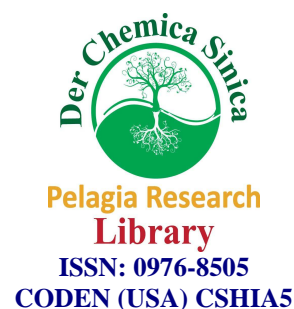




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Novel interacting blends based on amino terminated oligoimides by using N-phenylmaleimide with Michael addition reaction

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ABSTRACT

New amino terminated oligoimides (AOIs) were prepared by the Michael addition reaction of various bismaleimide (1), namely 1,1'-(1,4-phenylene)dipyrrolidine-2,5-dione with excess of various diamines(2a-c). These AOIs were characterized by elemental analysis, FT-IR spectral studies and number average molecular weight estimated by non-aqueous conductometric titrations. AOIs were then treated with acryloyl chloride and resultant acryl terminated oligoimides (AcOIs) samples were also characterized thermogravimetrically. Each of these AcOI was then combined with the N-phenyl maleimide (PM) in THF solvent. The resultant suspensions were then heated in the presence of azobisisobutyronitrile (AIBN) as an initiator. The AcOI and PM polymerized through double bond simultaneously and form interacting blends, which were analyzed thermogravimetrically. The glass fiber reinforced composites were fabricated by using the suspensions of the AcOI and PM. The composites of Interacting blends were analyzed for their mechanical, chemical and electrical properties.

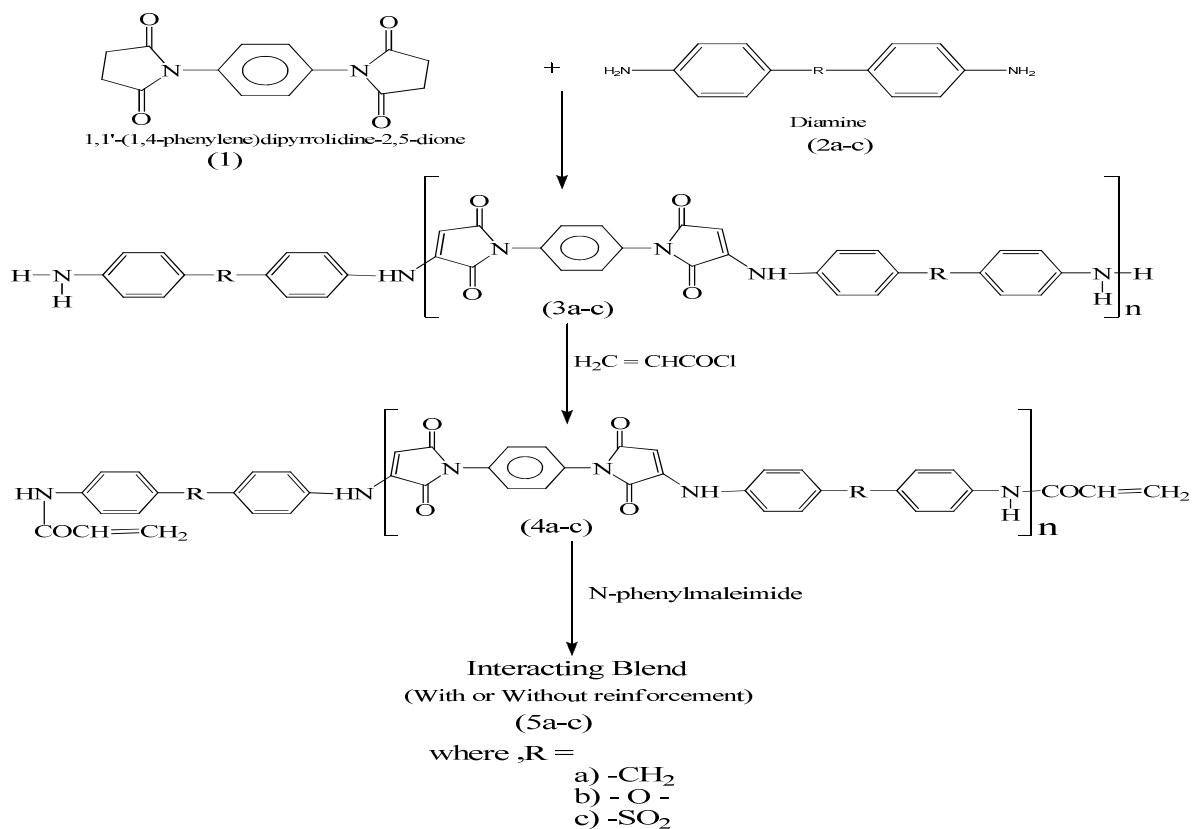
Key words: amino terminated oligoimides (AOIs), acryl end capped oligoimides (AcOIs), Michael addition reaction, *p*-xylylene diamine, acryl amide, AIBN and glass fiber reinforced composites.

INTRODUCTION

The polyimides as high performance polymers are well established [1]. Applications ranging from aerospace to microelectronics have utilized the outstanding thermo-oxidative stability of these polymers. Recently, the interest has accelerated in tailoring chemistry of polyimide So as to approach the optimum balance of properties required for ease of processing. Many aspects of research pertinent to various polyimide have been well documented [2-8].

Such approach can be received by interacting of thermoplasts i.e. acryl terminated oligoimides (AOIs) with thermosets i.e. poly N-phenyl maleimide. Such type of study has not been reported

so far. Though the styrene- N-phenyl maleimide (SPM) copolymers are reported for many applications [9-14]. So, the initial work has been carried out by present authors [15]. Thus in continuation of this work the present paper comprises the initial work about such interacting blends, scanned in scheme 1.



Scheme 1

MATERIALS AND METHODS

N- Phenyl maleimide, 1, 4-xylylene bismaleimide and diamines (2a-c) were used of A.R.grade. The diamine used for the synthesis of bismaleimides.Plain weave fibers, in the form of E-glass woven fabric (polyimide compatible) 0.25 mm thick (Unnati Chemicals, India) of a real weight 270 g/m² were used for composite fabrication. All the other chemicals used were of the laboratory grade.

Synthesis of bismaleimides

The bismaleimide 1,1'-(1,4-phenylene)dipyrrolidone-2,5-dione was synthesized by condensation of maleic anhydride and the 1,4-xylylene diamine following the reported methods [16,17].

Synthesis of amino terminated oligoimides

The amino terminated oligoimides (AOIs) were prepared by the Michael addition reaction between the bismaleimide and diamine (2a-c) at the molar ratio of 1:2. They were prepared according to the method reported [18]. All the three AOIs were designated as (3a-c).

Synthesis of acryl end capped oligoimides

To a suspension of AOIs (3a-c) (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 orange amorphous powder. All the three AcOIs were designated as (4a-c).

Synthesis of interacting blends of AOI-N-phenyl maleimide(PM)

Each of the AcOIs (4a-c) sample and N-phenyl maleimide (PM) with various weight percentages were prepared and shown in Table 1. To one of these mixtures, AIBN was added as an initiator and then the mixture was heated at 80° C for 2 hrs. and then at 200 °C for 1 h. The resulted cross linked of polyimide and was in the form of solid material. They were designated as (5a-c).

Composite fabrication

The composites were prepared from a typical method of composite fabrication is given below. Three ratios of AcOI to N-phenylmaleimide solution as shown in the below Table 1. A suspension of acryl end capped oligoimide (AcOI Scheme 1) and thermoset N-phenylmaleimide solution was prepared in tetrahydrofuran was prepared and stirred for 5-10 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 prepreges 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 prepreges stacks were cured by heating at 150 °C for 10 hrs. In an air circulated oven. The composite so obtained was cooled to 50-55 °C before the pressure was released. The specimens were made by cutting the composites and machining them to final dimensions.

Table 1. Various weight percentages

	I	II	III
AcOIs % (3a—c)	80	60	40
N-phenylmaleimide	20	40	60

Measurements

The C, H, N contents of all the amino terminated oligoimides (AOIs) (3a-c) and acryl end capped oligoimides (AcOIs) (4a-c) were estimated. Their results are furnished respectively, in Tables 2 and 3. IR spectra of AOIs and AcOIs were taken in KBr pellets using KBr as a reference on a Nicolet Impact 7600 D spectrophotometer.

The number average molecular weights of the AOIs (3a-c) were determined by the non-aqueous conductometric titration following the reported method[19, 20]. Formic acid-acetic acid mixture was used as the solvent and standard perchloric acid in acetic acid was used as a titration. A digital conductivity meter (Tosaniwal, India) was used for the titration. Their results are furnished in Table 2. AcOIs (3a-c) were also analyzed for their number of double bonds per repeating unit employing mercury catalyzed bromate-bromide titration method [21].The AOIs (3a-c) and AcOIs (4a-c) were also characterized thermo gravimetrically on a Du Pont 990 Thermal analyzer MK-III. Their results are furnished in Tables 2 and 3, respectively.

Table: 2 Characterization of amino terminated oligoimides(3a-c)

AOIs sample	Elemental Analysis Calc.(Found)				No. average molecular weight (Mn)	Percent weight loss at various temperatures				
	%C	%H	%N	%S		300	400	500	600	700
3a	72.71(72.73)	4.88(4.87)	12.72(12.75)	-	1935	39	51	86	93	98
3b	68.67(68.68)	4.25(4.27)	12.64(12.65)	-	2072	37	57	77	90	96
3c	59.99(59.97)	3.71(3.72)	11.05(11.03)	8.43(8.45)	1758	22	33	48	73	99

Table: 3 Characterization of acryl end capped oligoimides (4a-c)

AcOI sample	Elemental Analysis Calc.(Found)				No. of double bonds per unit	Percent weight loss at various temperatures				
	%C	%H	%N	%S		300	400	500	600	700
4a	71.86(71.85)	4.72(4.73)	10.93(10.96)	-	1.97	18	38	58	71	95
4b	68.39(68.37)	4.17(4.18)	10.88(10.89)	-	1.96	21	42	64	74	96
4c	60.82(60.85)	3.71(3.72)	9.67(9.68)	7.38(7.39)	1.99	24	45	68	78	99

Interacting blend Polyimide samples were subjected to thermo gravimetric analysis (TGA) on a Du Pont 990- thermal analyzer MK-III in air at a heating rate of 10 °C min⁻¹. The TGA data are furnished in Table 4. They were also subjected to the Differential thermal analysis to get their glass transition temperature. Their results are furnished in Table 4.

Table: 4 TGA of Interacting blends Polyimides

Interacting blend	AcOI-PM	Percent weight loss at various temperatures		
		300	450	750
5a I	80:20	30	43	73
5a II	60:40	32	44	75
5a III	40:60	30	45	76
5b I	80:20	31	46	78
5b II	60:40	35	48	83
5b III	40:60	38	51	80
5c I	80:20	33	49	77
5c II	60:40	36	53	85
5c III	40:60	37	54	88

Composite characterization Chemical resistance test

The chemical resistant test for the entire composite sample was performed according to ASTM D 543Y67. The composite sample dimensions were 25 x 25 x 3 mm. The samples were immersed in 25% v/v H₂SO₄, 25% v/v HCl 25% w/v NaOH, Ethanol, Acetone, DMF and THF for seven days at room temperature. After seven days the samples were taken out from the reagents and were analyzed for their percentage change in their thickness and weight. Their results are summarized in Table 5.

Mechanical test

All the mechanical and electrical tests were performed using three specimens and their average results are summarized in Table 6.

Table: 5 Chemical resistance tests of Interacting blends

Interacting blends polyimide	5a I % change		5a II % change		5a III % change		5b I % change		5b II % change		5b III % change		5c I % change		5c II % change		5c III % change	
	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.	Thi.	Wt.
25%H ₂ SO ₄	1.37	1.99	1.35	1.06	1.36	1.93	1.35	1.07	1.35	1.01	1.37	1.00	1.37	1.94	1.35	1.94	1.40	1.03
25%HCL	1.32	7.88	1.30	1.91	1.33	1.86	1.33	1.96	1.30	1.95	1.34	1.91	1.35	1.94	1.33	1.92	1.38	1.94
25%NaOH	0.87	1.30	0.89	1.32	0.95	1.37	0.86	1.30	0.87	1.31	0.84	1.33	0.87	1.37	0.92	1.28	0.83	1.34
Ethanol	0.62	1.24	0.68	1.26	0.65	1.29	0.67	1.21	0.71	1.29	0.77	1.23	0.75	1.31	0.77	1.25	0.71	1.30
Acetone	0.55	1.05	0.57	1.00	0.56	0.93	0.56	1.03	0.63	0.94	0.68	0.95	0.67	1.03	0.71	0.95	0.63	1.01
DMF	1.24	1.93	1.23	1.92	1.24	1.92	1.26	1.93	1.20	1.90	1.29	1.92	1.29	1.95	1.29	1.99	1.33	1.96
THF	1.01	1.84	0.98	0.99	0.95	1.89	1.04	1.87	1.06	1.89	1.08	1.84	1.05	1.79	0.98	1.88	0.98	1.84

Thi. = Thickness, *Wt.* = Weight

Table 6: Mechanical and electrical properties of interesting blend of polyimide

Interacting blend polyimides sample	Compressive strength (MPa)	Notched impact strength	Rockwell hardness (MPa)	Electrical strength in air (kV/mm)	Flexural strength (MPa)
5a I	295	293	131	16.8	307
5a II	299	296	134	16.9	306
5a III	303	298	135	17.4	298
5b I	302	299	136	17.7	305
5b II	305	297	135	17.5	303
5b III	307	295	137	18.4	297
5c I	305	298	132	17.7	293
5c II	309	299	133	18.7	289
5c III	307	302	138	18.2	286

The compressive strength was measured on a Universal Instron testing machine model no. A-74-37, at the room temperature according to ASTM D 695. The notched izod impact strength of the composites was measured on a Zwick Model no. 8900 Impact machine at the room temperature according to ASTM D256. Rockwell Hardness was measured on a Rockwell hardness tester model no. RAS/Saro Engg. Pvt. Ltd. India according to ASTM D 785 at room temperature. The measurement of Flexural strength was carried out with Universal Instron Testing Machine model no. A-74-37, at room temperature according to method of ASTM D790.

Electrical test

The measurement of dielectric strength was carried out on a high voltage tester machine oil test set.

RESULTS AND DISCUSSION

The syntheses of (AOIs) (3a-c) were performed by the reported method [18]. The oligoimides produced are in the form of orange powder. They were insoluble in organic solvents. The C, H and N contents Table 2 of all the oligoimides (3a-c) are consistent with their predicted structures (Scheme 1). Their results are furnished in Table 3. All the three oligoimides react to the red azo dye test, thereby confirming, and the presence of the terminal primary amino group. Examination of the IR Spectra (not shown) of the AOIs (3a-c) reveals that each spectrum comprises the strong bands around 1,700, 1,650, 1,050 and 730 cm^{-1} due to the presence of imide group [22]. The broad band around 3,300 cm^{-1} is attributed to -NH bonds. The inflections at 3,500 and 3,400 cm^{-1} may arise from terminal NH_2 groups. The medium bands at 2,950 and 2,840 cm^{-1} are attributed to the C-H of the $\text{CO-CH}_2\text{-CH}_2$ group present in the polymer chain.

The absence of the band at 3,040 cm^{-1} (attributed to the double bond present in AOIs) indicated that the Michael addition polymerization of the bismaleimides and DDM. The number average molecular weights (M_n) of the AOIs (3a-c) are furnished in Table 2.

TGA data (not shown) of the AOIs (3a-c) are given in Table 3.

Examination of the TGA data of AOIs reveals that the oligoimides begin to decompose at around 170 °C and loss almost 95% at around 700 °C. The amino terminated oligoimides AOIs (3a-c) were then reacted with acryloyl chloride to give acryl end-capped oligoimides (AcOIs) (4a-c). The C, H and N contents of all the AcOIs (4a-c) are consistent with their predicted structures (Scheme 1) (Table 3). The presence of double bonds in AcOIs (4a-c) are confirmed by the bromated bromide titration method [21] (Table 3).

The examination of the IR spectra of all AcOIs samples reveals that all the spectra are almost resemble to the spectra of corresponding AOIs samples only discernible difference is that the spectra of AcOIs contain the new band at 1,550 cm⁻¹ of amide group instead of bands at 3,500 and 3,400 cm⁻¹ to primary NH₂ group appeared in the spectra of AOIs. This confirms the acrylation reaction of amino terminated oligoimide. Examination of the TGA (Figure not shown) data (Table 3) reveals that the AcOIs (4a-c) starts their degradation around 180 °C and loss 90% around 750 °C. The AcOIs (4a-c) were mixed with a thermoplastic pyromellitic N-phenylmaleimide (PM) solution in different proportions. To this mixture AIBN was added as an initiator and then the mixture was heated at an elevated temperature. This create cross-linking reaction of AcOI as well as polyimide formation of N-phenylmaleimide, thus interacting blends were produced. The IR spectrum of IB is not obtained in well resolved form. While the spectrum comprises the bands due to imide group. The schematic diagram of such a system is shown in Scheme 1.

The Glass fibre reinforced composites were fabricated of this interesting blend of the polyimides of various proportions as in Table 1. These composites were analyzed for their chemical, mechanical and electrical properties. Examination of the data (Table 5) reveals that they have good resistance to common organic solvents like acetone, ethanol etc. They also have good mechanical strength. The electrical strength of these composites is between 15 to 16.5 kV/mm. Their results are furnished in Table 6. Because many factors such as processing, testing, reinforcement, environment and quality are known to significantly affect composite performance, it is very difficult if not impossible, to make a valid comparison of properties on the same material evaluated in different laboratories. In order to make a meaningful comparison of the properties between produced interesting blend those prepared by us these are shown in Table 7. It is evidenced that produced IBs have better mechanical properties and maintaining relatively easy processability. All of the raw materials necessary for the preparation of interesting blend are commercially available.

Table 7: Composite properties of Interacting blend(5a-c) compared with Interacting blend of Thermid 600 and NR150B2 constituent material [18].

Property	Interacting blend	ThamidLR-600 NR-150B2	Thermid AL-600, NR-150B2
Flexural strength MPa	288-309s	269	286

Interacting blend (reinforced with celining 6,000 graphite fibers)

CONCLUSION

The produced work indicates that synthesis of thermoset amino terminated oligoimide is easy. The synthesis of acryl end capped oligoimides and their polymerization are easy. The formation of new interesting blend polyimides system via acryl end capped oligoimide and Poly N-phenylmaleimide is feasible. The resultant interesting blend product has comparable properties with other of commercial polymer. The processing temperature is not much more than conventional polyimide composites. The glass reinforced composites could be prepared with good mechanical.

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