Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(1):492-500

Novel interacting blends based on acryl terminited oligoimides and vinyl monomers

Mukesh C. Patel* and Rita R.Patel

P.S. Science and H.D. Patel Arts College, Kadi Sarva Vishwavidhyalay University, Kadi-Gujarat, India

ABSTRACT

New amino terminated oligoimides (AOIs) were prepared by the Michael addition reaction of bismaleimide (1), namely [1, 1'-{1, 4-phenylenebis (methylene)}bis(1H-pyrrole-2,5-dione)] with excess of various diamines(2a-c). These AOIs were characterized by elemental analysis, FT-IR spectral studies, number average molecular weight estimated by non-aqueous conductometric titration and by thermogravimetry. AOIs were then treated with acrylol chloride and resultant acryl terminated oligoimides (AcOIs) samples were 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 may homo polymerized through double bond or may crosslinked simultaneously. Thus this 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.

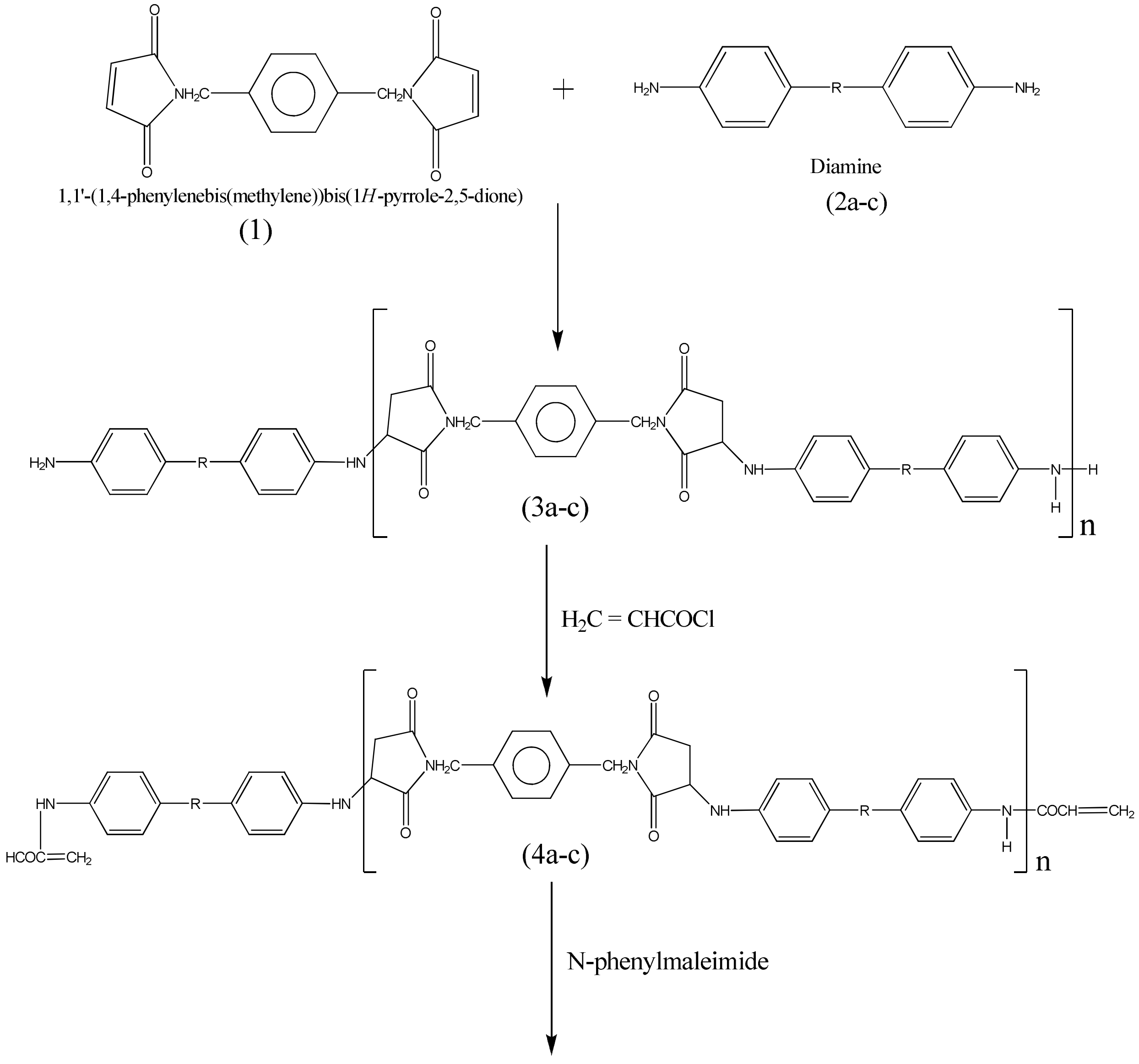
Key words: Amino terminated oligomides (AOIs), acryl end capped oligoimides (AcOIs), Michael addition reaction, *p*-xylylene diamine, acryl amide, AIBN, glass fiber reinforced composites, thermogravimetry.

INTRODUCTION

The polyimides known 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]. Looking to the good application of polyimides and SPM, it was thought to study AOIs-PM interacting blends.

Thus, the present paper comprises the initial work about such interacting blends, scanned in scheme 1.



Interacting Blend
(With or Without reinforcement)
(5a-c)

where ,R =
a) $-CH_2$
b) - O -
c) $-SO_2$

Scheme 1

EXPERIMENTAL SECTION

Material

N- Phenyl maleimide, the 1,4- xylylene diamines used for synthesis of 1, 4-xylylene bismaleimide and diamines (2a-c) were used of A.R.grade. 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-phenylenebis (methylene)}bis(1*H*-pyrrole-2,5-dione)] was synthesized by condensation of maleic anhydride and the 1,4-xylylene diamine following the reported methods [15,16].It was designated as 1.

Synthesis of amino terminated oligoimides

The amino terminated oligoimides (AOIs) **(3a-c)** were prepared by the Michael addition reaction between the bismaleimide **1** and diamine(2a-c)at the molar ratio of 1:2. They were prepared according to the method reported [17]. 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), acrylol chloride (0.05 mol) was added drop wise at room temperature. Then equivalent amount of K_2CO_3 was added to neutralize the resulting HCI. The resultant acryl end capped oligoimides (AcOIs) were obtained in the form of yellow amorphous powder. All the three AcOIs were designated as (4a-c).

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

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

Thus the nine systems of interacting blends of polyimides of were prepared.

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 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 °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

AOIs sample	Elemental Analysis Calc.(Found)				No.average molecular weight (Mn)	Percent weight loss at various temperatures ºC				
	%C	%H	%N	%S		300	400	500	600	700
3a	73.24(73.77)	5.27(5.26)	12.20(12.22)	-	1914	25	42	73	85	96
3b	72.71(72.68)	4.88(4.85)	12.72(12.70)	-	2058	24	48	63	79	93
3c	60.90(60.92)	4.09(4.08)	10.65(10.82)	8.13(8.12)	1743	10	20	37	62	98

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 method reported in the literature [18, 19]. 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 [20].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)

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

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 ºC				
	%C	%H	%N	%S		300	400	500	600	700
3a	72.35(72.33)	5.06(5.03)	10.55(10.58)	-	1.99	15	33	52	63	91
3b	68.99(69.01)	4.53(4.58)	10.49(10.47)	-	1.93	17	35	56	68	93
3c	61.60(61.62)	4.05(4.07)	9.37(9.39)	7.15(7.13)	1.97	20	40	63	72	97

Table:4 TGA of Interacting blends Polyimides

Interacting blend	AcOI-PM	Percent weight loss at various temperatures ºC		
		300	450	750
5a I	80:20	16	32	62
5a II	60:40	18	35	65
5a III	40:60	20	35	65
5b I	80:20	22	35	67
5b II	60:40	23	37	71
5b III	40:60	26	39	69
5c I	80:20	22	37	66
5c II	60:40	25	40	72
5c III	40:60	27	42	77

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_2SO_4	1.24	1.87	1.24	1.98	1.22	1.86	1.23	1.93	1.23	1.89	1.24	1.89	1.25	1.80	1.23	1.83	1.29	1.89
25%HCL	1.20	7.73	1.21	1.79	1.20	1.72	1.24	1.88	1.16	1.82	1.20	1.83	1.23	1.82	1.22	1.81	1.27	1.82
25%NaOH	0.78	1.19	0.76	1.19	0.81	1.24	0.78	1.19	0.75	1.19	0.75	1.20	0.78	1.24	0.80	1.19	0.77	1.23
Ethanol	0.53	1.10	0.56	1.17	0.53	1.15	0.56	1.09	0.59	1.15	0.63	1.12	0.67	1.19	0.63	1.16	0.63	1.19
Acetone	0.44	0.92	0.43	0.86	0.42	0.80	0.46	0.87	0.50	0.82	0.57	0.84	0.59	0.89	0.59	0.89	0.57	0.87
DMF	1.13	1.85	1.11	1.80	1.10	1.80	1.12	1.79	1.08	1.75	1.17	1.80	1.17	1.83	1.19	1.85	1.20	1.85
THF	0.93	1.73	0.90	0.90	0.88	1.76	0.95	1.72	0.93	1.76	0.96	1.71	0.98	1.67	0.92	1.77	0.89	1.73

Thi. = Thickness, Wt. = Weight

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-I. The TGA data are furnished in Table 5. They were also subjected to the Differential thermal analysis to get their glass transition temperature. Their results are furnished in Table 4.

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 H_2SO_4, 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.

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.

Table 6:Mechanical and electrical properties of interecting blend of polymides

Interecting blend polyimides sample	Compressive strength (MPa)	Notched impact strength	Rockwell hardness (MPa)	Electrical strength in air (kV/mm)	Flexural strength (MPa)
5a I	286	282	119	15.7	298
5a II	290	284	122	15.8	294
5a III	295	285	124	16.3	289
5b I	296	287	125	16.4	296
5b II	293	286	123	16.3	292
5b III	296	284	126	17.1	289
5c I	297	286	123	16.4	281
5c II	299	288	124	17.5	278
5c III	297	290	127	17.3	274

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 [17]. The oligoimides produced are in the form of yellow powder. They were insoluble in common 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 [21]. 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 are attributed to the C-H of the $CO-CH_2-CH_2$ 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 (Mn) 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 acrylol chloride to give acryl end-capped oligoimides (AcOIs) (4a-c). The C, Hand 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 [20] (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^{j1} of amide group instead of bands at 3,500 and 3,400 cm^{j1} to primary NH_2 group appeared in the spectra of AOIs. This confirms the acrylation reaction of amino terminated oligoemide. 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 pyromellatic N-phenylmeleimide (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-phenylmeleimide, 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 interecting 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 interecting blend those prepared by us and those reported elsewhere [22] 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 interecting blend are commercially available.

Table 7: Composite properties of Intrecting blend (5a-c) compared with Intrecting blend of Thermid 600 and NR150B2 constituent material [17].

Property	Intrecting blend	ThamidLR-600 NR-150B2	Thermid AL-600, NR-150B2
Flexural strength MPa	274-298s	255	278

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 interecting blend polyimides system via acryl end capped oligoimide and Poly N-phenylmeleimide is feasible. The resultant interecting 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.

REFRENCES

[1] D. Wilson, Polyimides, Blakie, Chapman and Halls, New York, **1990**.

[2] V.M.Neverov, S.N.Chvalun, D.Blackwell, Vysokomol. Soedin., Ser. A, **2000**, vol. 42(3), pp. 450 461.

[3] H.V.Nikalaichyk, A.A.Martsinkevich, N.R.Prokopchuk and E.T.Krutko, Abstracts of Papers, Third Int. Symp. on Polyimides and Other High Temperature Polymers: Synthesis, Characterization, and Applications, Orlando, December 17 19, **2003**, p. 21.

[4] B. A. Zhubanov, V. D. Kravtsova, R. F. Mukhamedova, and K. Kh. Bekmagambetova, **“***Russian Journal of Applied Chemistry”*, **2006**, Vol. 79(11), pp. 1869-1874.

[5] A. A. Berlina; B. I. Liogon'kiia; B. I. Zapadinskiia; E. A. Kazantzevaa; A. O. Stankevich, *“J. MACROMOL. XI.-CHEM.”*, **1977**, All(l), pp. 1-28.

[6] Liliana Burakowski Noharaa, Michelle Leali Costaa,b, Mauro Angelo Alvesb,Marta Ferreira Koyama Takahashic, Evandro Luís Noharad, Mirabel Cerqueira Rezendeb, *“Materials Research”*, **2010**, 13(2), pp.245-252.

[7] D. E. Rajsfus, M.B. Meador and A.A. Frimer, *“Macromolecules”*, **2010**, 43, pp.5971–5980.

[8] R. Hoogenboom, U. S. Schubert, *“Macromol. Rapid Commun.”* **2007**, 28, pp.368–386.

[9] A. Oishi, H. Matsuoka, T. Yasuda, M. watanabe, *“J.Material Chemistry”* , **2009**,19, pp 514-521.

[10] I.E.Serhatli, A.B. Duz and Y.Yagci, *“Polymer Bulletin”*, **2000,** 44(3),pp.261-268.

[11] Y. Lu, W. Sun and Z. shen, *“European Polymer Journal”*, **2002**, 38(7), pp 1275-1279.

[12] G. Liu, X. Li, L. Zhang, X. Qu, P. Liu, L. yang, J. gao, *“Journal of Applied Polymer Science”* , **2002**, 83(2), pp.417-422.

[13] D.R.Suwier, P.A.M.Steeman, M.N.Yeerenstra, M.A.J.Schellekens, B.Vanhaecht, M.J.Monterio and C.E. Kohing, *“Macromolecules”*, **2002**, 35(16), pp.6210-6216.

[14] F.Ylimaz, L.Cidnga, Y.Gunner, L.Toppare, Y.Yagci, *“Polymer”*, **2004**,45, pp.5765-5774.

[15] J. V. Crivello, *Chem. Ed.*, **1976,** 14, pp.159.

[16] N. E. Searle and H. W. Arnold, US Patent 2467835, Chem. Abast., **1976**, 43, pp.4421b .

[17] H. S. Patel and V. J. Shah, *J. Macromol. Sci., Part A*, **1995**, A32(3), pp.405.

[18] S. K. Chatterji and V. B. Agrawal, *J. Polym. Sci., Part A*, **1971**, Al(9),pp.3225.

[19] R. N. Patel and S. R. Patel, *Angew. Makromol. Chem.*, **1981**,96, pp.85.

[20] A. I. Vogel, Quantitative Organic Analysis, II Edn, CBS, New Delhi,**1998**.

[21] J. R. Dyer, Application of Absorption Spectroscopy of Organic Compounds, CBS, New Delhi, **1987**.

[22] R. H. Pater, ANTEC’ 1304 , **1990**.