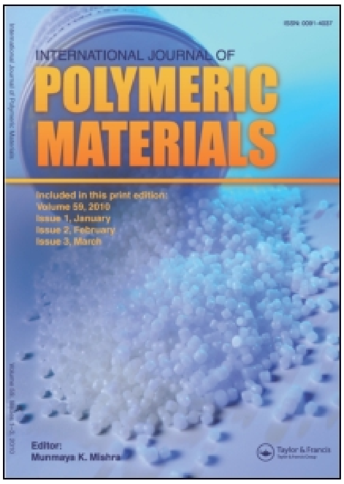

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Novel Semi-Interpenetrating Polyimide Network Based on Acryl End Capped Oligoimides

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Amino terminated oligoimides (AOIs) were prepared by the Michael addition reaction of various bismaleimides with excess of 4,4′-diamino diphenyl methane (DDM). These AOIs were characterized by elemental analysis, FT-IR spectral studies, and number average molecular weight estimated by non-aqueous conductometric titrations. The AOIs were then reacted with acrylol chloride and the resultant acryl end capped oligoimides (AcOIs) were also characterized thermogravimetrically. Each of these AcOI was then combined with a commercially available thermoplastic polyamic acid solution in various proportions. The resultant suspensions were then heated in the presence of azobisisobutyronitrile (AIBN) as a catalyst. The AcOI polymerized through double bond and the polyamic acid was cyclized to form SEMI-IPN polymides, which were analyzed thermogravimetrically. Glass fiber reinforced composites were fabricated by using the suspensions of the AcOI and polyamic acid solution. The composites of SEMI IPN polymides were analyzed for their mechanical, chemical, and electrical properties.

Keywords: acryl capped oligoimides, AIBN, amino terminated oligoimides, bismaleimides, 4,4′-diamino diphenyl methane, glass fiber reinforced composites, Michael addition reaction, polyamic acid, SEMI-IPN

INTRODUCTION

The importance of polyimides in the spectrum of the thermally stable polymers is well recognized [1]. Applications ranging from aerospace

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to microelectronics have utilized the outstanding thermo-oxidative stability of these polymers. In the past decade the interest has accelerated in tailoring the chemistry of polyimides so as to approach the optimum balance of thermal, mechanical, and electrical properties required for processing and performance in specific advanced technologies. Many aspects of research pursuits to various polyimides have been well documented [1–2].

One approach for polyimides designed for varied applications is to attain an optimum balance of properties. This would be possible by a combination of a thermoset and a thermoplastic polyimides. Such a combination, say, interpenetrating polymer network (IPN), has been considered for use as composite matrix and as adhesive in aerospace structures and electronic applications. Considing one the easily processable but brittle thermosetting polyimide with a more tough but difficult to process linear thermoplastic polyimide would afford a SEMI-IPN with ease of processing and good toughness.

This concept has been successfully applied to develop a variety of SEMI-IPNs. Such SEMI-IPNs, are reported for PMR-15 [3], acetylene terminated polyimide [4], bismaleimides [5–6], polytetrazine [7], epoxy [8], and phthalocyanine [9–10] based materials. Looking to the excellent properties of the SEMI-IPNs mentioned earlier, it was thought interesting to explore the field of polyimide SEMI-IPNs. The present article comprises the initial work about such IPNs.

EXPERIMENTAL

Materials

Commercially available pyromellitic anhydride -4,4′-diaminodiphenyl methane based polyamic acid solution in DMSO was received from Guru-krupa Paper Board, Vapi. The diamines (Analar grade) used for the synthesis of bismaleimides are: (a) 1,3-Phenylene diamine, (b) 1,4-Phenylene diamine, and (c) Benzidine. Plan 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/m^2 were used for composite fabrication. All other chemicals used were of the laboratory grade.

Synthesis of Bismaleimides

The bismaleimides (shown in Table 1) were synthesized by condensation of maleic anhydride and the diamines mentioned earlier following the reported methods [6,11]. The three bismaleimides were designated as (la–c).

TABLE 1 Bismaleimides Used

No.	Bis(maleimide) compounds	Molecular weight	Melting point (°C)
1a	1,3 phenylene bismaleimide	268	202–203
1b	1,4 phenylene bismaleimide	268	300
1c	Benzidine bismaleimide	344	300

Synthesis of Amino Terminated Oligoimides

The amino terminated oligoimides (AOIs) were prepared by the Michael addition reaction between the bismaleimides (la–c) and 4,4′-diamino diphenyl methane at the molar ratio of 1:2. They were prepared according to the method reported by one of the authors (HSP) [12]. The three AOls were designated as (2a–c).

Synthesis of Acryl End Capped Oligoimides

To a suspension of AOI (2a–c) (0.05 mole) in THF (100 ml), acrylol chloride (0.05 mole) was added dropwise at room temperature. Then an 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. The three AcOIs were designated as (3a–c).

Synthesis of SEMI-IPN Polyimide

Each of the AcOI (3a–c) samples and polyamic acid solution (P.A.) in various weight percentage were prepared as shown in Table 2. To each of these mixtures, 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 SEMI-IPN of polymide was in the form of solid hard material. They were designated as 4(a–c).

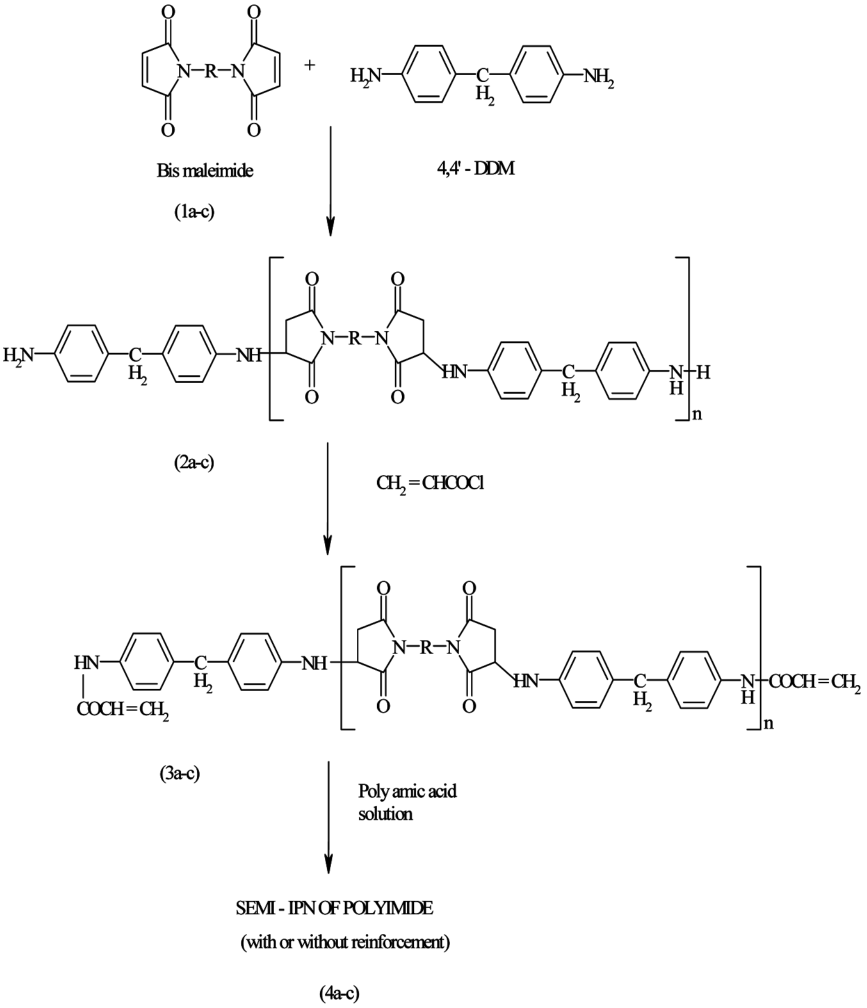
Thus, nine systems of SEMI-IPN of polyimides were prepared.

TABLE 2 Various Weight Percentage

	I	II	III
AcOI% (3a–c)	80	60	40
Polyamic acid	20	40	60

COMPOSITE FABRICATION

The composites were prepared by a typical method of composite fabrication as given in what follows. Three ratios of AcOI to polyamic acid solution were used as shown in Table 2. A suspension of acryl end



Where, R =
- a) 1,3-phenylene diamine
- b) 1,4-phenylene diamine
- c) Benzidin

SCHEME 1

capped oligoimide (AcOI Scheme 1) and thermoplastic polyamic acid solution was prepared in tetrahydrofuran and stirred for 5 min. To this, AIBN was added as a catalyst and was stirred well for a few minutes. The suspension was then applied with a brush on a 150 mm × 150 mm glass cloth. The 10 dried prepgregs 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 in a press under 70 psi (0.4 Mpa) pressure. The prepgregs stacks were cured by heating at 150°C for 10 h in an air circulated oven. The composites so obtained was cooled to 50°C before the pressure was released. Specimens were made by cutting the composites and machining them to final dimensions.

MEASUREMENTS

The C, H, N contents of all the amino terminated oligoimides (2a–c) and acryl end capped oligoimides (AcOI) (3a–c) were estimated by means of a Carlo Erba Elemental Analyzer (Italy). The results are furnished, respectively, in Tables 3 and 4. IR spectra of AOls and AcOls were taken in KBr pellets using KBr as a reference on a Nicolet Impact 400D spectrophotometer.

The number average molecular weights of the AOI (2a–c) were determined by a nonaqueous conductometric titration following the method reported in the literature [13–14]. Formic acid–acetic acid mixture was used as the solvent and standard perchloric acid in acetic acid was used as a titrant. A digital conductivity meter (Tosaniwal, India) was used for the titration. The results are furnished in Table 3. AcOls (3a–c) were also analyzed for their number of double bonds per repeating unit employing mercury catalyzed bromate-bromide titration method [15].

TABLE 3 Characterization of Amino Terminated Oligoimides (2a–c)

	Elemental analysis Calc. (Found)			Number average molecular weight	% Weight loss at various temperatures				
AOI samples	%C	%H	%N	($\overline{Mn}$)	200	300	400	500	600
2a	71.64 (70.50)	6.26 (6.25)	12.53 (12.40)	1469	16	40	71	82	94.50
2b	71.64 (71.01)	6.28 (6.29)	12.51 (11.92)	1170	12	42	64	78	93
2c	74.79 (73.78)	5.14 (5.11)	11.38 (11.36)	1997	3	17.5	30	56.5	90

TABLE 4 Characterization of Acryl End Capped Oligoimides (3a–c)

AOI samples	Elemental analysis Calc. (Found) %C	%H	%N	Number of double bonds per unit	% Weight loss at various temperatures 200	300	400	500	600
3a	71.69 (71.50)	4.94 (4.11)	10.91 (10.50)	1.92	8.5	28	46	57	85
3b	71.68 (70.50)	4.93 (4.41)	10.92 (10.86)	1.98	9.5	29	49	59	86
3c	73.76 (73.66)	5.32 (5.35)	9.93 (9.83)	2.10	10	31	52	60	89

The AOls (2a–c) and AcOls (3a–c) were also characterized thermogravimetrically on a Du Pont 990 Thermal analyzer MK-III. The results are furnished in Tables 3 and 4, respectively.

SEMI-IPN Polyimides samples were subjected to thermogravimetric analysis (TGA) on a Du Pont 990-thermal analyzer MK-III in air at a heating rate of 10°C/min. The TGA data are furnished in Table 5. They were also subjected to the Differential thermal analysis to get their glass transition temperature. The results are furnished in Table 5.

COMPOSITE CHARACTERIZATION

Chemical Resistance Test

The chemical resistant test for all the composite samples was performed according to ASTM D 543–67. The composite sample dimension were

TABLE 5 TGA of SEMI-IPN Polyimides

SEMI-IPN	AcOI-PA	Tg	% Weight loss at various temperature 300	450	600
4a I	80:20	239	16	29	60
4a II	60:40	250	17	32	64
4a III	40:60	229	18	31	63
4b I	80:20	240	20	31	64
4b II	60:40	227	23	35	67
4b III	40:60	249	24	36	65
4c I	80:20	270	21	34	65
4c II	60:40	210	23	37	66
4c III	40:60	216	27	39	70

25 mm × 25mm × 3 mm. The samples were immersed in 25% v/v H_2SO_4, 25% v/v HCI 25% w/v NaOH, Ethanol, Acetone, DMF, and THF for 7 days at room temperature. After 7 days the samples were taken out from the reagents and were analyzed for the percentage change in their thickness and weight. The results are summarized in Table 6.

Mechanical Tests

All the mechanical tests were performed using three specimens and their average results are summarized in Table 7.

The compressive strength was measured on a Universal Instron testing machine model no. A-74-37, at 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. The results are summarized in Table 7.

RESULTS AND DISCUSSION

The synthesis of bismaleimides-DDM amino terminated oligoimides (AOI) (2a–c) was performed by the reported method [12]. The oligoimides produced are in the form of yellow powder. They were insoluble in common organic solvents. The C, H, and N contents of the oligoimides (2a–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 the presence of the terminal primary amino group. Examination of the IR Spectra (typical in Figure 1) of the AOIs (2a–c) reveals that each spectrum comprises the strong bands around 1700, 1650, 1050, and 730 cm^{-1}; due to the presence of imide group [16]. The broad band around 3300 cm^{-1} is attributed to –NH bonds. The inflections at 3500 and 3400 cm^{-1} may

TABLE 6 Chemical Resistance Test of SEMI-IPN Polyimides

SEMI-IPN polyimide sample	4a I % Change		4a II % Change		4a III % Change		4b I % Change		4b II % Change		4b III % Change		4c I % Change		4c II % Change		4c III % Change	
	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.	Thickness	Wt.
25% H_2SO_4	1.23	1.89	1.22	1.98	1.20	1.85	1.26	1.89	1.24	1.86	1.26	1.84	1.23	1.81	1.27	1.83	1.26	1.87
25% HCl	1.18	7.79	1.20	1.77	1.17	1.76	1.21	1.82	1.19	1.79	1.23	1.80	1.22	1.81	1.20	1.80	1.24	1.82
25% NaOH	.074	1.16	0.77	1.15	0.80	1.21	0.76	1.18	0.77	1.16	0.79	1.19	0.74	1.21	0.75	1.17	0.78	1.19
Ethanol	0.50	1.0	0.53	1.12	0.52	1.09	0.56	1.10	0.57	1.12	0.60	1.14	0.61	1.17	0.59	1.15	0.62	1.16
Acetone	0.44	0.91	0.41	0.81	0.39	0.75	0.46	0.80	0.49	0.81	0.52	0.84	0.54	0.87	0.55	0.86	0.57	0.88
DMF	1.10	1.81	1.05	1.78	1.06	1.76	1.08	1.77	1.07	1.75	1.10	1.81	1.13	1.82	1.15	1.83	1.17	1.85
THF	0.9	1.69	0.88	0.88	0.87	1.71	0.93	1.72	0.91	1.71	0.92	1.69	0.93	1.68	0.91	1.73	0.89	1.71

TABLE 7 Mechanical and Electrical Properties of SEMI-IPN of Polymides

SEMI-IPN polyimides samples	Compressive strength (Mpa)	Notched impact strength	Rockwell hardness (Mpa)	Electrical strength in air (kv/mm)	Flexural strength (Mpa)
4a I	283	279	112	15.5	299
4a II	287	280	116	15.9	294
4a III	290	281	117	16.1	289
4b I	291	282	118	16.3	295
4b II	290	281	117	16.2	291
4b III	291	280	119	16.0	288
4c I	293	283	116	16.3	281
4c II	294	285	119	16.4	279
4c III	292	286	120	16.2	275

arise from terminal NH_2 groups. The medium bands at 2950 and 2840 cm^{-1} 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 3040 cm^{-1} (attributed to the double bond present in AOI) indicated that the Michael addition polymerization of the bismaleimides and DDM. The number average molecular weights (Mn) of the AOIs (2ac) are furnished in Table 3.

TGA data (Figure 2) of the AOIs (2a–c) are given in Table 3. Examination of the TGA data of AOIs reveals that the oligoimides begin to decompose at around 150°C. The rate of decomposition increases rapidly between 250 and 450°C and they are 95% decomposed at around 600°C. The amino terminated oligoimides AOIs (2a–c) were then reacted with acrylol chloride to give acryl end capped oligoimides (AcOI) (3a–c). The C, H, and N contents of all the AcOIs (3a–c) are consistent with their predicted structures (Scheme 1). Their results are furnished in Table 4. The presence of double bonds in AcOI (3a–c) is confirmed by the bromate-bromide titration method [15]. The results are furnished in Table 4.

A typical IR spectrum of AcOI sample is given in Figure 1. The examination of the IR spectra of all AcOI samples reveals that all the spectra are almost dentical to the spectra of corresponding AOI samples and the only discernible difference is that the spectra of AcOI contain a new band at 1550 cm^{-1} of amide group instead of bands at 3500 and 3400 cm^{-1}. This confirms the acrylation reaction of amino terminated oligoimide.

TGA data for the AcOI (3a–c) (Figure 2) are given in Table 4. Examination of the data reveals that the AcOI (3a–c) starts their degradation at around 150°C. The rate of decomposition increases very rapidly

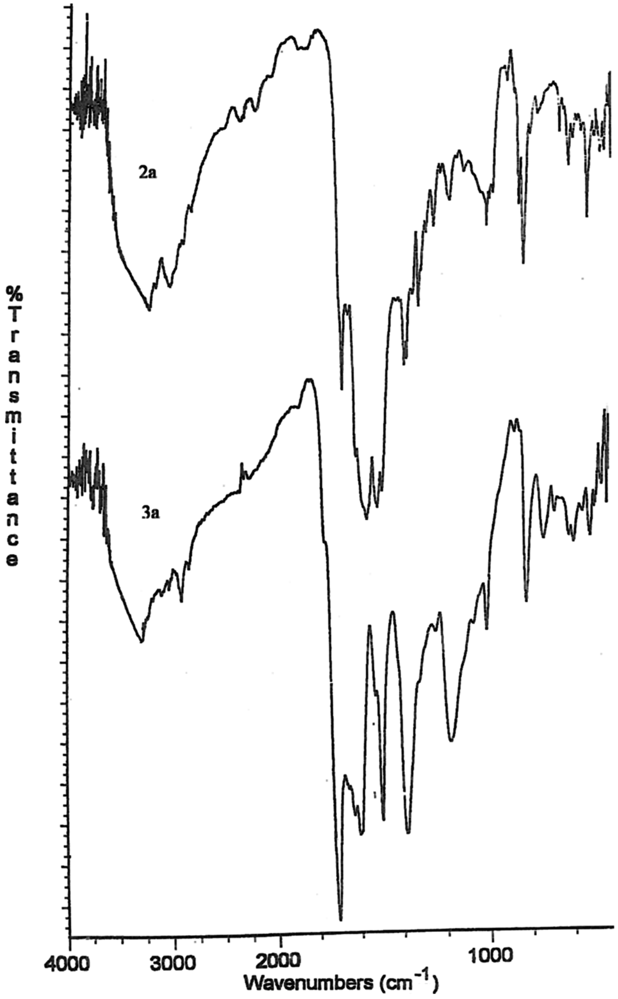


FIGURE 1 IR spectra of sample 2a and 3a.

between 250–500°C and they are 90% decomposed at around 650°C. Comparison of the decomposition data of the AOI (2a–c) and AcOI (3a–c) reveals that the decomposition rate of AcOI (3a–c) is slightly lower than that of the AOls (2a–c). The thermosetting AcOI (3a–c) were mixed with a thermoplastic pyromellitic anhydride–based polyamic acid solution in different proportions. To this, AIBN was added as an initiator and then the mixture was heated at an elevated temperature. This initiates a crosslinking polymerization reaction

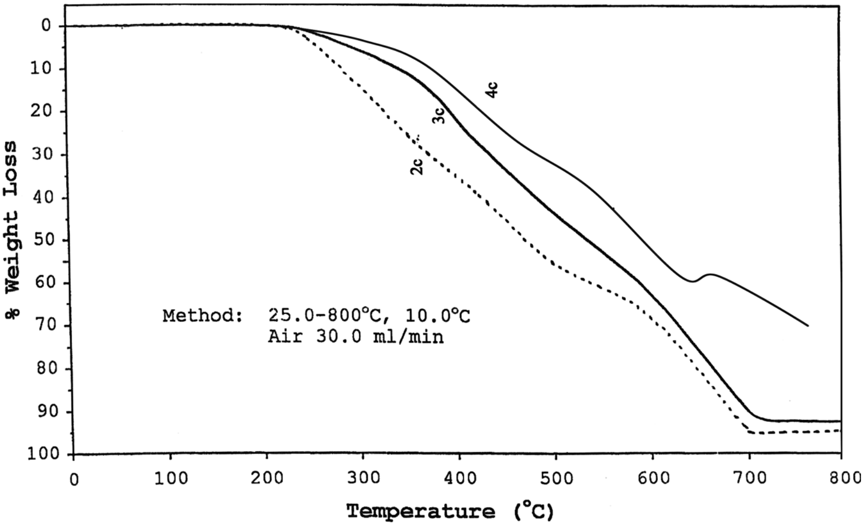


FIGURE 2 TG thermo gram of 2c, 3c, 4c.

although at higher temperature the cyclization of the polyamic acid takes place to give insoluble linear polyimide. As the IPN system forms a more and more corsslinked material is obtained. Thus the IR spectrum of IPN is not obtained in well-resolved form. Although the spectrum comprises the bands due to imide group, the band at 1680 cm^{-1} due to carboxylic acid group present in amic acid is not observed. Thus cyclization of polyamic acid is present. Thus the resultant polymer system is designated as a SEMI IPN (Figure 3) Polyimide. The schematic diagram of such a system is shown in Scheme 1. They were analyzed by a Differential thermal analyzer (DTA) (figure not shown). The results are furnished in Table 5. Examination of the results reveals that there is only one Tg for the produced SEMI IPNs of the Polyimides. Hence a homogenous SEMI-IPNs of Polyimides are formed. They were also subjected to a thermogravimetric analysis. The results are furnished in Table 5. Examination of the data reveals that all the polyimide systems show about 20% weight loss at 300°C. Their maximum weight loss is between 450–600°C and about 65% weight loss is observed at 600°C.

The glass fiber–reinforced composites were fabricated of the SEMI-IPNs of the polyimides of various proportions as in Table 2. These composites were analyzed for their chemical, mechanical, and electrical properties. Examination of the data reveals that they have good resistance to common organic solvents like acetone, ethanol, and

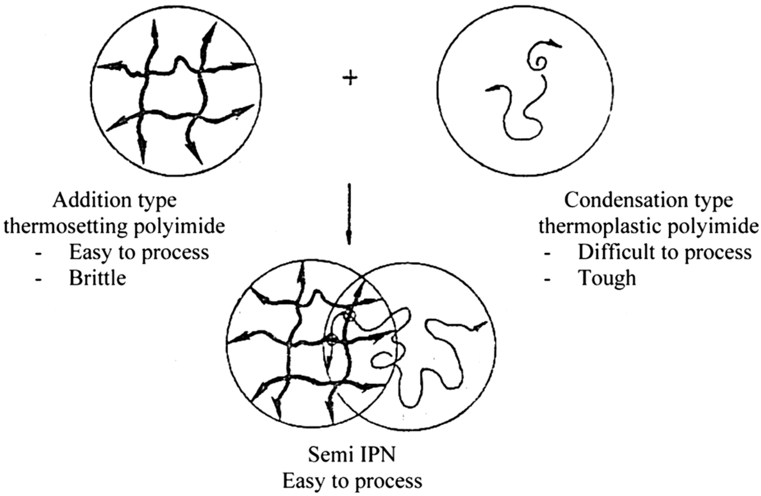


FIGURE 3 Proposed structure of SEMI-IPN polyimide.

so on. They also have good mechanical strength. The electrical strength of these composites is between 15 to 16.5 kv/mm. The results are furnished in Table 7.

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 SEMI-IPNs, those prepared by the authors and those reported elswhere are shown in Table 8. It is evident that the present IPNs have better mechanical properties and maintain relatively easy processability. All of the raw materials necessary for the preparation of SEMI-IPNs are commercially available.

TABLE 8 Composite Properties of SEMI-IPN (4a–c) Compared with SEMI IPN of Thermid 600 and NR150B2 Constituent Material. SEMI IPN[a]

Property	SEMI IPN	Thermid LR-600 NR-150B2	Thermid AL-600, NR-150B2	Thermid MC-600 NR 150B2
Flexural strength MPa	275–299	254	279	293

[a] Reinforced with celining 6,000 graphite fibers.

CONCLUSION

The produced work indicates that:

1. Synthesis of thermoset amino terminated oligoimide is easy.
2. The synthesis of acryl end capped oligoimides and their polymereization are easy.
3. The formation of new SEMI-IPN polyimides system via acryl end capped oligoimide and polyamic acid is feasible. The resultant IPN product has comparable properties with those of commercial polymer.
4. The processing temperature is not much more than conventional copolymide composites. Glass-reinforced composites could be prepared with good mechanical strength.

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