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Alloys of polyimides with varying degree of crosslinking through antimony salts: mechanical properties characterization

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Abstract

Polyimides with unique thermomechanical characteristics and film forming capabilities have emerged as choice material for diversified applications in advanced technologies. Wide ranging properties could be achieved for polyimides by incorporating them with many metal salts, complexes or organic materials. The inadvertent crosslinking was introduced due to metal salt incorporation and unique polyimide alloys are prepared by blending the crosslinked and uncrosslinked polyamic acid components followed by thermal imidization. The blend components were synthesized by the reaction of polyamic acid with varying concentrations of a crosslinker (here antimony pentachloride or APC) as high as 1.67×10^{-2} mole/dm^3 (i.e. hypothetically calculated Critical Crosslinker Concentration) up to lowest of 1.67×10^{-6} mole/dm^3. This communication delves into the synthesis and characterization of polyimide blends and alloys prepared by varying degrees of crosslinking introduced via APC–Amic Acid reactions. The polyimide alloys were prepared by thermal imidization of polyamic acid blends at different curing temperature starting from 50° to 350°C. The degree of imidization, mechanical properties and the residual solvent content for blends having varying mole fractions of crosslinked or uncrosslinked components have been studied. The resultant APC-PI blends have exhibited synergism on mechanical properties. The feasibility of preparing polyimide alloys with synergistic combinations of crosslinked and uncrosslinked polyimide components was concluded.

Keywords: Polyimide; Alloys; Crosslinked network

1. Introduction

The research in the area of polymeric blends, alloys, composites and interpenetrating network systems has been very active in both academic and industrial fields. The value addition of commercial polymers (both commodity and speciality grades) and avenues for fundamental research in these emerging fields have culminated in tailoring of the properties of the polymers to meet very specific technological requirements. Polymer blends and alloys are relatively economical to produce and generally cause a lower technical risk than developing a new polymer or polymeric composition [1]. Alloys are defined as synergistic polymer combinations with real property advantages derived from a high level of compatibility between blend components. Alloys exhibit strong intermolecular forces and form single phase systems with one glass transition temperature. The discovery of new polymeric alloys by blending commercially available polymer is an exciting trend in material development. The ability to tailor existing material to a new/unique set of property/performance/price specifications through combination of materials is the key reason for this growth. Polyimides—the polymers containing cyclic imide groups in the main macromolecular chain have emerged as potential high temperature resistant materials finding myriads of applications in frontier technologies like aerospace, microelectronics and advanced composites [2]. The blending or alloying in polyimide fields are very limited [3] and that could be attributed to their intractable character. In multiphase polyimide systems, molecular composites [4] and polyimide ceramers [5] have recently been reported.

As a consequence of the extensive studies [6–9] in our laboratory involving the modification of polyimides by metal salts and organic crosslinkers, a new approach to the synthesis of polyimide blends/alloys has emerged. In this new concept, a blend of polyamic acid with the varying degree of crosslinking is in situ produced and alloys of polyimides are produced from thermal cyclization. A very lightly crosslinked polyamic acid is produced from the reaction of a very highly functionalized polyamic acid with a hypothetically calculated concentration of crosslinker (either organic or metal salt). A hypothetical concentration has been calculated based on the concept of critical branching coefficients, and the crosslinked polyamic acid

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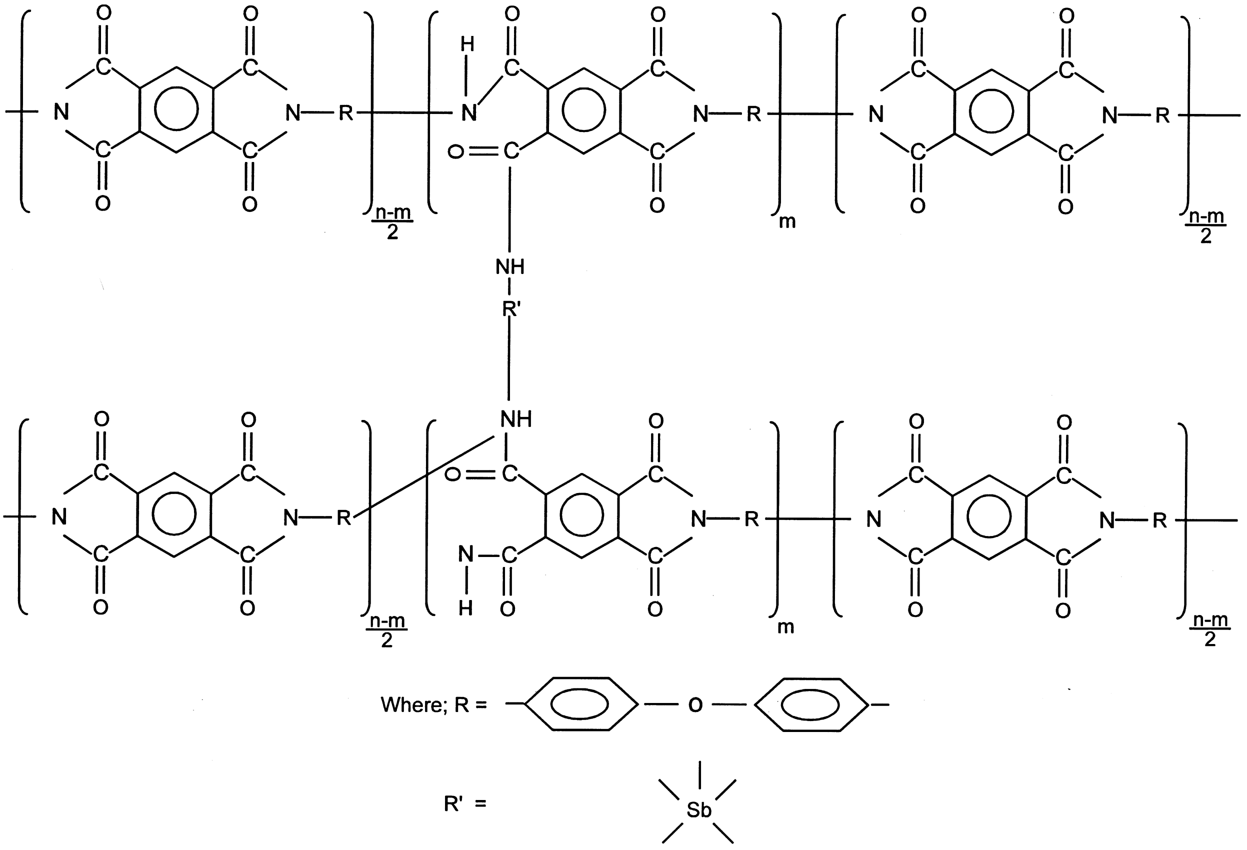

Fig. 1. Probable chemical structure of the crosslinked PI molecule.

component is produced from existing polyamic acid molecules. The blend of the polyamic acids thus obtained has been thermally imidized to have polyimide alloys. The synergistic improvement in thermal and water uptake characteristics [10] had already been demonstrated and an attempt to elucidate the mechanism responsible for these properties has been made and also currently undertaken to strengthen this new concept of making alloys and blends of polyimides.

Poly(4,4′-oxydiphenylene) pyromellitamic acid was chosen for this study in view of its excellent mechanical, thermal and electrical properties. Polyfunctional polyamic acid could be crosslinked with a crosslinking agent like Antimony Pentachloride and an infinite network structure could be achieved with extremely low concentrations of crosslinker agent. The present communication is based on the evaluation of the mechanical properties coupled with physico-chemical characterization like the degree of imidization and solvent interaction in the polymeric alloys.

2. Experimental

2.1. Materials and instruments used

Polypyromellitamic acid—a precursor of polypyromellitimide was used as 10% solution in Dimethyl Acetamide (DMAC) solvent. The intrinsic viscosity of the polyamic acid was measured to be 0.86 dl/g. The crosslinker antimony pentachloride (APC) was obtained from M/s Fluka, Switzerland and was used as received. The solvent DMAC reagent grade (BP—165°C) was supplied by CDH Laboratories, Bombay, India. DMAC was purified by distillation in the presence of P_2O_5 and the fraction between 162–166°C was collected and was always kept in a closed container. The intrinsic viscosity of the PAA solution was determined using a Ubbelohde Viscometer.

The degree of imidization of all samples were determined by IR spectroscopic techniques. Spectra of PAA/polyimide films were recorded using a Perkin-Elmer FTIR Spectrophotometer (model 1720X). A band ratio method was adopted wherein the area of symmetric carbonyl stretch at $1776\ \mathrm{cm}^{-1}$ was ratioed with area of reference aromatic vibration at $1012\ \mathrm{cm}^{-1}$. The solvent content was determined by the weight difference method using the electronic digital balance having least count of 0.001 mg. Mechanical properties were determined according to ASTM test method D 882. Instron Universal Testing Machine (model 4202) was used and a cross head speed of 0.5 mm/min was adopted.

2.2. Synthesis and preparation

Polypyromellitamic acid was formed upon acylation of oxydianiline with pyromellitic dianhydride in amide

Table 1
Solvent content of APC-PI alloys at different time–temperature profiles (TTP)

S. No.	Concentration of antimony pentachloride (mole/dm^3)	Solvent content at different TTPs						
		PROF50	PROF 100	PROF 150	PROF 200	PROF 250	PROF 300	PROF 350
1	0.0 (neat PI)	49.3	30.8	15.96	10.5	9.3	3.6	0.0
2	1.67×10^{-6}	45.0	26.1	14.61	9.6	8.9	3.4	0.0
3	1.67×10^{-5}	42.6	24.8	14.28	9.2	8.1	3.3	0.0
4	1.67×10^{-4}	39.7	22.9	13.70	9.0	7.9	3.0	0.0
5	1.67×10^{-3}	36.6	19.6	12.97	8.6	7.6	2.9	0.0
6	1.67×10^{-2}	30.4	16.6	11.94	8.1	6.9	2.6	0.0

solvent. Calculated quantities of APC in DMAC were mixed in Polyamic acid solution in different molar ratios so as to result in polyimide alloy films of 25 μm thickness having varying concentrations of APC viz; 1.67×10^{-2}, 1.67×10^{-3}, 1.67×10^{-4}, 1.67×10^{-5} and 1.67×10^{-6} mole/dm^3 of polyimide, respectively. Antimony pentachloride and polyamic acid solutions were mixed thoroughly and spread over glass plates with the help of a Doctor's blade. Samples were heated independently at different curing temperatures (i.e. at 50°C, 100°C, 150°C, 200°C, 250°C, 300°C and 350°C) for 2 h and each curing temperature was designated as PROF-50, PROF-100, PROF-150, PROF-200, PROF-250, PROF-300 and PROF-350, respectively. Samples were taken out from the glass plates and were designated as APC-PI alloys.

3. Results and discussion

Polyamic acid (PAA) could be considered as polyfunctional polymers in terms of amide and carbonyl functionalities and an average functionality can vary from 200 to 600 depending upon its molecular weight. With the following relationship of intrinsic viscosity (η) with molecular weight (M), the average molecular weight of the PAA was calculated as per Eq. (1):

$$[\eta] = kM^{\alpha} \quad (1)$$

where k and α are the Mark–Kuhn–Hauwink constants. In our studies, values of k and α have been taken as 2.3×10^{-4} and 0.78 respectively as reported elsewhere [11,12]. Since the average molecular weight of the PAA used here is approximately 4.2×10^4, its functionality is equal to 400, if both the functional groups are considered reactive.

Any reactive material having functionality two or more can crosslink the polyamic acid resulting in a high molecular weight crosslinked polymeric network. The formation of an infinite network in such polyfunctional branching units [13] will be governed by the critical branching coefficient (i.e. α_c) by its simple correlation as given below:

$$\alpha_c = 1/f - 1 \quad (2)$$

where 'f' is the functionality of the branching unit like PAA.

According to this theory, even the introduction of a single crosslink between two molecules of PAA may result in a high molecular weight network structure. On the basis of this theory, it is inferred that antimony pentachloride having labile chloride can react with polyamic acid and introduce a crosslinking resulting in in situ generation of the polymeric blend. Reaction of other metal ions with polyamic acid forming metal salts of polyamic acid have been established by Linde et al. [14] and accordingly, the probable chemical structure of the crosslinked PI molecule may be shown as in Fig. 1.

In order to quantitatively assess the impact of incorporation of APC in polyimide, a hypothetical concentration of antimony pentachloride was used. This hypothetical concentration was termed as the Critical Crosslinker Concentration (C.C.C.) which has been defined as the

Table 2
Degree of imidization of APC-PI alloys

S. No.	Time temp. profile	Degree of imidization at different concentrations of APC in alloys					
		0.0	1.67×10^{-6}	1.67×10^{-5}	1.67×10^{-4}	1.67×10^{-3}	1.67×10^{-2}
1	PROF 50	0.0	0.0	0.0	0.0	0.0	0.0
2	PROF 100	38.29	36.84	34.6	32.51	32.08	29.19
3	PROF 150	69.16	65.11	55.23	53.92	52.61	52.26
4	PROF 200	74.41	72.62	70.39	69.94	69.38	67.15
5	PROF 250	83.02	78.50	75.74	73.42	74.42	72.10
6	PROF 300	98.37	95.02	94.08	93.77	93.36	90.24
7	PROF 350	100.00	94.4	93.8	92.6	91.5	89.2

Table 3
Tensile strength of APC-PI alloys

S. No.	Concentration of antimony pentachloride (mole/dm^3	Tensile strength (MPa) at different TTPs					
		PROF 50	PROF 100	PROF 150	PROF 200	PROF 250	PROF 300
1	0.0 (neat PI)	2.45	13.33	51.94	56.84	56.84	59.29
2	1.67×10^{-6}	24.01	47.04	57.82	62.72	71.54	76.44
3	1.67×10^{-5}	82.12	87.22	85.16	92.32	96.63	67.03
4	1.67×10^{-4}	89.47	90.16	91.63	92.12	94.08	50.96
5	1.67×10^{-3}	79.38	77.42	80.85	78.60	81.34	49.59
6	1.67×10^{-2}	77.32	73.50	72.72	75.95	80.07	42.14

minimum concentration of antimony pentachloride in mole/dm^3 (of polyimide) required to introduce single crosslinking between two independent molecules of polyamic acid. The critical crosslinker concentration was calculated to be 1.67×10^{-2} mole/dm^3. Accordingly, in this study, the incorporation of APC in polyimide was made at a concentration below or equal to C.C.C.

The incorporation of APC was found to influence the ultimate properties and curing process of the alloys of polyimide films. These products were characterised for physicochemical, photophysical, elemental analysis, mechanical, electrical, thermal and water uptake properties [15]. In this communication, only the results of the effect on the imidization process and mechanical properties are presented.

The degree of imidization determined by FTIR spectroscopy and suitable correction for the solvent content was made using the data given in Table 1. The imide content for various APC-PI alloys having APC concentrations equal to or below C.C.C. are shown in Table 2. It can be seen from Table 2 that the incorporation of APC made the process of imidization a little sluggish and an increase in the concentration of APC decreases the achievable degree of imidization at a given temperature. Like neat polyimide, no imidization took place at 50°C and the process of imidization commenced at 100°C.

The difference of approximately 26% was observed between the neat polyimide and the alloy having highest concentration. This gap in the imide content narrowed further with decrease in the APC concentration and only a gap of 1.5% was found between neat polyimide and alloy having 1.67×10^{-6} mole/dm^3 concentration. This gap of almost the same order existed at all cure temperatures. This observation established that the total loss of a certain part of functionality is responsible for the reduction in imide content which took place at 100°C itself. This also favours the crosslinking reaction between APC and polyimide. The same trend was found in almost all the concentration ranges of antimony pentachloride in polyimide.

The change in mechanical properties of APC-PI alloys were determined for the alloys cured at temperatures from 50°C to 300°C. The evaluation of the mechanical properties was undertaken for three parameters viz; tensile strength (max), elongation at break (%) and modulus (initial). The results for these parameters are given in Tables 3–5, respectively.

Since the antimony pentachloride is added at the polyamic acid stage, the possibility of its reaction with amic acid functionality of the polyamic acid could not be ruled out and the structural integrity of the polymeric alloys are characterized by their mechanical properties. As observed from Table 3, the mechanical property (i.e. tensile strength) increases in the case of alloys cured at 50°C.

The overall improvements in the mechanical properties of APC-PI alloys were observed for all the concentrations of APC. There had been manifold enhancement in the mechanical properties even with very low concentrations of antimony pentachloride. This trend could be seen distinctly at lower cure temperatures and no significant variation was observed with increase in cure temperature. The reduction

Table 4
Elongation (at break) of APC-PI alloys

S. No.	Concentration of antimony pentachloride (mole/dm^3)	Elongation (%) of APC-PI alloys at different TTPS					
		PROF 50	PROF 100	PROF 150	PROF 200	PROF 250	PROF 300
1	0.0 (neat PI)	2.5	2.5	5.2	6.1	7.3	9.3
2	1.67×10^{-6}	2.9	3.2	5.4	7.2	8.1	10.5
3	1.67×10^{-5}	3.0	2.9	4.8	8.0	6.8	2.9
4	1.67×10^{-4}	3.3	3.4	3.8	5.7	7.2	3.4
5	1.67×10^{-3}	1.7	2.5	3.6	5.8	4.5	5.8
6	1.67×10^{-2}	1.6	2.1	3.1	3.0	3.9	4.2

Table 5
Initial modulus (GPa) at different TTPs

S. No.	Concentration of antimony pentachloride (mole/dm^3)	Initial modulus (GPa) at different TTPs					
		PROF 50	PROF 100	PROF 150	PROF 200	PROF 250	PROF 300
1	0.0 (neat PI)	0.3038	0.5194	0.735	0.9604	1.078	1.5778
2	1.67×10^{-6}	0.8869	1.225	1.372	1.5288	1.666	1.813
3	1.67×10^{-5}	1.9404	2.2636	2.2442	2.2834	2.1952	1.7738
4	1.67×10^{-4}	2.058	2.2001	2.352	2.4941	2.4001	1.4896
5	1.67×10^{-3}	2.156	2.107	2.0188	2.6754	2.6754	1.5748
6	1.67×10^{-2}	1.862	1.9698	1.8522	2.058	2.7636	0.3969

in APC concentration is expected to decrease the degree of crosslinking in the APC-PI alloy which results in improvement in mechanical properties. The formation of an alloy of the crosslinked and uncrosslinked polymeric molecule offers the synergism of the properties resulting in the improvement of mechanical properties. As the improvement in mechanical properties is explained by the charge transfer complexes in polyimide by previous authors [16–18], the charge transfer complex between crosslinked and uncrosslinked polyimide molecules may be also responsible for the improvement in properties.

4. Conclusions

The incorporation of a metal salt like antimony pentachloride introduced crosslinking polyamic acid yielding a blend of crosslinked and uncrosslinked molecules. The thermal imidization of crosslinked and uncrosslinked polyamic acid has resulted in polyimide alloys that exhibit synergism in mechanical properties while retaining the inherent features of unmodified polyimides. The improvement in mechanical properties are noteworthy at low temperature cures and also at relatively low degrees of imidization.

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