

EXECUTIVE SUMMARY OF THE PROJECT REPORT

UGC Minor Research Project: F.NO. 47-088/07 (WRO); Dated- 16/01/2008

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1.1 Preparation of bismaleimides:

The bismaleimide monomers were prepared by using different diamines (4-aminomethyl-benzyl amine, 4-4-Aminomethyl-benzyl-benzylamine, and 4,4'-diamino-diphenyl-methane) and maleic anhydride to get bismaleimic acid, followed by their cyclodehydration with acetic anhydride and fused sodium acetate, followed by a slightly modified procedure earlier.

To a vigorously stirred solution of diamines (4-aminomethyl-benzyl amine, 4-4-aminomethyl-benzyl)-benzylamine, 4,4'-diamino-diphenyl-methane) (0.1 mol) in dry acetone, the maleic anhydride (0.2 mol) in dry acetone, was added drop wise in a nitrogen atmosphere at 5⁰C, within 30 minutes. The pale yellow or white precipitate of bismaleimic acid was obtained on the addition of maleic anhydride. The reaction mixture was vigorously stirred for one hour after the completion of the addition of maleic anhydride. The reaction mixture was then kept for one hour with stirring at room temperature. To this reaction mixture, fused sodium acetate (6 g) and acetic anhydride (70 ml) was added while continuing the stirring. The reaction mixture was then heated up to its refluxing temperature for three hours until the solution became clear. The clear brownish colored solution was poured over crushed ice and repeatedly washed with water and dried quickly in air.

1.2 Preparation of Bismaleimide-diamine-oligomers (i.e Amino terminated oligoimides) [AOIs]:

Synthesis of polyimides based on Michael addition reaction of bismaleimide and diamine [4,4'-diamino-diphenyl-methane, 4,4'-diamino-diphenyl-ether, 4,4'-diamino-diphenyl-sulfone, 4,4'-diamino-diphenyl-amide, 4,4'-diamino-diphenyl-sulfonamide, 4,4'-diamino-aza-diphenyl, 4-methyl-1,3-di amino benzene, 4-methoxy-1,3-di amino benzene, and 4-chloro-1,3-di amino benzene] at equimolar or higher molar ratios of bismaleimide and diamine has been reported so far. The Michael addition reaction method has been adopted for

the synthesis of produced oligoimides from lower ratio of bismaleimide and diamine. As the 4,4'-diamino biphenyl methane is well known as epoxy curing agent, so it was selected as diamine reactant and various bismaleimide as variant. Synthesis of oligoimides was carried out by varying the molar ratios of bismaleimide to diamine. The molar ratios of bismaleimide to diamine used were 1:2.

To a well stirred molten state of diamine, bismaleimide was added gradually at 125-130⁰C over a period of 30 minute. The resultant homogeneous viscous mass was poured immediately into a large amount of solvent ether cooled by ice. The ether was decanted and washed twice with more ether to remove unreacted diamine. The dried powder was then washed with hot DMF (20 ml) to remove unreacted bismaleimides. The resultant oligoimides was then dried in vacuum oven.

1.3 Preparation of acryl terminated oligoimides (i.e ACOIs):

To a suspension of amino terminated oligoimides [AOIs] (0.05 mol) in THF (100 ml), acryloyl chloride (0.05 mol) was added drop wise at room temperature. Then equivalent amount of K₂CO₃ was added to neutralize the resulting HCl. The resultant acryl end capped oligoimides (AcOIs) were obtained in the form of yellow amorphous powder.

1.4 Characterization of ATOs and AcOIs:

The prepared amino terminated oligoimides (AOIs) and acryl terminated oligoimides (AcOIs) were characterized by elemental analysis, Infrared spectroscopy. In addition to this thermo gravimetric study was performed.

1.4.1 Elemental analysis:

Elemental analysis was carried out with a C, H, N elemental analyzer (ThermoFinnigan Flash 1101 FA, Italy).

1.4.2 IR Spectroscopic analysis:

IR spectra of the polymer samples were recorded in KBr. Carefully purified and dried KBr was used for purpose. The pellet for the IR study was prepared by mixing uniformly 2-3 mg of polymer sample with 1gm of pure crushed KBr. This mixture is compressed to a disc at a

pressure of 15,000 psi in vacuum. The spectrum of pellet was scanned on “Nicolet 760D” IR spectrometer.

1.4.3 Thermogravimetric study:

The thermogravimetric analysis (TGA) of AOIs and AcOIs samples has been carried out by using a “Universal V 3.0 G TA Instrument Thermo gravimetric analyzer” in a slow stream of air. The boat prepared from the platinum foil holds the polymer sample that is to be analyzed. It was properly washed and dried. It was suspended on the quartz rod in the TGA balance. The sample (about 5 mg) was placed in the boat. The sample in the boat is covered by quartz tube in which the flow of air was maintained. The weight of the sample was noted on the TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was started by heating the system at a constant heating rate of 10 °C / min. Simultaneous change in the weight was recorded automatically with time (temperature). This will reveal the percentage weight loss of the material as a function of time and also of the temperature. The experiment was stopped at about 800°C. The thermograms were analyzed to obtain the information about the percentage weight at different temperatures.

2.1 Synthesis of Interacting Blends of ATOs (7a-o) with N-phenyl maleimide Monomer:

When the acid value of acryl terminated oligoimides falls below 60 mg KOH /g, 0.05 % of the weight of the above, hydroquinone was added as an inhibitor. The whole reaction mixture was stirred well for few minutes maintaining the temperature at 85°C. Then the temperature was lowered to 80°C and 50% of the total weight of the above, N-phenyl maleimide monomer was added. The reaction mixture was then continuously stirred at 80°C for one hour. It is then discharged to give the-NPM blends. All the blends were in form of viscous resinous syrup. The Infrared spectra of acryl terminated oligoimides-NPM blends are obtained to characterize them.

2.2 Thermal analysis by differential scanning calorimeter (DSC):

DSC technique is employed to study the curing reaction of acryl terminated oligoimides NPM using benzoyl peroxide as a catalyst. The curing reaction was monitored on Universal V3.0G TA instruments.

The curing study of all the (6a-o)-NPM blends was carried out by using benzoyl peroxide (BPO) as a catalyst. 0.05 % benzoyl peroxide based on the total weight of the resin sample was added. Examination of the DSC Thermogram of all the NPM blends revealed that all the NPM blends with BPO as a catalyst gave a single exothermic peak in the range of 90 to 175 °C. The weak endothermic peak observed in some the DSC thermograms of blends. This indicates the minor formation of homopolymer. From the DSC thermograms, the cure onset temperature (T_i) in the range of 95 to 115 °C, peak exotherm temperature (T_p) in the range of 125 to 140 °C and the temperature of completion (T_f) in the range of 150 to 175 °C for each of the NPM blends were obtained. From the DSC thermograms the values of kinetic parameters such as activation energy (E_a) in the range of 100 to 165 kJ/mol. and the order of reaction (n) in the range of 2.15 to 3.30 were also obtained.

2.3 Characterization of Unreinforced Cured-NPM Blends:

The unreinforced cured-NPM blends were characterized thermo gravimetrically. The cured samples were prepared by carrying out the cross linking reaction between-NPM blends with benzoyl peroxide (0.05 % of the weight of resin) as a catalyst. This mixture was heated in a porcelain disc at their respective curing temperature for about an hour. The porcelain disc was allowed to cool to the room temperature. The cross linked material was collected and was subjected to the thermo gravimetric study on a Universal V3.0G TA instruments. Thermogravimetric analysis of all the unreinforced cured-NPM blends revealed that all the resins degrade in a single step. All the resins started their degradation at about 300 °C and their initial weight loss was about 2 - 20 %. This weight loss may have been due to either insufficient curing of the components used or due to the catalyst used. The rate of degradation for all the NPM blends increases very rapidly between 300 – 450 °C, where about 20 to 73 % weight loss is observed. The weight loss of about 65 to 75 % for all the NPM blends is observed at 600 °C.

2.4 Fabrication of Glass Fibre Reinforced Composites:

The process for making glass fibre reinforced composites (GRC) comprises of:

- (a) Formation of resin and curing agent solution for impregnation of the prepregs.
- (b) Wet hand lay-up of prepregs with the above formulated resin solution.

(c) Laid up prepregs stacks and to cure by heating.

The composites were made from woven E-type plain glass cloth by using wet hand lay-up prepregs technique using the following materials:

- I. Three ratios of Acryl terminated Oligoimides to N-phenyl maleimide solution were used as resin matrices for the fabrication of glass fibre reinforced composites.
- II. Woven E-type plain glass cloth was obtained from Unnati Corporation, Ahmedabad.
- III. Azobisisobutyronitrile (AIBN) and solvent THF used were of laboratory grade.

2.4.1 Composite fabrication:

The composites were prepared from a typical method of composite fabrication is given below. Three ratios of AcOI to N-phenylmaleimide solution. A suspension of acryl end capped oligoimide (AcOI) and thermoset N- phenylmaleimide solution was prepared in tetrahydrofuran was prepared and stirred for 5 min. To this, AIBN was added as an initiator and was stirred well for few minutes. The suspension was then applied with a brush on a 150 mm x 150 mm glass cloth. The 10 dried prepreg prepared by these way were then stacked one on top of another and pressed between the steel plates coated with a Teflon film release sheet and compressed in a flat platen under 70 psi (0.4 MPa) pressure the prepreg stacks were cured by heating at 150 °C for 10 hrs in an air circulated oven. The composite so obtained was cooled to 50°C before the pressure was released. The specimens were made by cutting the composites and machining them to final dimensions according to ASTM standards. The processing parameters for the composite fabrication are as follows:

Glass fiber cloth : Resin mixture Ratio = 60 : 40 w/w	
Reinforcing material	E-glass cloth, 15mile, 10 layers
Resin content	40 ± 2 %
Initiator	Azobisisobutyronitrile (AIBN)
Composite size	150 mm × 150 mm
Curing temperature	150 °C
Curing time	10 hours
Pressure	70 psi

2.5 Characterization of the prepared Composites:

The use of the composites for different applications depends upon the properties of that particular composite fabricated by employing a particular resin. Hence here, the fabricated

glass fibre reinforced composites from (7a-o) were characterized for their physical, mechanical, electrical and chemical properties.

2.5.1 Physical Properties: The glass fibre reinforced composites of (7a-o) were evaluated for their physical properties such as density and colour. They were also evaluated for the properties such as resin content, water absorption and boiling water absorption.

2.5.1.1 Resin content: The resin contents of the composites were determined according to the following method. The dry weighed sample of the composite (1 cm × 1 cm) was heated at around 600°C for about 2.5 hours till a constant weight is obtained in electric furnace and weighing the residue. The resin content was calculated as:

$$\text{Resin content (\%)} = [1 - (\text{Weight of Residue} / \text{Weight of Sample})] \times 100$$

2.5.1.2 Water absorption: The dry weighed sample piece of the composite (2 cm × 2 cm) was immersed in water for 24 hours at room temperature. The sample was then wiped out with the filter paper and weighed. The water absorption was calculated as:

$$\text{Water absorption (\%)} = (\text{Increase in weight of sample} / \text{Weight of sample}) \times 100$$

2.5.1.3 Boiling water absorption: It was determined by immersing the dry weighed sample of the composite (2 cm × 2 cm) in the boiling water for one hour. The boiling water absorption was calculated using the same above equation.

2.5.2 Electrical properties: The composites prepared from various mixture of acryl terminated oligoimide and N-phenyl maleimide were also analyzed for their mechanical properties using ASTM methods.

2.5.3 Mechanical properties: All the acryl terminated oligoimide based composites have better mechanical properties. There is not much variation in the mechanical properties in all the series. The structure of the glass cloth core fibers in the direction of the core plane is almost random. There are relatively very few fibres oriented in the direction perpendicular to the plane. During compression, the fibre structure oriented perpendicular to the plane is diminished during compression.

The composites were fabricated from acryl terminated oligoimide + N-phenyl maleimide (7a-o) using AIBN as a initiator. Resin content of the fabricated composites was determined by a reported method for all the composites and was found in the range of 37.5 to 39 %. From the

results, it is observed that around 1-4 % loss of the matrix system took place during the workup of composite fabrication. Examination of the result reveals that for such type of acryl terminated based composites absorb about 2.10 to 3.13 % of water. Results also reveals that, all composites, the percentage water absorption is more in that resin systems. The results of the boiling water absorption test reveal that there is 2.90 to 4.10 of boiling water absorption in all the composites. Results also reveals that, the percentage boiling water absorption is more in that resin systems.

The electrical strength of the composites is in the range of 20.3 to 23.8 kv/mm respectively. As there is no appreciable change in the electrical strength, no attempt was made to interpret this data. However, the values of the electrical strength of the composites of acryl terminated oligoimide type of resins are rather low. This could result in a charred path, over which subsequent discharge could take place a minute leakage of current may arise from surface contamination.

The results of the chemical resistance test of the composites fabricated from acryl terminated oligoimide have revealed that all the composites are very negligibly affected by the common organic solvents like ethanol, acetone etc. However, considerable percentage change in thickness and weight is observed in DMF, H₂SO₄ and NaOH for all the composites.

List of Publications:

1. "Novel Interacting Blends On Acryl Terminated Oligoimides and Vinyl monomers", *J. Chem. Pharm. Res.* R R.Patel and **M. C. Patel**, **2011**, 3(1); 492-500.(ISSN: 0975-7384)[**H Index: 15**]
2. **Patel M C** and Patel R R, "Novel Interacting Blends Based On Amino Terminated Oligoimides-II", *E J. Chem.* **2012**; 9(4); 1960-1967.(ISSN: 0973-4945) [I F: **0.696**]
3. Interecting Blends Based on Amino Terminited Oligoimides by Using Michael Addition Reaction, *Alfa Univarsal: Int. J Chem.*, R R.Patel and **Mukesh C. Patel** , **2011**, 2(3), 174-180 (**2011**).) [IF: Still computing] (ISSN: 2229-4775).
4. , "Novel Interacting Blends Based On Amino Terminated Oligoimdes-II", *Adv. In applied Sci. Res.* **2011**; 2(4); 472-479. [IF: Still computing] (ISSN: 0976 – 8610)

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