealed an improved mechanical property[6]. IPNs are prepared in the form of film, alloy, foam and glass fiber reinforced composites[11-14]. Many IPNs have been also reported from novolac resin and/or thermoplastic resin[15-17]. Some work have been reported on phenolic type resins containing acetone-formaldehyde (AF) moiety[18-21] and observed that they have better chemical, mechanical and electrical properties than conventional phenolics (PF). Introduction of such resin into interpenetrating polymer networks (IPNs) may alter the properties of such resin to some extent. Also some work have been reported IPNs of[18-20] in order to improve chemical, mechanical and electrical properties[22-24]. In extension of this work[18-21] recently present author (BKP) has also reported some modification[25]. In extension of this work[25] the present article comprises IPNs based on acetone-formldehyde-1,5-dihydroxynaphthalene, diglycidylether of bisphenol-A (DGEBA) and methyl methacrylate monomer (vinyl monomer). The synthetic steps are scanned in Scheme 1.



Scheme 1. Synthetic steps

Experimental

Commercially available epoxy resin, diglycidylether of bisphenol-A (DGEBA) was obtained from synpol products Ltd.

The specifications of diglycidylether of bisphenol-A (DGEBA) are as follows:

1. Epoxy equivalent weight, 190.
2. Viscosity 40-100 poise at 25 ^{0}C.
3. Density at 25 ^{0}C, 1.16-1.17 g/cm.

E-type of glass woven fabric 0.25 mm thick was obtained from Unnati Chemicals, India used for glass reinforcement. All other chemicals used were of pure grade.

Preparation of acetone-formaldehyde resin

Acetone-formaldehyde (AF) resin was prepared by slight modification following the method reported in earlier communication[25]. The general procedure for the preparation of acetone-formaldehyde resin is as follows:

A mixture of acetone and formaldehyde in 1:1 mole ration with 5% alcoholic KOH was heated at 40-50 ^{0}C with constant stirring for 15 minutes. The resultant mixture was cooled at room temperature. The so-called resin obtained was a colorless thick liquid. It was neutralized by formic acid.

Preparation of acetone-formaldehyde-1,5-dihydroxynaphthalene (AFDN) resin

Acetone-formaldehyde-1,5-dihydroxynaphthalene (AFDN) resin have been prepared by method reported in literature[25]. The general procedure is as follows. Acetone-formaldehyde (AF) resin and 1,5-dihydroxynaphthalene (DN) in molar ration of 1:1 was refluxed in dioxane solvent using 2.5% KOH of the total weight for 2 h. The resulting solution is then poured immediately into distilled water and washed several times with distilled water in order to remove unreacted reactants.

Preparation of three component IPNs syrup

Three component syrup systems were prepared by dissolving acetone-formaldehyde-1, 5-dihydroxynaphthalene (AFDN) resin and diglycidylether of bisphenol-A (DGEBA) in methyl methacrylate (MMA) monomer in different proportions. To this curing catalyst, hexamethy-lenetetramine (HEXA) (0.5% wt. of AFDN resin), initiator 2,2’-azobisisobutyronitrile (AIBN) 2% wt. of MMA) and 4,4’-diaminodiphenyl methane (DDM) (2% wt. of epoxy resin) were added under continuous stirring and stirred well for 15 minutes to form a homogeneous syrup. Three such different syrup systems were prepared with different compositions (**1a-c**). In a similar manner three component syrups were also prepared by dissolving Acetone-Formaldehyde (AFDN) resin and diglycidylether of bisphenol-A (DGEBA) in methyl methacrylate (MMA) monomer containing 1% ethylene glycol dimethacrylate (EGDMA) a vinyl monomer cross linker (**1d-f**).

Composite fabrication

Glass fiber reinforced composites (GFRC) were prepared using *E*-type of glass fiber. Suspensions mixture of above syrup was prepared in tetrahydrofuran (THF). The mixture was applied with a brush to a 200 mm × 200 mm glass cloth and the solvent was allowed to evaporate. The ten dried prepregs prepared in this way were then stacked one on top of another and pressed between steel plates coated with a “Teflon” film release sheet and compressed under 70 psi pressure. The prepregs stacks were cured by heating it in an autoclave oven at 180±5 ^{0}C for 40 minutes and post cured for further 1 hour at 190±5 ^{0}C. The composites so obtained were cooled to 45-50 ^{0}C before the pressure was released. Composites were designated as C1-6. Test specimens were made by cutting the composites.

Curing study

A DuPont 900 DSC was used for the curing study of **1a-f** systems. The instrument was calibrated using standard indium metal with known heat of fusion (ΔH=28.45J/g). Curing was carried out using a single heating rate of 10 ^{0}C /min in air. The sample weight for this investigation used was in the range of 4-5 mg along with an empty reference cell.

Unreinforced cured samples were subjected to thermogravimetric analysis (TGA) using DuPont 950 thermogravimetric analyzer at a heating rate of 10 ^{0}C /min in air. The sample weight for this investigation used was in the range of 4-5 mg.

Composite characterization

All the chemical, mechanical and electrical tests on composites were conducted according to ASTM methods (as listed below) using three test specimens for each test.

Chemical resistance test

The resistances against chemicals of the composite samples were measured according to ASTM D 543.

Mechanical testing

Flexural strength

The flexural strength of the composites was measured on the Universal Instron Testing Machine of the model number A-7437. The tests were performed according to ASTM D-790 method at room temperature.

Compressive strength

The compressive strength of the composites was measured on a Universal Instron Testing Machine of the model number A-7437. The tests were performed according to ASTM D-695 method at room temperature.

Impact strength

The izod impact strength of the composites was measured on a ZWICK model number 8900 impact machine. The tests were performed according to ASTM D-256 method at room temperature.

Rockwell hardness

The rockwell hardness test of the composites was performed on a rockwell hardness tester model RAS / Saro Eng. Pvt. Ltd., India. The tests were performed at the room temperature. The rockwell hardness is obtained directly from the M scale dial reading.

Electrical resistances property

A Hewlett-Packed 4329 a high resistance meter was used to measure the resistivity of the composite samples, following the method of ASTM D 149.

Results and Discussion

The cure reaction (IPN systems) of AFDN:DGEBA:MMA and AFDN:DGEBA:MMA (1% EGDMA) were studied on a differential scanning calorimeter (DSC) for different proportions (Table 1). Results shows that all AFDN:DGEBA:MMA cured systems gave a single exothermic peak in the range of 159 to 219 ^{0}C, depending upon the nature of the IPN syrup. This indicates miscibility between three components. The AFDN:DGEBA:MMA (1% EGDMA) cured system also gave a single exothermic peak in the range of 165 to 228 ^{0}C. From the curing characteristics of varying syrup systems it is observed that curing temperature increases when % of AFDN resin is higher and % of DGEBA is lower but at the same time activation energy is low, indicating lower reactivity of such systems. When cross linker of vinyl monomer EGDMA with methyl methacrylate monomer. The kinetic parameters such as activation energy (Ea) were calculated by assuming that the curing reaction obeys the Arrhenius type kinetics and that the peak maximum represents a point of constant conversion. DSC for IPN sample 1d is shown in Figure 1.

Table 1. Curing characterization of IPNs

IPNs	Composition (% by weight)				Kick off Temp Ti, ^{0}C	Peak Temp Tp, ^{0}C	Final Temp Tf, ^{0}C	Activation Energy (Ea) kJ/mol
	AFDN	DGEBA	MMA	EGDMA				
1a	20	60	20	---	159	178	198	127
1b	40	40	20	---	160	194	207	128
1c	60	20	20	---	163	197	219	119
1d	20	60	20	1%	165	199	209	134
1e	40	40	20	1%	167	201	223	131
1f	60	20	20	1%	169	206	228	129

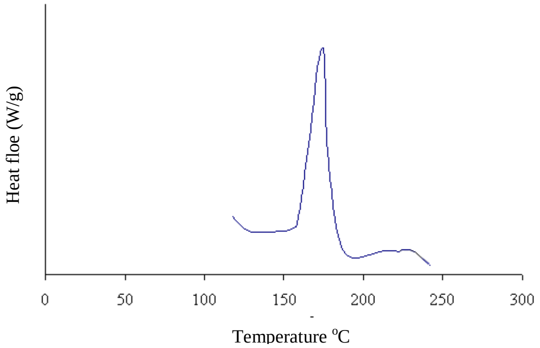


Figure 1. DSC of IPN (**1d**)

All the unreinforced IPNs are dark brown in color and insoluble in almost all common organic solvents. The TGA data of all the unreinforced IPNs are given in Table 2. TGA for IPN sample **1a** is shown in Figure 2.

Table 2. TGA of unreinforced cured IPNs

IPNs	% Weight loss at Various Temperatures, ^{0}C from TGA					
	200	300	400	500	600	700
1a	2.3	18	28	47	68	96
1b	2.1	12	24	41	60	92
1c	1.8	11	23	40	59	91
1d	2.4	13	25	42	65	92
1e	2.3	16	31	46	70	94
1f	2.2	11	24	41	65	92

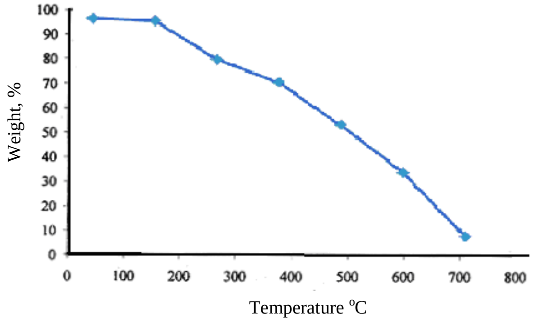


Figure 2. TGA of unreinforced cured IPN (**1a**)

Glass fiber reinforced composites prepared from IPNs are in the form of dark brown sheets. The densities were in the range of 1.43 to 1.47 g/cm^3. The higher densities of the composites are attributed to interpenetration and entanglement among polymeric chains[26]. The chemical resistance study at room temperature indicates that the composites prepared from IPNs were not affected by immersion in organic solvents for 24 hour (Alcohol, Ketone, DMSO, DMF, 1,4-Dioxane, THF). It was also noted that concentrated HCl (25% V/V) did not affect the composites. However, exposures to concentrated NaOH (25% W/V) results in slight change in the thickness and cause weight loss of about 0.9 to 1.1% (shown in Table 3). The chemical resistivity of all the composites may be due to the presence of aromatic rings and interpenetration of epoxy resin, PMMA and AFDN resin.

Table 3. Chemical, mechanical and electrical properties of glass fiber reinforced composites (GFRC) based on IPNs

GFRC	% Change on exposure to 25% (W/V) NaOH		Density g/cm^3	Flexural strength (MPa)	Compressive strength (MPa)	Impact strength (MPa)	Rockwell hardness (R)	Electrical strength (in air) kV/mm
	Thickness	Weight						
C1	0.9	1.0	1.44	281	283	290	114	19.3
C2	1.0	1.1	1.43	279	284	289	113	19.5
C3	1.0	1.1	1.43	276	285	289	112	19.7
C4	0.8	0.9	1.44	274	287	292	117	20.5
C5	0.8	0.9	1.45	273	289	292	116	20.7
C6	0.9	1.0	1.47	270	291	291	115	20.9

The mechanical properties of all composites are given in Table 3. The results suggest that composites prepared from IPNs, have good mechanical properties because of interpenetration and compatibility of the component networks. The presence of flexible segments of epoxy resin, PMMA and aliphatic ketone of AFDN resin in produced IPNs increases mechanical properties. Further, more mechanical properties of all the IPNs increases due to incorporation of EGDMA cross linker of vinyl monomer; this increase might be due to greater interpenetration. The electrical strength of all the composites has been found in the range of 19.3 to 20.9 kV/mm.

Conclusion

Following conclusions have been made from the prepared IPNs: The prepared composite gives good chemical and mechanical resistance properties. Easy of fabrication and processability. Better mechanical properties than those of epoxy-based composites. The produced IPNs can be used for metal coating, impact resistance plastics, foam, plastics and glass fiber reinforced composites (GFRC).

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