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Studies on Dynamic Mechanical Analysis and Morphology of Carbon Soot Filled Un saturated Polyester Graded Composites

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Abstract— Dynamic mechanical behaviour of carbon soot filled polyester graded composites was determined with reference to carbon soot concentration present at different positions of the graded composites. At lower temperatures ,E' values are maximum for unsaturated polyester resin whereas above Tg E' values of graded composites are higher than the pure polyester resin . The loss modulus peaks values decreased on increasing the carbon soot concentration .Tg values increased with increase in sootconcentration . Apparent activation energy of the relaxation process of different composites were analysed

Index terms: carbon soot, un saturated polyester, DMA,Storage modulus,Activation energy.

Introduction

In last few decades use of filled and reinforced polymer composites has increased rapidly because these composites exhibit high performance [1]. Considerable amount of work has been reported in the literarture on the viscoelastic properties of particulate polymer composites [2-4]. Recently Chand and Nigrawal [1] have developed HAF carbon filled polyester graded composites and reported their electrical properties. Polymeric composites offer excellent positional properties. Lee and Jang [5] studied glass reinforced polypropylene composites having spatially-graded distributions of fibers . Dynamic mechanical analysis (DMA) is an excellent method to characterize the viscoelastic properties of filled polymers. Recently dynamic mechanical behavior of carbon black filled styrene and butyl methacrylate was reported at low strain amplitude and frequency [6]. Shaffer and Windle [7] reported DMA analysis of carbon nanotube/poly(vinyl alcohol) (PVA) composites and found significant increase in elastic modulus on incorporation of carbon nanotubes [7].Dynamic mechanical behaviour of unsaturated polyester at 1 Hz frequency was determined by Lionetto and Maffezzoli [8].They observed a relaxation during heating at 2 °C /min after Tg of the polyester resin due to the molecular mobility of the residual reactive groups and a decrease in storage modulus.There is no study on the dynamic mechanical analysis behaviour with respect to concentration of carbon soot in polyester.In this paper dynamic mechanical behaviour of carbon soot filled polyester graded composites has been determined .Dynamic mechanical behaviour and morphology of carbon soot filled polyester graded composites have been reported.

I. Materials and methods

Carbon soot powder used in this study was obtained from GNFC India. Carbon soot filled polyester gradient composites were developed by using centrifugation process. In this process centrifugal force was applied in the X direction. Graded composites were prepared from the mix of carbon soot powder filled having 3 wt.% of carbon soot. Carbon soot was added to a mix of unsaturated polyester resin. Polyester resin had 1.5% accelerator and 1.5wt.% hardener in it . Details of set up and process of making gradient composites were reported earlier (Chand and Hashmi) [9]. The total mix was filled in a pin mould to make sample. The sample filled mould was kept in a holder and rotated at 800 + 50 RPM and at a radius of 130 mm. Samples were removed after one hour from the mould and kept for post curing at room temperature for 24 hours. Slicing of pin was done into four discs.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was carried out with a Dynamic mechanical spectrometer model (DMS 6100 SSI Nanotechnology Inc). Measurement of the storage modulus (E'), loss modulus(E'') and tanδ of the samples was carried out under compression mode at 1,2,5 and 10 Hz frequencies in the temperature range from 30°C to 190°C.

Density Measurements

Density values of carbon soot filled polyester graded composite discs ,sliced from different positions were

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determined by using a Mettler Toledo precision balance.

Results and Discussion

Dynamic mechanical analysis plays an important role in understanding the storage modulus and tan δ behaviour of the composite under a wide range of temperature and frequency.

Table 1 lists the density values of sliced graded samples obtained from center (sample1) to periphery (sample 3). This table shows that sample 3 has maximum and 1has minimum density, which corresponds to the carbon soot content present in the samples.

Figs. 1-3 show the variation of dynamic mechanical parameters such as E', E" and tan δ with temperature for samples 1-3 respectively. Decrease in E' value for sample 1 occurs at 46.3, 51.2, 53.5 and at 55.9 °C respectively corresponding to 1, 2, 5 and 10 Hz frequencies. Table 3 a lists the storage modulus values for sample 1 to 3. As the temperature rose, the material initially softened, causing the storage modulus to fall and then it became constant. Loss modulus (E") is due to the viscous response of the composite. It is the dissipation of energy into heat when a material deforms. In case of sample 1 loss moduli increases on increasing the temperature due to the increase in internal friction that increases the dissipation of energy.

tan δ is defined as the ratio of loss modulus to the storage modulus . tan δ peak appears at 69.9, 74.4, 76.3 and at 81.2 °C respectively corresponding to 1, 2, 5 and 10 Hz frequencies. tan δ and E" peaks shifted towards right hand side on increase in frequency. This behaviour is due to α relaxation of polyester resin. In case of pure polyester frequency had a direct impact on the E', E" and on tan δ. E' dropped around 60°C.If a polymer is subjected to a constant stress its elastic modulus decreases with time due to molecular rearrangement to mininmize the localized stresses [10].The storage modulus of a polymer decreases rapidly whereas the loss modulus and tan δ reach a maximum when the polymer is heated up through the glass transition (T_g) region.

In case of sample 2, which had higher concentration of carbon soot as compared to sample 1 (Fig 2). Fall in E' for sample 2 as compared to sample 1 occurs at 45.6, 50.8, 56.5 and at 59.1°C temperatures respectively corresponding to 1, 2, 5 and 10 Hz frequencies. E' values increase on increasing the frequency and temperature .tan δ transition appears at 70.9, 75.6, 77.6 and at 82.5 °C respectively corresponding to 1, 2, 5 and 10 Hz frequencies.

For sample 3, which has maximum concentration of carbon soot in the composite exhibits the tan δ peak s at 70.9, 75.6, 77.7 and at 83.8°C respectively corresponding to 1, 2, 5 and 10 Hz frequencies (Fig 3). This shows that addition of carbon soot shifted the Tg of polyester towards the higher temperature side due to it's higher thermal stability as compared to pure polyester resin [10]. With the increase in temperature damping increases, and reaches to a maximum in the transition region and then decreases in the rubbery region. Because in the rubbery region, the molecular segments are quite free to move and hence the damping is low . Decrease in E' value with increasing in the concentration of carbon soot in the composite reduces the elastic component (polyester).Sharp fall in $E^{''}$ value at the glass transition can be attributed to the increase in molecular mobility of the polymer chains above Tg.

It can be seen in fig.1-3 that both $E^{'}$ $E^{''}$ and tan δ became independent of frequency and temperature at higher temperatures. It was observed that tan δ peak temperature increases from sample1 to sample 3 due to the increase in concentration of carbon soot from sample 1to sample 3 showing relaxation behaviour.The shifting of Tg to higher temperatures can be associated with the decreased mobility of the chains by the increase of carbon soot .Elevation of Tg can be taken as a measure of the interfacial interaction in addition, the stress field surrounding the carbon soot particles induces the shift in Tg [11].

The T_g value is also shifted towards higher temperature region with frequency. The effect of frequency on T_g of the composites can be well explained by Arrehenius relationship. The apparent activation energy (E) for the relaxation process at glass transition region can be calculated using the following equation [12].

$$\log f = \log f_0 - E/2.303RT$$

where f is the measuring frequency, f_0 is the frequency when T approaches infinity, T is the tan δ_{max} temperature and R is the universal gas constant. The slope of the plot obtained from the log f vs reciprocal temperature will give the activation energy for the relaxation process. The E values thus obtained are given in table 2 .The activation energy of the composites is decreased on increasing filler content.

In order to confirm the graded distribution of carbon soot in the composite, it was necessary to observe the surfaces of different positioned samples. Surface microstructures of samples 1, 2 and 3 were observed by using a SEM and are shown in Figs 4-6. Microstructure shown in Figs.4a-c depict the dominance of polyester resin, in some places carbon soot particles are dispersed in the matrix. Fig. 5a-c shows carbon soot particles distribution through out the sample, even in this case there is a segregation of carbon soot particles at one place.Fig.5c shows further increase in concentration of carbon particles and network formation in the microstructures. Maximum number of carbon particles are visible in microstructure of sample 3 (Fig.6d), in this figure the networking is best. This shows that there is a grading of carbon particles distribution in the composites. Sample 1 has minimum carbon content and sample 3 has maximum carbon content.

Figures and Tables

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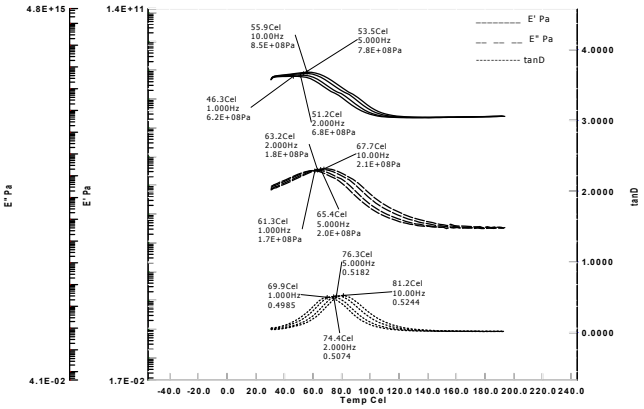
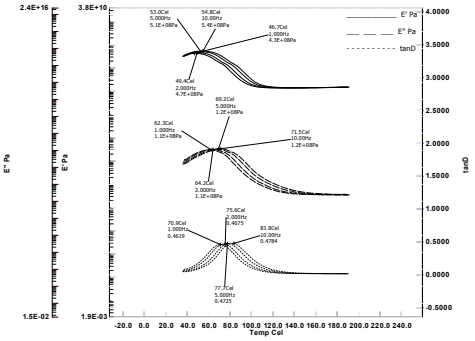


Carbon Soot Polyester Gradient-1



Carbon Soot Polyester Gradient-2

Table 1	**Density of carbon soot filled polyester gradient composites**	
	Sample Designation	**Density (g/cc)**
	Sample 1	**1.22**
	Sample 2	**1.24**
	Sample 3	**1.25**

Table

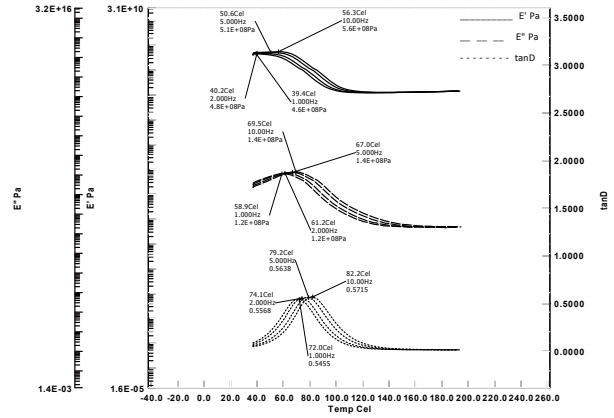
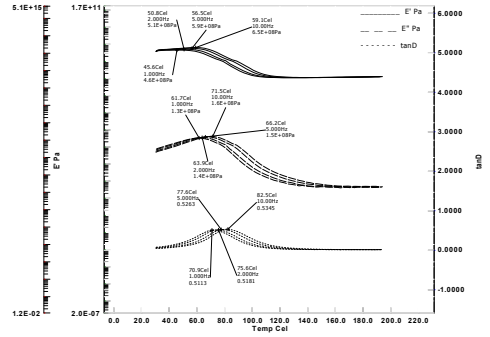


Table 3a

Values of storage modulus

S.No.	Sample Name	Frequency (Hz)	$E^{'}$ Temp. (°C)	$E^{'}$ (Pa)
1.	Carbon Soot Polyester Gradient-1	1	46.3	6.2E+08
		2	51.2	6.0E+08
		5	53.5	7.8E+08
		10	55.9	8.5E+08
2.	Carbon Soot Polyester Gradient-2	1	45.6	4.6E+08
		2	50.8	5.1E+08
		5	56.5	5.9E+08
		10	59.1	6.5E+08
3.	Carbon Soot Polyester Gradient-3	1	46.7	4.3E+08
		2	49.4	4.7E+08
		5	53.0	5.1E+08
		10	54.8	5.4E+08



Carbon Soot Polyester Gradient-3

Table 3b

Values of loss modulus

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S.No.	Sample Name	Frequency (Hz)	E'' Temp. (°C)	E'' Values (Pa)
1.	Carbon Soot Polyester Gradient-1	1	61.3	1.7E+08
		2	63.2	1.8E+08
		5	65.4	2.0E+08
		10	67.7	2.1E+08
2.	Carbon Soot Polyester Gradient-2	1	61.7	1.3E+08
		2	63.9	1.4E+08
		5	66.2	1.5E+08
		10	71.5	1.6E+08
3.	Carbon Soot Polyester Gradient-3	1	62.3	1.1E+08
		2	64.2	1.1E+08
		5	69.2	1.2E+08
		10	71.5	1.2E+08

Table 3c

Values of tan δ Values

S.No.	Sample Name	Frequency (Hz)	tan δ Temp. (°C)	tan δ Values
1.	Carbon Soot Polyester Gradient-1	1	69.9	0.4985
		2	74.4	0.5074
		5	76.3	0.5182
		10	81.2	0.5244
2.	Carbon Soot Polyester Gradient-2	1	70.9	0.5113
		2	75.6	0.5181
		5	77.6	0.5263
		10	82.5	0.5345
3.	Carbon Soot Polyester Gradient-3	1	70.9	0.4619
		2	75.6	0.4675
		5	77.7	0.4725
		10	83.8	0.4784

Conclusions

1.At lower temperatures ,E' values are maximum for unsaturated polyester resin whereas above Tg E' values of graded composites are higher than the pure polyester resin .

2. The loss modulus peaks values decreased on increasing the carbon soot concentration 3.Tg values increased with increase in soot concentration .

4.Activation energy of the composites decreased on increasing the concentration of carbon soot.

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