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EFFECT OF NANO-BARIUM TITANATE ON THERMAL STABILITY OF FERRITE FILLED POLY-ETHER-ETHER-KETONE (PEEK) COMPOSITES

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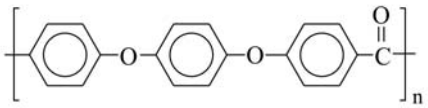
Abstract

The reinforcement of nano-barium titanate in ferrite filled poly-ether-ether-ketone (PEEK) composites caused a shift in the decomposition temperature, at which maximum mass loss occurred, to higher side and enhancement in char yield in thermogravimetric analysis. Loss tangent and glass transition temperature of ferrite filled PEEK composites were also found to be increased with the reinforcement of nano barium titanate. The effect of nano barium titanate on the melting behaviour of ferrite filled PEEK composites was negligible.

Keywords: DMA, DSC, ferrite, nano-barium titanate, PEEK, TG

Introduction

Poly-ether-ether-ketone (PEEK) is a known high-performance thermoplastic which is used as neat polymer, blends and matrix material in various applications. It is semicrystalline and highly aromatic thermoplastic belonging to the class of polymers known as poly(aryl-ether-ketone)s. PEEK is made up of the following repeating unit [1]:



PEEK can be obtained in amorphous and semicrystalline form, depending on the processing conditions employed from the molten state [2–4]. The natural grade of PEEK is 35% crystalline. It has been reported [5–7] that thermal treatment at high

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temperatures in the presence of oxygen may give rise to crosslinking of PEEK. The estimated maximum continuous working temperature of PEEK is 250°C and it retains useful mechanical properties up to 300°C [8]. For brief usage, it can withstand a temperature in excess of 300°C. Under nitrogen atmosphere, PEEK shows a good thermal stability at temperatures as high as 550–580°C beyond which significant mass loss occurs with the decomposition products being phenol and benzoquinone.

The glass transition temperature (T_g) of PEEK is 143°C and crystalline melting point is 334°C. The maximum rate of crystallization of PEEK occurs at around 230°C of annealing temperature [2], which is roughly halfway between the glass transition temperature and melting point.

PEEK is one the best blending materials for high performance applications. It has been blended with many polymers. Its blends offer wide range of properties. In polytetrafluoroethylene (PTFE)/PEEK blends, a shift (towards higher temperature) in the melting peak of the PEEK phase was reported with increasing proportion of PTFE in blend [9].

PEEK is an inert polymer under normal storage conditions and there are no known dust hazards in the handling of fully compounded granules as supplied by M/s.ICI Inc. [10]. When handling PEEK powders or in other situations where dust may be generated, precaution should be taken to prevent dust accumulation and the threshold limit value (TLV), for nuisance particulates, of 30 million particles/ft^3 should be observed [11].

Experimental

Materials

Fine powder grade of PEEK (grade: 450 PF), used in this study, was supplied by M/s. ICI Inc., UK. Ferrite and nano-barium titanate, used in this experiment, were indigenous. The ferrite used in these experiments was cobalt–silicon (Co–Si) doped barium hexa-ferrite having molecular formula, $BaCo_xSi_xFe_{12-2x}$ [12]. The particle size of barium titanate was ~25 nm. In all the composites, fast extrusion furnace (FEF) carbon black as per ASTM D 1765 No. 550, was used. This provided moderate reinforcement and stability against oxidative thermal degradation.

Preparation of mouldings

The moulding of samples was carried out in compression moulding machine. The charge was weighed, mixed and dried at 200°C for 2 h. The matched die mould made out of tool grade steel was used to fabricate composite sheets. Charging of the mould cavity was carried out carefully as the bulk factor of powdered PEEK was high. The charge was compacted many times to remove entrapped air and obtain voids free composite sheets. The moulding was carried out at maximum temperature of 400°C and pressure of 100 kg cm^{-2}.

Designation of samples

Table 1 defines the designation of the samples and their constituents for ferrite filled PEEK composites and, ferrite and nano-barium titanate filled PEEK composites moulded for this study.

Table 1 Designation and constituents of samples

No.	Sample designation	Composition/%			
		PEEK	Ferrite	Nano-barium titanate	Carbon black
1a	PFM2	97	2	0	1
1b	PFBM2	96	2	1	1
2a	PFM4	95	4	0	1
2b	PFBM4	94	4	1	1
3a	PFM6	93	6	0	1
3b	PFBM6	92	6	1	1
4a	PFM8	91	8	0	1
4b	PFBM8	90	8	1	1
5a	PFM10	89	10	0	1
5b	PFBM10	88	10	1	1

Thermogravimetric analysis (TG)

Thermogravimetric analyser (Product code; Hi-Res TGA 2950; manufactured by: M/s TA Instruments, USA) was used for the experiments [13]. The test samples were prepared in the form of small particles using hand operated crimping and shearing machine. The heating rate was kept 10°C min^{-1} and temperature range was kept from ambient to 800°C, for the samples of all compositions in nitrogen atmosphere.

Dynamic mechanical analysis (DMA)

In this study, forced oscillation was used in flexural mode. Dynamic mechanical analyzer (Product code: DMA 2980, manufactured by: M/s TA Instruments, USA) was used for the experiments. The test samples were prepared using the electrically operated circular cutting saw (specs.: motor power: 3 HP, manufactured by M/s. Bharat Bijli, Corp. Ltd.; rpm: 2800; 3 phase, AC, 440 V; belt drive; brass cutting wheel of 8" diameter; wooden platform). The heating rate was kept 10°C min^{-1} and temperature range was kept from ambient to 300°C, for the samples of all compositions. DMA test was carried out on two different frequencies of 1 and 10 Hz. The glass transition temperature (T_g) was evaluated as the extrapolated onset temperature of the transition.

Differential scanning calorimetry (DSC)

Modulated DSC (product code: DSC 2920; manufactured by: M/s TA Instruments, USA) with thermal analyser (product code: Thermal Analyst 2100; manufactured by:

M/s TA Instruments, USA) was used for the experiments [14]. The temperature range of the equipment was –70 to 700°C. The mass of the sample was required to be within the range of 10±1 mg. The test samples were prepared in the form of small particles using hand operated crimping and shearing machine. The heating rate was kept 10°C min^{-1} and temperature range was kept from ambient to 400°C, for the samples of all compositions.

Results and discussion

Thermal stability

Thermal stability was studied using thermal gravimetric technique. The comparison of the results of thermogravimetric traces of ferrite filled PEEK composites, and ferrite and nano-barium titanate filled PEEK composites is given in Table 2. Thermogravimetric traces of PFM10 and PFBM10 are mentioned at Figs 1a, b, respectively, as representative thermogravimetric traces.

Single step decomposition was observed in all the compositions. On increasing the content of ferrite in the matrix, the initial decomposition temperature (T_i) has increased significantly. The char yield at 600°C of all the composites ranged from 59–66%. The char yields have shown an increasing trend on increasing the proportion of ferrite. This shows that thermal stability has improved on increase of ferrite into the PEEK matrix. This effect is more pronounced with the reinforcement of nano-barium titanate. This reason is attributed to the reinforcing effect of nano-barium titanate. The T_i of PFBM samples has shifted to higher side corresponding to PFM samples. Similarly, T_m, at which the maximum rate of mass loss occurred has shifted to higher side for PFBM samples than PFM samples indicating the higher thermal stability for nano-barium titanate reiforced composites. Incorporation of carbon black has also improved the thermal stability of all the samples.

Table 2 Comparison of the results of thermogravimetric traces

No.	Sample designation	Initial decompositon temperature, T_i/°C	Temperature at peak value, T_m/°C	Char yield at 600°C/%
1a	PFM2	534.94	557.16	59.1
1b	PFBM2	534.86	558.23	60.2
2a	PFM4	539.95	554.95	60.9
2b	PFBM4	540.56	557.72	61.6
3a	PFM6	539.47	558.35	61.8
3b	PFBM6	543.97	559.03	62.8
4a	PFM8	540.63	562.19	63.2
4b	PFBM8	553.55	571.88	66.1
5a	PFM10	540.23	562.19	63.6
5b	PFBM10	558.83	576.55	66.3

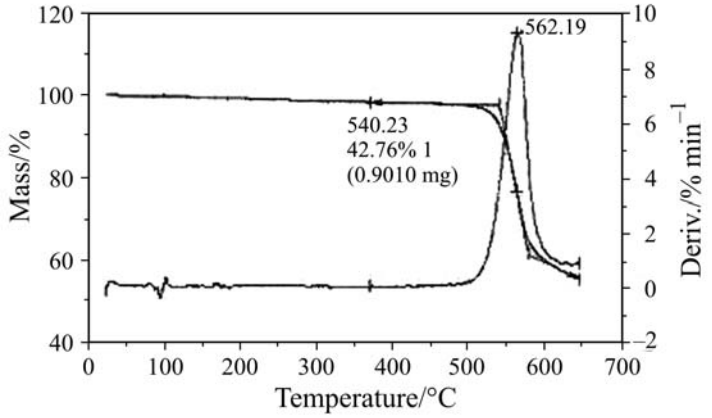

Fig. 1a Thermogravimetric trace of PFM10 samples

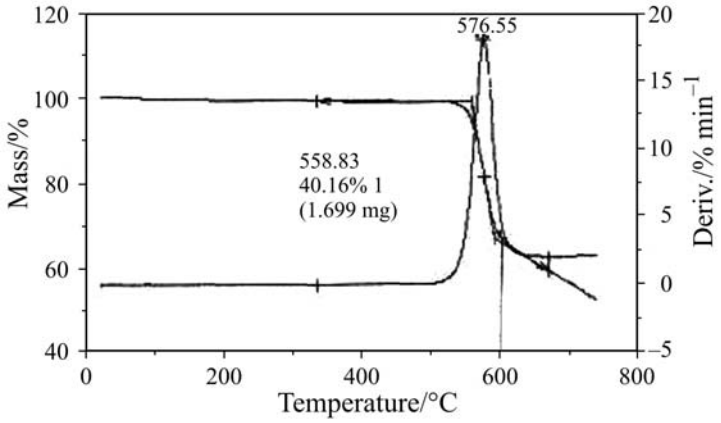

Fig. 1b Thermogravimetric trace of PFBM10 samples

DMA

The comparison of the results of DMA of ferrite filled PEEK composites, and ferrite and nano-barium titanate filled PEEK composites for 1 and 10 Hz frequencies, is given in Table 3. DMA curves, of PFM10 at 1 and 10 Hz frequency are mentioned at Figs 2a, b, and of PFBM10 at 1 and 10 Hz frequency are mentioned at Figs 3a, b, respectively, as representative DMA curves.

An increase in loss tangent was observed in ferrite and barium titanate filled PEEK composites as compared to ferrite filled PEEK composites. This was more pronounced at 10 Hz frequency. A marginal increase in glass transition temperature (T_g) was observed in PFBM samples over PFM samples. This was due to reinforcing effect of nano-barium titanate and filling up of micro voids in the composite, which caused some restriction of translational motion of polymeric chains of PEEK.

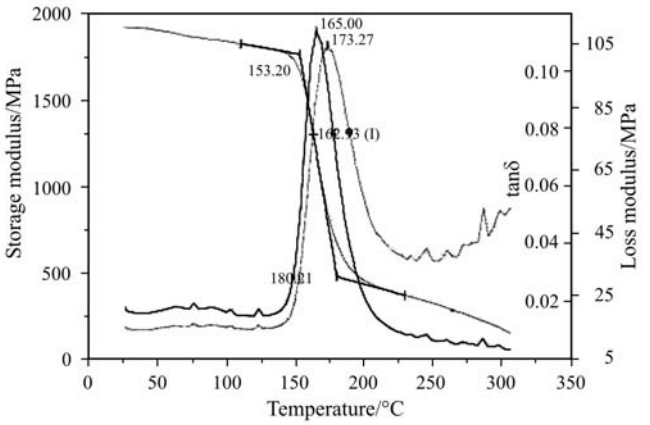

Fig. 2a DMA curve of PFM10 sample at 1 Hz frequency

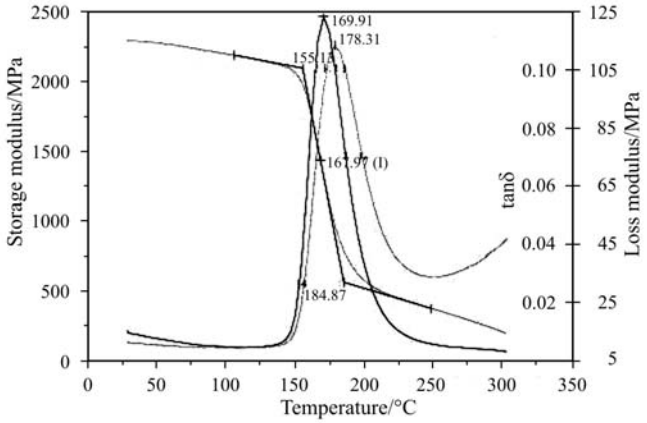

Fig. 2b DMA curve of PFM10 sample at 10 Hz frequency

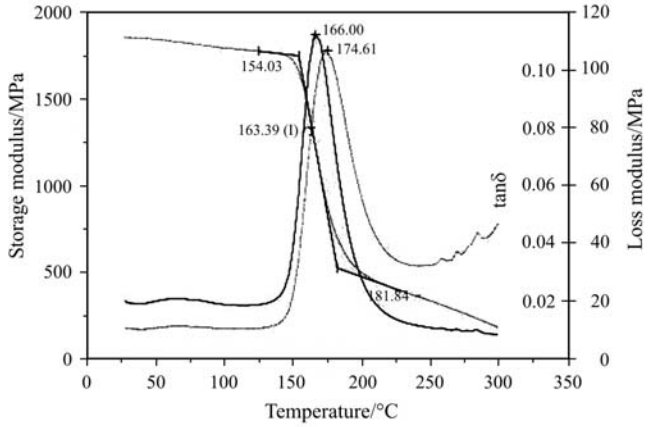

Fig. 3a DMA curve of PFBM10 sample at 1 Hz frequency

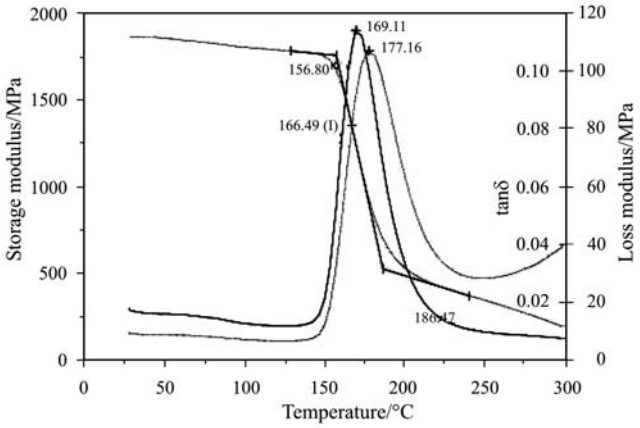

Fig. 3b DMA curve of PFBM10 sample at 10 Hz frequency

Table 3 Comparison of the results of DMA at 1 and 10 Hz

No.	Sample designation	Loss tangent, tanδ		Glass transition temperature, T_g/°C	
		1 Hz	10 Hz	1 Hz	10 Hz
1a	PFM2	0.0556	0.0568	151.27	152.09
1b	PFBM2	0.0600	0.0608	152.62	150.35
2a	PFM4	0.0572	0.0608	151.00	153.24
2b	PFBM4	0.0672	0.0711	153.29	155.65
3a	PFM6	0.0592	0.0648	151.70	155.50
3b	PFBM6	0.0714	0.0752	153.51	155.60
4a	PFM8	0.0612	0.0692	153.13	153.23
4b	PFBM8	0.0736	0.0808	154.55	156.91
5a	PFM10	0.0722	0.0808	153.20	155.13
5b	PFBM10	0.0928	0.0986	154.03	156.80

Melting behaviour

The melting behaviour was studied by using differential scanning calorimetry (DSC). The comparison of the results of DSC scans of ferrite filled PEEK composites, and ferrite and nano-barium titanate filled PEEK composites is given in Table 4. DSC scans of PFM10 and PFBM10 are mentioned at Figs 4a, b, respectively, as representative DSC scans.

An endothermic peak was observed in the range of 334–358°C for all the composites. It was observed that melting peaks were small and this reason may be attributed to absorption and conduction of energy by ferrite in PEEK matrix. Effect of nano-barium titanate on the melting behaviour of ferrite filled PEEK composites was

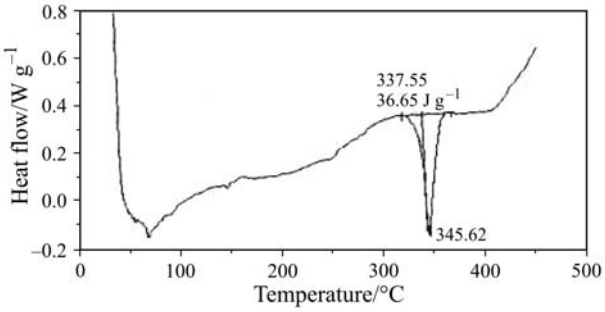

Fig. 4a DSC scan of PFM10 sample

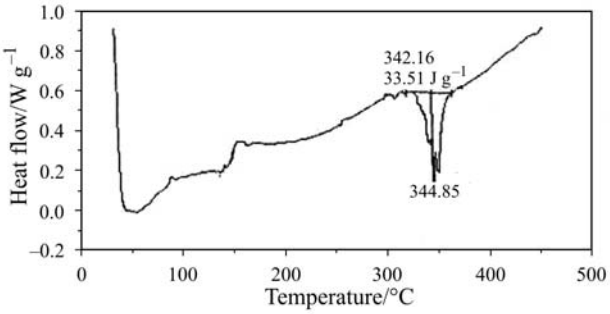

Fig. 4b DSC scan of PFBM10 sample

Table 4 Comparison of the results of DSC

No.	Sample designation	Initial melting temp., T_i/°C	Melting temperature, T_m/°C	Final melting temp., T_f/°C
1a	PFM2	334.30	345.65	356.61
1b	PFBM2	335.46	344.94	356.16
2a	PFM4	334.91	346.10	358.91
2b	PFBM4	335.65	346.67	355.88
3a	PFM6	335.01	345.37	357.44
3b	PFBM6	337.97	346.09	355.56
4a	PFM8	335.04	346.62	358.33
4b	PFBM8	340.11	346.59	357.89
5a	PFM10	337.55	345.52	357.11
5b	PFBM10	342.16	344.85	357.13

marginal. Significant deviation in melting peak was not observed even after the reinforcement of nano-barium titanate. The reason may be attributed to the fact that melting temperature of thermoplastic matrix is grossly independent to its reinforcement.

Conclusions

Nano-barium titanate, due to its reinforcing effect, has caused an enhancement in the values of char yield and initial temperature of decomposition of ferrite filled PEEK composites. However, melting temperature of composites remained unaffected with the reinforcement of nano-barium titanate. Overall, the reinforcement of nano-barium titanate in ferrite filled PEEK composites has caused an improvement in the thermal stability of the composites.

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