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Thermal analysis of polysiloxanes, aromatic polyimide and their blends

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Abstract

Low molecular weight poly(dimethylsiloxane) and poly(methylphenylsiloxane) were synthesized and blended with polyimide (PI) at its precursor poly(amic acid) stage. FTIR analysis has proven the retention of polysiloxanes in polyimide after the ultimate curing of blends. Differential scanning calorimetric analysis was performed on polysiloxanes to elucidate the structures present in polymers while thermogravimetric analysis (TGA) was performed on polysiloxanes, polyimide as well as their blends to evaluate the thermal stability and to analyze the effect of polysiloxane incorporation in blends. Blends have shown synergistic improvement as compared to neat polyimide.

Keywords: Poly(dimethylsiloxane); Poly(methylphenylsiloxane); Polyimide; Blending; Thermal analysis; Energy of activation

1. Introduction

Aromatic polyimide (PI), a condensation product from the reaction of pyromelliticdianhydride and oxydianiline finds use in myriad of technical and industrial field such as dielectric materials for microelectronics, high temperature adhesives, photoresists, nonlinear optical materials, membranes for separation technology, atomic oxygen resistant polymers for low earth orbit spacecrafts and Langmuir–Blodgett (LB) films. These applications arise as polyimides are associated with excellent mechanical properties, low relative permitivity, high breakdown voltage, low losses over a wide range of frequency, good planarization, good processability, wear resistance, inertness to solvents, good adhesion properties, low thermal expansion, good hydrolytic stability, and long term stability [1]. Similar to polyimides, polysiloxanes do possess unique properties which cover a wide range of applications for electrical insulation to biomaterials and use in space research as they combine the advantages of synthetic variability of organic polymer with thermal and oxidative stability of inorganic polymers. Despite of many outstanding properties of polysiloxanes, these show cold flow characteristics even when the molecular weight of the chain is as high as 1 million and thus necessitating the use of the crosslinker to provide rigidity [2]. Hence, it was realized long back that the combination of polyimide and polysiloxane could be used to draw the benefit from both the polymers.

Thermal stability and degradation of polyimide backbone has been an area of extensive research [3–12]. Tsimpris and Mayhan [13] have reported thermal analysis for the cyclization of polyamic acid (PAA) to polyimide and thereafter its decomposition in both oxidative and nonoxidative atmosphere. Bishop and Smith [14] have studied thermal degradation of aromatic polyimide in nitrogen atmosphere using pyrolysis gas chromatography, infrared spectroscopy, and radiochemical techniques. Degradation mechanism has also been postulated by these workers and found major degradation products were carbon dioxide and carbon monoxide, while hydrogen, methane, ammonia, water, hydrogen cyanide, and benzene were also formed along with small amount of phenol and benzonitrile. Bruck [15] has reported an excellent study on thermal degradation of aromatic polypyromelitimide in air as well as in vacuum and calculated their respective rate constant along with the activation energies.

Due to high applicability of silicone fluid/polymers, their thermal stability has also been widely studied by many researchers [16–18]. In a series of papers by Semlyen and coworkers [19–23], various techniques for the synthesis

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of polysiloxanes, their characterization along with thermal stability has been reported. Thomas and Kendrcik [24,25] have investigated the thermal degradation of poly(methylphenylsiloxane) in controlled atmosphere and analyzed the kinetics aspects associated with the decomposition process. Clarson and Semlyen [26] have reported the high temperature thermal behavior of cyclic and linear PDMS using differential scanning calorimetry (DSC) and thermogravimetirc analysis. Lee and Meier [27] had reported the synthesis of diarylsiloxane as well as arylmethylsiloxane and investigated their thermal behavior.

Apart from the individual studies on both the polymers, i.e. polyimide and polysiloxane, investigation has also been made on the combination of both these moieties. Spectrum of research findings has been published by Arnold et al. [28–32]. Classic review articles by McGrath and coworkers [33,34] indicate the applicability of the polysiloxane segmented polyimide along with their thermal stability for elevated temperature usage. In most of the cases reported so far, combination of both the polymers were achieved by segmenting polysiloxane to polyimide backbone via reactive end group reactions and no study has been made on blends of both the components. The inability to use siloxane and polyimide as blend components may be probably due to the reason that process involves optimization of too many parameters at the same time to produce a successful blend. In this study, an attempt has been made to analyze the effect of polysiloxane on thermal stability of polyimide–polysiloxane blends.

2. Experimental

2.1. Materials used

Analytical grade benzene, 1,2,4,5-tetracarboxylic, 1,2,4,5-dianhydride, and 4,4′-diaminodiphenyl ether (ODA) were supplied by Merck, Germany and were used as such. Analytical grade tetrahydrofuran and *N*,*N*′-dimethylacetamide were supplied by Aldrich and were purified by distillation under reduced pressure and dried over calcium hydride for 24 h. Analytical grade dimethyldichlorosilane was supplied by Across Chemical Ltd. and was 99.7% pure, hence was used as such. Water used in this study was double distilled.

2.2. Synthesis of polyamic acid (PAA)

Into a 500-ml three-necked round bottom flask fitted with mechanical stirrer, nitrogen inlet, and drying tube of $CaCl_2$, was taken 0.05 mol of 4,4′-diaminodiphenyl ether in 188 g of dry dimethylacetamide (DMAC). Benzene–1,2,4,5-tetracarboxylic–1,2,4,5-dianhydride (PMDA) (0.05 mol) was added slowly to the above solution with vigorous mixing. After complete addition, reaction mixture was stirred for additional 2 h in nitrogen atmosphere. The concentration of solution was 10% having intrinsic viscosity of 29.37 dl/g at 26 °C when stored at −10 °C temperature.

2.3. Synthesis of polydimethylsiloxane (PDMS)

NaCl was added to double distilled water in ratio of 2:1 (by volume) to make a supersaturated solution. Polydimethylsiloxane was synthesized by dropwise addition of 25 ml dimethyldichlorosilane to the above prepared saturated aqueous solution of NaCl in a three-necked round bottom flask fitted with a nitrogen inlet, water condenser and magnetic stirrer. Temperature of the reaction was kept at 0 °C during entire process. Products obtained after hydrolysis were extracted with diethylether and washed several times with water and finally with very dilute solution of Na_2CO_3 to remove last traces of acid. The mixture of cyclic and linear polymer so obtained was subjected to fractional distillation at 200 °C and 200 mg Hg. The fraction obtained after 200 °C was linear poly(dimethyl siloxane diol), free from cyclics. The linear PDMS was purified by repeated washing in distilled water followed by passing it repeatedly through silica gel column to ensure complete removal of absorbed water molecules. Polymer obtained was transparent low viscous having intrinsic viscosity of 16.15 dl/g and density 0.981 g/cm^3.

2.4. Synthesis of polymethylphenylsiloxane (PMPS)

Poly(methylphenylsiloxane) was synthesized by the hydrolysis of 25 ml dichlorophenylmethylsilane with icy cold water in a three-necked round bottom flask equipped with nitrogen inlet, water condenser, and magnetic stirrer. Resultant viscous oily layer was extracted with diethylether and washed several times with water and finally with very dilute solution of Na_2CO_3 to remove last traces of acid. Polymer obtained was transparent low viscous having intrinsic viscosity of 13.14 dl/g and density 0.97 g/cm^3.

2.5. Preparation of poly(dimethylsiloxane-imide) or DMSI and poly(methylphenylsiloxane-imide) or PMSI blends

PDMS and PMPS in various concentrations were taken in a known volume of tetrahydofuron (THF) and added to the fixed quantity of polyamic acid to result into the blends of required concentrations and were designated as DMSI and PMSI—3, 5, 10, 15, 20, and 25, respectively, where numerals denote the percentage of polysiloxanes in blends. THF was chosen as solvent on the basis of its miscibility with DMAC and its use as a solvent for the preparation of PAA. Additionally, it was also necessary to ensure that two solvents should not interact each other. Various blends compositions comprising two polymers were prepared by mixing them for 2 h with the help of electric motor operating at 3.33 rph in flowing nitrogen atmosphere. Resultant blends were kept under the blanket of nitrogen at 10 °C for 48 h. These blends were used for casting and curing process.

2.6. Casting and curing

Calculated quantities of different blend compositions were spread over clean dry glass plate in a dust free chamber by means of a doctors blade to ensure uniform ultimate thickness of 25 ± 2 μm. The films on glass plate were kept overnight at ~50 °C followed by soft backing upto 100 °C and thereon retained for 1 h at this temperature. The films were then heated in steps, i.e. at 160 °C for 2 h (to ensure slow removal of DMAC), 200 °C for 1 h (to ensure cyclization or imidization), and ultimately at 300 °C for 2 h (to ensure the maximum possible ordering and crystal growth). Polyimide films so obtained were cooled to room temperature and removed from the glass plates.

3. Characterization

3.1. FTIR spectroscopy

FTIR spectra were measured on a Perkin-Elmer model 720X instrument, using cured films and cast films on KBr discs. The polymer films were dried in oven at 100 °C for 1 h before FTIR measurements. The spectra were recorded on Spectrum one software.

3.2. Thermal analysis

Differential scanning calorimetry was performed on a duPont USA, instrument. Scan were run at 10 °C/min in flowing nitrogen atmosphere for heating cycle and 5 °C/min for cooling cycle. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 instrument using Pyris software. The heating rate was 20 °C/min in air and nitrogen atmosphere. All analysis was conducted on samples in the form of 300 °C cured films and synthesized polymer.

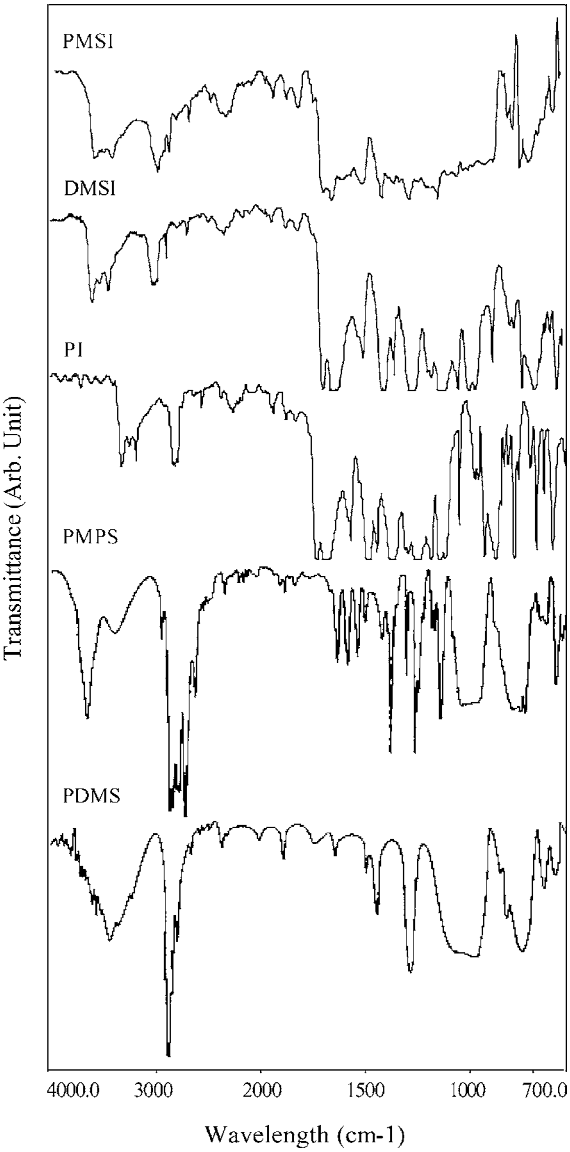

Fig. 1. FTIR analysis of PDMS, PMPS, PI, DMSI and PMSI.

4. Results and discussion

4.1. FTIR analysis of PDMS, PMPS, PI, and their blends, i.e. DMSI and PMSI

Molecular confirmation of the synthesized polymers and their blends were drawn from FTIR analysis. FTIR spectras of synthesized PDMS, PMPS, PI, and their blends are shown in Fig. 1. Strong peak at 551 and 1050 cm^{-1} corresponding to symmetrical Si–O–Si stretching can be seen in case of polysiloxanes. Asymmetric C–Si–O stretching for linear polymer $(Me_2Sio)_x$ type, was seen in both these polymers at 1263 cm^{-1} [35]. Characteristic symmetrical and asymmetrical methyl stretching was also found in both these polymers around 2900 and 2964 cm^{-1}, respectively. Peaks and strong hump concentrating around 4000–3400 cm^{-1} corresponding to the presence of Si–OH group was found in both the polysiloxane samples while in case of PMPS, Si–ph stretching was found at 1429 cm^{-1} [36]. In case of cured neat PI, sharp band around 3440 cm^{-1} has been found for primary and secondary amine stretching while imide stretching at 1777 cm^{-1}. DMSI spectra show strong absorptions at 1776, 1726, and 755 cm^{-1} suggesting that essentially imidized structures were obtained. Strong evidences for the existence of silicone in polymeric blends can be inferred from the appearance of methyl group stretching at 2900 cm^{-1} and disappearance of one of the imide band at 776 cm^{-1} [37]. FTIR spectra for PMSI blends shows sharp band at 1777 cm^{-1} indicating that an imidized structure is obtained, while clear methyl group stretching at 2900 cm^{-1} and phenyl group at 1428 cm^{-1} indicates the incorporation of PMPS in PI, hence proving that PMPS and PDMS retains their identity even after the complete curing cycle of the blends to 300 °C.

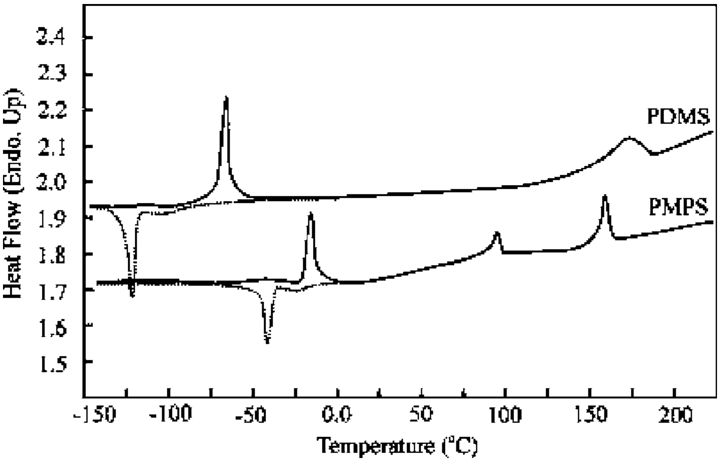

Fig. 2. DSC traces of PDMS and PMPS for heating and cooling cycles. Dotted line for cooling cycle while solid line represents heating cycle. Scan were run at 10 °C/min in flowing nitrogen atmosphere for heating cycle and 5 °C/min for cooling cycle.

4.2. DSC analysis of PDMS and PMPS

Differential scanning calorimetric study was performed on PDMS and PMPS to reveal the structures present in the polymers. Samples were first cooled to freezing point and finally the cooling cycle was reversed to heating to melt the crystallites formed at low temperature. DSC heating traces of the PDMS and PMPS are shown in Fig. 2. Both the curves (i.e. for heating and cooling cycle) are shown for better understanding. In case of PDMS a weak transition at −113 °C and a sharp transition around −125 °C has been found, corresponding to glass transition temperature (T_g) and crystallization, in cooling cycle, while a transition around −70 °C in reverse cycle (heating) corresponds to the melting of solid crystalline PDMS formed during the cooling cycle [38–40]. A broad transition at 172 °C in heating cycle has been observed and may be attributed to the equilibration process and chain elongation of PDMS. In case of PMPS a weak transition at −26 °C and a sharp transition around −41 °C corresponds to the glass transition temperature (T_g) and crystallization, respectively, results similar to these are reported elsewhere [40,41]. Another transition observed in reverse cycle at −22 °C was attributed to the melting of crystalline PMPS formed in cooling cycle. Addition to these two more transitions were observed at +91 and +163 °C, corresponding to the depolymerization of few low molecular mass moieties present in the sample and equilibration process of cyclic and linear structures of PMPS, respectively.

4.3. Thermogravimetric analysis and PDMS and PMPS

Inert and air atmosphere thermograms of PDMS and PMPS are shown in Figs. 3 and 4, respectively. Characteristic degradation temperatures and corresponding associated parameters obtained from these thermograms are summarized in Table 1. $D_{0.1}$ indicates the temperature at which the 10% of decomposition occurs, while $D_{1/2}$ indicates the temperature at which half of decomposition occurs and

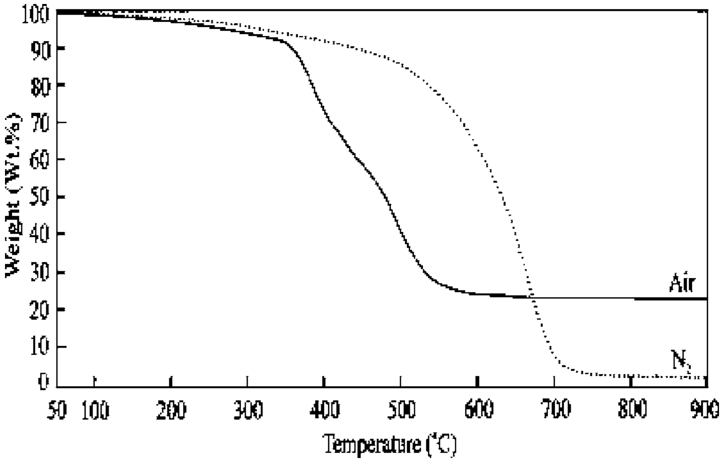

Fig. 3. Inert and air atmosphere thermogravimetric analysis of PDMS. Scan were run at 20 °C/min in inert and air atmosphere.

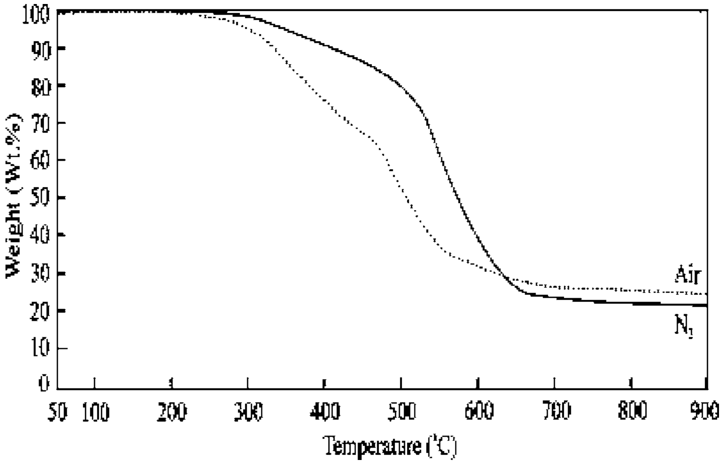

Fig. 4. Inert and air atmosphere thermogravimetric analysis of PMPS. Scan were run at 20 °C/min in inert and air atmosphere.

MRDT is the maximum rate of decomposition (MRD) temperature. It can be seen from the Fig. 3, that PDMS shows good thermal stability as $D_{0.1}$ value in inert atmosphere was found to be 440 °C while in air atmosphere its value was found to be 377 °C. Temperature for half of decomposition $D_{1/2}$ was found to be nearly 184 °C higher for inert atmosphere as compared to air atmosphere. Residue obtained after the complete decomposition of PDMS to 900 °C was found to be 2.50 wt.% in inert atmosphere probably due to the formation of ceramic type of structure, while the residue in air atmosphere was around 30.50 wt.% which may be attributed to the formation of silica in form of SiO_2. Two-step decomposition, hence two derivatograms were found in inert as well as for air atmosphere. In two-step decomposition, first decomposition step may be probably due to the presence of few lower molecular weight linear polymeric chains, which might decompose at slightly lower temperature, while second step may be a contribution from relatively higher molecular weight products.

Thermal degradation of polymethylphenylsiloxane (PMPS) differs in numerous aspects than that of polydimethylslioxane (PDMS). It is known that nature and number of chain ends influences the rate and extent of thermal degradation of polymer. Hydroxyl group terminated PMPS structure has shown greater stability than that trimethylslioxyl-terminated structure which is opposite to that in case of PDMS [42]. Hence, at elevated temperature, the principal effect of hydroxyl end group in PMPS is not to accelerate depolymerization but to assist in the cleavage of Si–ph bond. This written premise has been strengthened by the fact that an appreciable amount of benzene is formed at high temperature degradation of polymer while the rate of formation and amount of benzene formed increases with the decrease in molecular weight at high temperature, probably due to the increase in liability of the phenyl group adjacent to the hydroxyl group. Initial decomposition temperature (IDT) or $D_{0.1}$ value was found around 340 °C for PMPS in air while 413 °C for inert atmosphere indicating that polymer is comparatively more stable in inert atmospheres. Polymer decomposes rapidly to half of its initial weight in air atmosphere than in inert conditions and the same is supported by maximum rate of decomposition temperature. Residue obtained after the complete decomposition was 31.36 wt.% in air atmosphere and directly corresponds to the formation of silica. Residue obtained in inert atmosphere was 23.18 wt.%, a value much higher as compared to that in case of PDMS (2.3 wt.%). This higher residual content may be attributed to the existence of aromatic group in PMPS and its degradation to carbonaceous product at high temperature. Reason for the increment in residue for air atmosphere as compared to inert atmosphere is not clear and mechanism is still under intense investigation.

4.4. Thermogravimetric analysis of PDMS/PI or DMSI blends

Curing of blends to 300 °C leads to a polymeric system having best of possible physicomechanical properties [43]. Additionally, it was the temperature at which maximum possible imidization in polyimide has been achieved

Table 1
Inert and air atmosphere TGA derived parameters of polysiloxanes

Sample designation	Inert atmosphere parameters (°C)			Air atmosphere parameters (°C)			Residue analysis (%)	
	$D_{0.1}$	$D_{1/2}$	MRDT	$D_{0.1}$	$D_{1/2}$	MRDT	Inert atmosphere	Air atmosphere
PDMS	440.68	630.51	667.80	376.82	446.63	655.41	2.50	30.50
PMPS	412.52	550.00	523.20	340.68	477.60	488.24	23.18	31.36

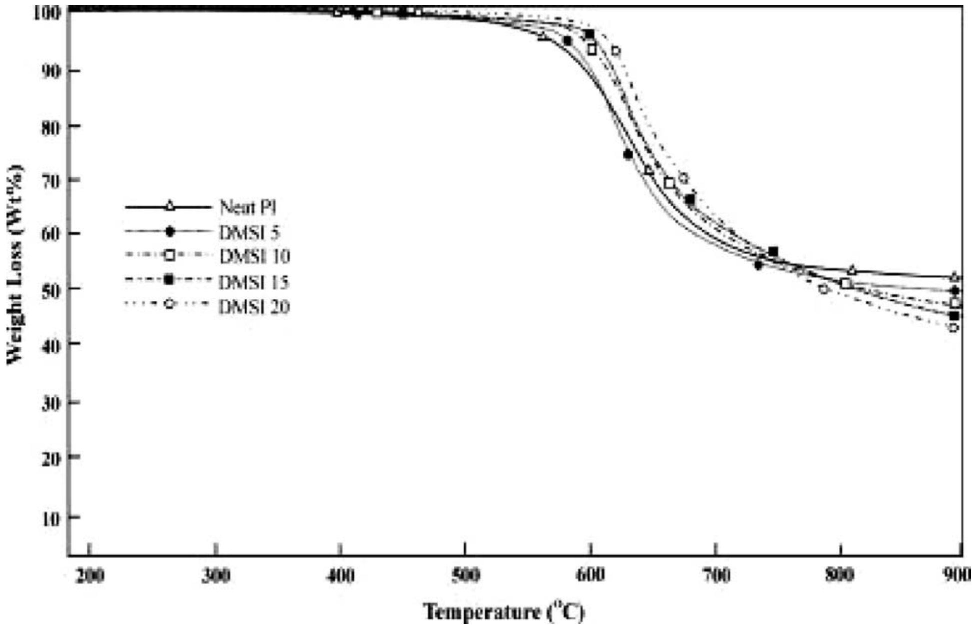

Fig. 5. Inert atmosphere thermogravimetric analysis of DMSI blends. Scan were run at 20 °C/min in inert atmosphere.

[44–46]. Hence, most of the properties reported here are for 300 °C-cured blends. Incorporation of flexible polysiloxane having relatively lower thermal stability than polyimide may result in lowering of thermal stability in ultimate blend compositions as reported earlier [47,48], but the reverse was observed as blends have shown better thermal stability than the neat polyimide.

In inert atmosphere, $D_{0.1}$ value increases for blends (Fig. 5) with the increase in PDMS concentration and maximum value was found for DMSI-20 as nearly 18 °C rise was achieved for this composition as compared to neat polyimide. The above reported increment may not seem pronounced at first sight, but careful studies has shown that thermal stability was approximately 196 °C higher for these blends as compared to the values reported elsewhere for the identical concentration of silicone in polyimide [48]. MRD temperature increases (Table 2) with the increases in polysiloxane concentration and finally falls beyond 20 wt.% of polysiloxane concentration in blends. This increase in MRD temperature suggests that the role of polysiloxane in polyimide blend is to prevent the thermal degradation of polyimide backbone. Additionally, in this case, polysiloxane do not form part of polyimide backbone as in case of polysiloxane-segmented polyimide reported elsewhere [48]. Feasibility and facility of rotation along the Si–O linkage can compel polysiloxane molecule to absorb a part of heat energy and thereby raising the requirement of temperature. A single derivatogram was obtained for each composition of blend consistent with both blend components decomposing following an identical kinetic pathway. It was also seen that maximum rate of decomposition decreases with the increase in polysiloxane in blends as MRD value was 10.2%/min at 582 °C for neat polyimide which decreases to 8.3%/min at 618 °C for DMSI-25, supporting the argument that presence of polysiloxane retards the decomposition of blends.

In air atmosphere (Fig. 6), both the components, i.e. polyimide and polysiloxane have shown stability slightly towards the lower side as compared to that in inert atmosphere. The organic linkages present in polymers may tend to show less susceptibility to elevated temperature and presence of

Table 2
Inert and air atmosphere TGA derived parameters of DMSI blends

Sample designation	Inert atmosphere parameters (°C)			Air atmosphere parameters (°C)			Residue analysis (%)	
	$D_{0.1}$	$D_{1/2}$	MRDT	$D_{0.1}$	$D_{1/2}$	MRDT	Inert atmosphere	Air atmosphere
PI	600.00	632.02	582.10	536.66	593.24	545.00	53.00	0
DMSI-3	604.03	635.43	602.75	545.21	602.54	557.58	51.50	0.90
DMSI-5	606.17	633.71	610.26	551.34	607.37	569.83	50.57	1.63
DMSI-10	610.82	638.47	614.23	558.57	611.21	566.72	48.38	3.12
DMSI-15	616.55	640.44	617.37	563.42	619.66	570.72	46.37	4.95
DMSI-20	618.26	642.74	620.78	566.91	625.44	576.26	44.51	6.79
DMSI-25	617.14	639.66	618.08	563.33	630.23	583.35	42.82	8.20

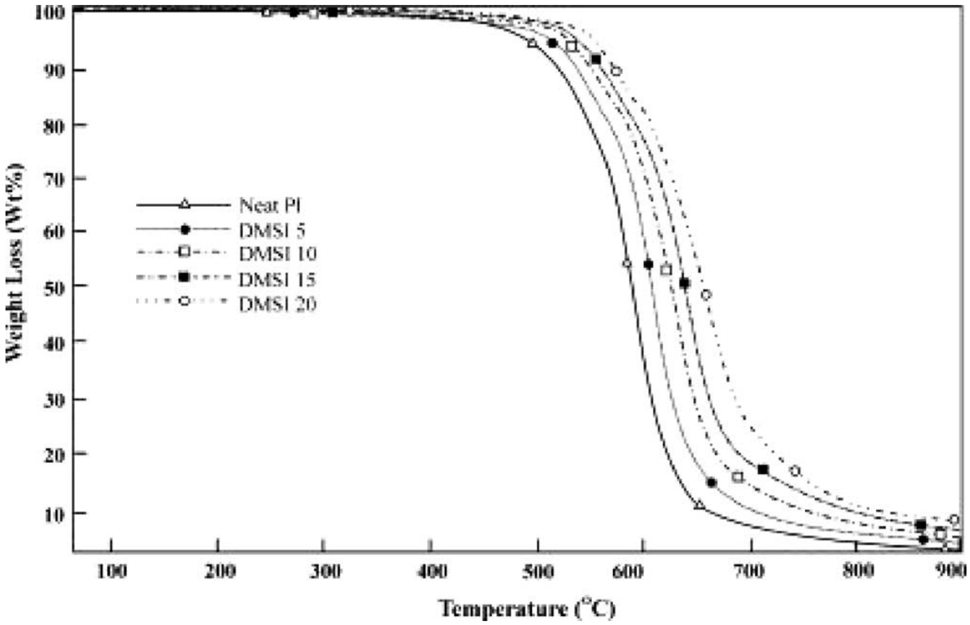

Fig. 6. Air atmosphere thermogravimetric analysis of DMSI blends. Scan were run at 20 °C/min in air atmosphere.

oxygen in air. Although, the thermal stability was found lower as compared to inert atmosphere but still the trend was same for all the blend compositions as stability increases with the increase in concentration of polysiloxane in blends and stability in each case was found higher than that of neat polyimide. Nearly 30 °C rise in $D_{0.1}$ value (567 °C) was obtained in case of DMSI-20 and can be attributed to some protective mechanism of polysiloxane present in bulk. Two clear derivatograms were obtained corresponding to two-step decomposition in blends. Area under the derivatogram curves gives an idea about the nature of the polymeric chains hence their degradation in blends. Similar to inert atmosphere, maximum rate of decomposition decreases with the increase in polysiloxane in blends as MRD value was 7.3%/min at 583 °C for DMSI-25. Results indicate that conversion of PDMS domains to silica at elevated temperature acts as heat sink and makes the surrounding polymeric chains to experience less temperature than actual.

4.5. Thermal stability of PMPS/PI or PMSI blends

Inert and air atmosphere thermograms of poly(methylphenylslioxane-imide) blends have been shown in Figs. 7 and 8, while the corresponding parameters are given in

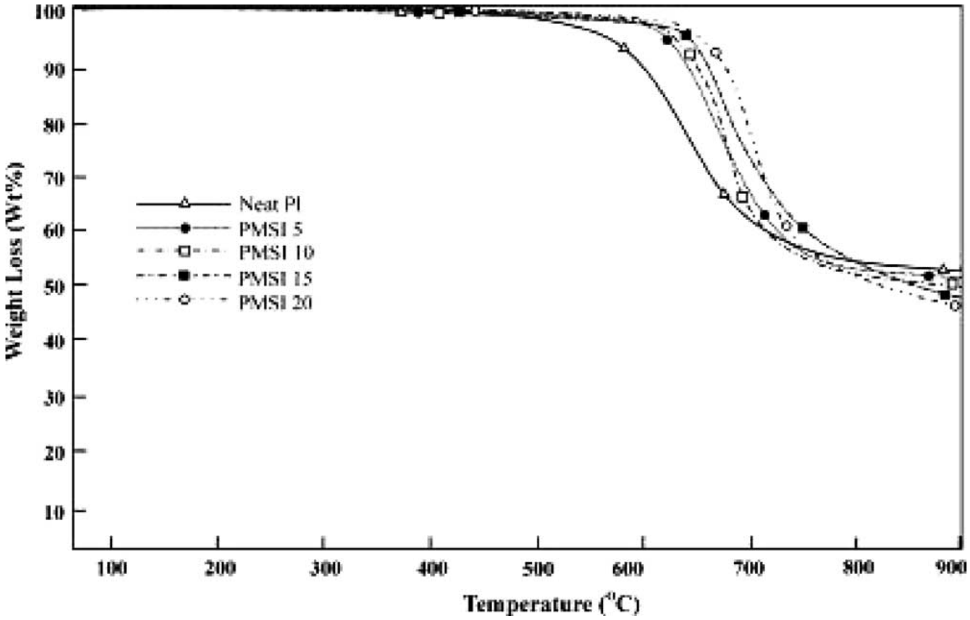

Fig. 7. Inert atmosphere thermogravimetric analysis of PMSI blends. Scan were run at 20 °C/min in inert atmosphere.

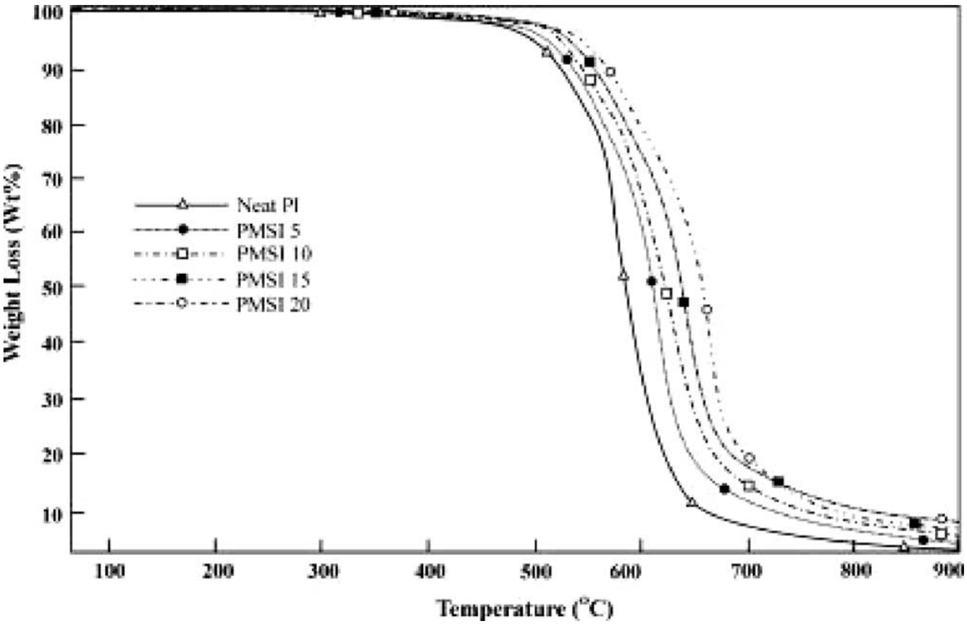

Fig. 8. Air atmosphere thermogravimetric analysis of PMSI blends. Scan were run at 20 °C/min in air atmosphere.

Table 3. As symbolized from Fig. 7, thermal stability of blend composition increases with the increases in PMPS concentration for insert atmosphere. A hike of 82 °C has been found for PMSI-20 as compared to neat polyimide and may be attributed to the protective mechanism of PMPS. It appears that the requirement of high temperature for the degradation of blends arises due to the increase in potential energy barrier formed by the electrostatic attraction between the polyimide molecules and silicone moiety. Our previous studies have indicated that elevated temperature curing of these blends results into the decomposition of few silicone aryl linkages and thereby the formation of highly charged electronic domains around the silicone premises [49]. These domains may interact with the excited electronic states in polyimide molecules thereby resulting into the formation of charge transfer complexes. These complexes may enhance the potential energy barrier for the degradation, which can only be overcomed by the supply of energy higher than the normal. Temperature for half of decomposition increases with the increase in polysiloxane concentration in blends and a maximum value (691 °C) was found for PMSI-25. Similar to that in case of DMSI blends, decomposition of PMSI blends was found to occur in single step and thus, producing single derivatogram. MRD value was 7.8%/min in case of PMSI-20 at 692 °C, indicating that presence of polysiloxane retards the degradation of polyimide macromolecule probably by mechanism discussed above.

In air atmosphere, degradation of blend was found slow as compared to neat polyimide as thermal stability increases with the increase in polysiloxane concentration. Nearly 76 °C rise in $D_{0.1}$ value was found for PMSI-25, as compared to neat polyimide degradation in air atmosphere. $D_{1/2}$ temperature also increases with the increase in polysiloxane concentration in blends. Maximum rate of decomposition was found to be 9.1%/min at 698 °C in case of PMSI-25 and value for the same in case of neat polyimide was 15.5%/min at 560 °C suggesting that the presence of polysiloxane between the layers of polyimide macromolecule deaccelerates the decomposition pattern of the blend constituents. In each case of blend, a dual step decomposition pattern has been seen, giving rise to two derivatograms. Study of area under the derivatograms indicates that decomposition pattern of

Table 3
Inert and air atmosphere TGA derived parameters of PMSI blends

Sample designation	Inert atmosphere parameters (°C)			Air atmosphere parameters (°C)			Residue analysis (%)	
	$D_{0.1}$	$D_{1/2}$	MRDT	$D_{0.1}$	$D_{1/2}$	MRDT	Inert atmosphere	Air atmosphere
PI	600.00	632.02	582.10	536.66	593.24	545.00	53.00	0
PMSI-3	635.60	656.72	649.27	563.67	613.22	612.73	55.41	0.97
PMSI-5	664.41	674.58	664.19	574.88	634.17	656.60	57.50	2.00
PMSI-10	668.54	672.88	674.41	584.28	640.11	693.60	57.75	4.41
PMSI-15	679.66	683.39	688.92	590.25	647.24	695.20	59.00	6.92
PMSI-20	682.02	688.50	691.97	610.65	654.33	697.72	60.02	9.93
PMSI-25	681.31	691.10	690.82	612.00	658.36	698.47	63.15	11.35

polymeric chains is strictly governed by the nature of forces between the blend components that hold them intact.

4.6. Effect of blend ratio on energy of activation for decomposition

The activation energy for the decomposition of polymers and their blends can be calculated using integral equation of Coats and Redfern [50].

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2}\right] = \log_{10}\frac{R}{\Delta E_a}\left[1-\frac{2RT}{E_a}\right]-\frac{E_a}{2.303RT} \quad (1)$$

In above equation, T is the absolute temperature in Kelvin, E_a the activation energy in cal/mol, R the gas constant having value 1.987 cal/(mol K), n the order of reaction, and α is the fraction decomposed at that particular temperature calculated as:

$$\alpha = \frac{w_i - w_t}{w_i - w_f} \quad (2)$$

where w_i is the initial weight of the sample, w_t the weight at given temperature and w_f is the final weight of the sample. The best-fit value of 'n' was obtained by plotting for the first order kinetics [$\ln(1-\alpha) = -kt$]. A kinetic plot of $-\ln(1-\alpha)$ versus time of decomposition or conversion gives a straight line indicating that decomposition of blends follows first order kinetics. It was observed from the kinetic analysis that decomposition reaction of PDMS, PMPS, PI, and their blends follows similar kinetics and reaction order was independent of the level of polysiloxane in polyimide. Eq. (1) is valid for order of reaction other than $n = 1$, for which equation reduces to

$$\log_{10}\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right] = \log_{10}\frac{R}{\Delta E_a}\left[1-\frac{2RT}{E_a}\right]-\frac{E_a}{2.303RT} \quad (3)$$

From the kinetic plots, value of n was found 1 and thus $-\log_{10}[-\log_{10}(1-\alpha)/T^2]$ was plotted against $1000/T$ (K) for each polymer and their blends. Finally the value of activation energy (E_a) was calculated from the slope of the above plot as

$$E_a = 2.303R \times \text{slope} \quad (4)$$

Fig. 9 shows plot of activation energy of different blend compositions for air as well as inert atmosphere. In case of each blend E_a value increases with the increase in polysiloxane concentration in polyimide. E_a value increases to 39.03 kcal/mol for DMSI-25 as compared to neat polyimide having value 32.10 kcal/mol in an inert atmosphere while for air atmosphere this value was 29.96 kcal/mol for the same blend composition; further strengthening the fact that presence of PDMS in polyimide as a blend component increases thermal stability of blends to an appreciable extent. Similar to that in case of DMSI blends, E_a value rises linearly with the increase in PMPS concentration in PMSI blends. An E_a value increment to 42.58 kcal/mol was found for PMSI-25 as compared to neat polyimide having E_a value of 32.10 kcal/mol in inert atmosphere, while this increment was very high (E_a = 41.18 kcal/mol) in case of same blend composition for air atmosphere. Large increase in E_a value for air atmosphere may be probably, a result of high-energy requirement to be met for the decomposition of polymeric chains. This high-energy requirement to trigger the decomposition of PMSI blends may be attributed to some protective shielding mechanism as a result of PMPS decomposition in polyimide leaving behind higher residue and unknown byproducts in air atmosphere. Slope of the E_a plot, shown in Fig. 9, also indicates that energy required to activate the decomposition in case of PMSI blends enhances as a result of increase in aromatic content in blends.

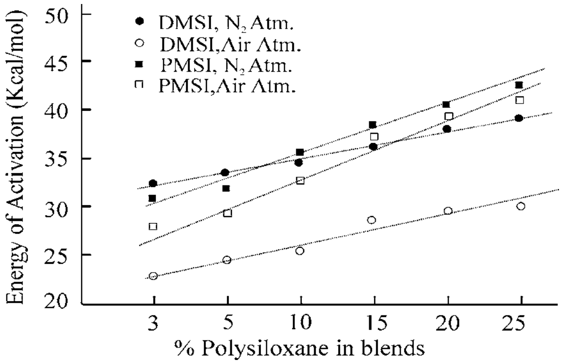

Fig. 9. Energy of activation (E_a) vs. polysiloxane concentration (%) in DMSI and PMSI blends.

4.7. Residue analysis

Residue obtained after the complete decomposition at 900 °C are shown in Tables 1–3 and gives an idea about the mode of thermal decomposition in blends. In case of neat polyimide, residue content was 53% in inert atmosphere while in air atmosphere polyimide decomposes to zero residues. As appears from Tables 2 and 3, residue obtained in each case of blend directly corresponds to the remaining of polysiloxane to silica given in Table 1. A slight higher residue content (as compared to theoretical value) was obtained in each case of blend and may be attributed to the probable formation of ceramic type of structure or as a result of decomposition to polysiloxane crabbed graphitized structure of polyimide reported earlier [51].

5. Conclusion

Thermal studies on polysiloxanes, polyimide, and their blends have been made. Blends have shown synergistic improvement in thermal stability. Mechanism of thermal degradation for blends is not very clear at this point but it appears that decomposition of blends has been retarded due to the presence of dispersed polysiloxane and the same has been supported by the increase in energy of activation for the decomposition with the increase in polysiloxane content in blends. Mechanism of degradation and the kinetic pathways are still to be explored and will be communicated very soon.

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