Mechanical and thermal properties of PEEK / Polycarbosilane coated MWCNT

Vishal Verma[1], Vijai Kumar[2], A. K. Saxena[3]
[1] Central Institute of Plastics Engineering & Technology, Lucknow
[2] Central Institute of Plastics Engineering & Technology, Bhopal
[3] DMSRDE, Kanpur

Abstract- *The present studies aim to develop composites reinforced with multiwalled carbon nanotubes (MWCNTs) coated with polycarbosilane (PCS) derived β silicon carbide (SiC) by melt mixing process with the help of co-rotating twin screw extruder. Modification of MWCNTs by PCS derived SiC particles has provided an excellent route to provide the dispersion of MWCNTs in polyetheretherketone (PEEK) matrix. It has been observed that there is remarkable enhancement in mechanical properties of the nanocomposites with the incorporation of MWCNTs at varied loadings in PEEK matrix. Mechanical properties results demonstrate that the incorporation of 0.3 % PCS coated MWCNTs gives rise an appreciable enhancement in mechanical properties (tensile strength, tensile strength, flexural strength, flexural modulus, Impact strength, hardness etc). This increase in mechanical properties may be because of higher aspect ratio and surface area of MWCNTs. Higher surface area of MWCNTs may provide an excellent interaction and orientation of nanofillers with PEEK matrix. Heat deflection temperatures of developed nanocomposites have been studied. The test results depict a significant enhancement in HDT value with the incorporation of MWCNTs in polymer matrix. The increase in the HDT may be due to the incorporation of MWCNTs which reduces the chain mobility of the PEEK matrix by imposing vast number of restricted sites that reduces the thermal vibration of C-C bond.*

Keywords: PEEK, MWCNTs, PCS, SiC, Nanocomposites, Mechanical Properties.

I. INTRODUCTION

Poly (ether ether ketone) belongs to a family of semi-crystalline polymers by containing various sequences aryl ether and aryl ketone functionalities in polymer backbone. This family of materials find their applications in various fields. PEEK possess superior mechanical properties, chemical resistance, solvent resistance and thermal stability [1, 2]. Among the development fields, high performance polymer is of great interest [3-5]. Among various polymers PEEK is thought to be one of the most promising materials for engineering applications because of its outstanding properties and high glass transition temperature and melting point (Tg~143^{o} C, Tm~343^{o}C) [6-8]. In order to have excellent mechanical properties, thermal stability etc, it is essential to reinforce PEEK matrix with various reinforcing agent such as carbon nanotube, graphene, graphene oxide, carbon nanofibres etc. In particular, the incorporation of small amount of MWCNTs in PEEK matrix leads to a significant increase in mechanical properties and degradation temperature of the matrix [9, 10].

Carbon nanotubes incorporated polymeric composites have attracted great attention over the past two decade because of their remarkable industrial applications [11-15]. It is very difficult to disperse CNTs in polymer matrix because of their strong tendency to gather and forms bundles. To improve their distribution through the matrix, different processing rouets such as solution mixing [16], and in situ polymerization [17] have been employed over the last two decade. Many studies have been reported on the structural [18], mechanical properties [19] and thermal [20] characterization of their linear aromatic polymers. Enormous amount of work has been carried out on PEEK based composites, the most relevant are those published by Shaffers et al. [21], Deng et al. [22] Song et al. [23], Jin et al.[24], Gao et al. [25], Rzatiki et al. [26], Hwang et al. [27], and Ashrafi et al. [28].

The present investigation deals with the study of PEEK/MWCNTs reinforced composites. The MWCNT has been chemically treated with poly-carbosilane so that it should have a coating of β-silicon carbide for their excellent dispersion in PEEK matrix. The mechanical properties, thermal properties and morphological properties have been determined with the help of sophisticated analytical equipment such as DSC, DMA, TGA, SEM, FTIR, XRD etc.

II. MATERIALS AND METHODS

2.1. Materials

PEEK (grade Ketaspire 820 NT) purchased from solvay chemicals alpheretta(USA) is used as metrix materials. The multiwalled carbon nano tubes (MWCNT) and polycarbosilane(PCS) were synthesises by DMSRDE ,

Kanpur. MWCNT having a diameter 2-4 nm nad length 20-30 micrometer and the aspect ratio 10,000.

2.2. Coating of inorganic polymer on MWCNT

Took 2 liter tetra hydro furan (THF) and 100gm KOH pass it over 500 gm Alumina to remove the moisture , press sodium in this solution and leave the solution for two days a bluish colour is produced. Distillation of this solution was done and then took 100 ML of this solution in a bottle and add 100 mg PCS in it. Now took 40 ML of the above solution and add 0.4 gm MWNT in it then reflux it for 6 to 7 hours. Now distillation of the above solution is done at 90^0C then they obtained residues is heated up to 25^0C and then leave it to cool as a result we get PCS coated MWCNT.

2.3 Dispersion of inorganic polymer coated MWCNT'ₛ

Before incorporation of PCS coated MWCNT'ₛ from 0.1 to 0.3 phr in PEI . The nanotubes have been sonicated in 10 ml of toluene for a period of 30 minutes to separate the agglomerated polycarbosilane coated MWCNT's at in order to induce an efficient dispersion of nanotubes.

2.4 Preparation of organic/inorganic polymer Nanocomposite

Before mixing, the organic polymer (PEEK) was dried under vacuum at 80^0C for at least 12 hrs. Then after organic polymer and inorganic polymer with nanoclay (Polycarbosilane coated MWCNT) were blended in twin screw extruder (at RPM 144) at temperature processing condition given in Table 2.1 for PEEK blend with inorganic polymer as per formulation Table 2.2. Testing specimens were prepared using injection moulding machine at temperature 340°C for PEEK & PEEK/PEI blend with inorganic polymer / nanoclay.

Table – 2.1 Processing temperature of Twin Screw Extruder during the compounding of PEEK nanocomposites

Heating Zone	PEEK
Zone 1	340 °C
Zone 2	366 °C
Zone 3	385°C
Zone 4	386°C
Zone 5	390°C
Die	398°C

Table – 2.2 Formulation of the nanocomposite based on PEEK/PCS coated MWCNT blend

Sr. No.	PEEK (gm)	PCS coated MWCNT (%)
1.	500	0.1
2.	500	0.3
3.	500	0.5

2.5 Testing and characterization

Test specimens were prepared by injection moulding for the analysis of Mechanical and thermal properties.

2.5.1 Mechanical & Thermal properties

Density were measured as per ASTMD 792, Tensile properties were determined using dumbbell shaped specimen as per ASTMD 638, Flexural properties were measured as per ASTMD 790 using universal testing machine (model INSTRON 3382, USA). The thermal properties heat deflection temperature (HDT) was measured at 1.82 MPa as per ASTMD 648. During testing the test atmosphere was maintained at 23+/- 2 deg C and 50+/- 5 RH.

2.5.2 Morphological Studies

Scanning electron microscopy (SEM) techniques was used to analyse the morphological properties of PEEK/ Polycarbosilane coated MWCNT. Prior to SEM analysis the tensile strength broken samples were gold coated with the help of gold sputtering unit for avoiding charge effect. SEM studies were done using Carl Zeiss EVO-50*VP low volume scanning electron microscopy.

III. RESULTS AND DISCUSSION

3.1 Mechanical and Thermal Properties

The variation of density and hardness were increased with the addition of filler content at optimum label and have shown in Table 3.1. Tensile strength, tensile modulus and elongation % have shown in Table 3.2, It is clearly found that tensile properties are increased with the addition of polycarbosilane coated MWCNT in to the PEEK. The flexural properties have shown in Table 3.3, Flexural modulus increased at 3 wt % loading as compared to virgin PEEK. Impact strength also increased as other mechanical properties increased. SEM micrograph also shows that the mechanical properties increased due to better dispersion of nano filler in to polymer matrix. The thermal properties HDT also increasing with the addition of filler in to matrix.

Table 3.1: Density, Rockwell hardness of PEEK with Inorganic polymer coated MWCNT composite

Composition		Density, g/cc (PEEK density – 1.28 g/cc)	Rockwell Hardness, (M Scale) (PEEK Hardness – 96)
PEEK, gm	Filler %	PCS coated MWCNT	
500	0.1	1.29	102
500	0.3	1.3	106
500	0.5	1.3	100

Table 3.2: Tensile Strength, Elongation and Modulus of PEEK with Inorganic polymer coated MWCNT composite

Composition		Tensile strength, MPa (PEEK Tensile Strength – 93.42 MPa)	Tensile Elongation, % (PEEK Tensile Elongation – 5.6%)	Tensile Modulus, MPa (PEEK Tensile Modulus – 3498 MPa)
PEEK, gm	Filler %	PCS coated MWCNT		
500	0.1	103.24	5.3	3817.28
500	0.3	108.21	5.1	3982.12
500	0.5	105.72	5.2	3926.41

Table 3.3: Flexural Strength & Modulus of PEEK with Inorganic polymer coated MWCNT composite

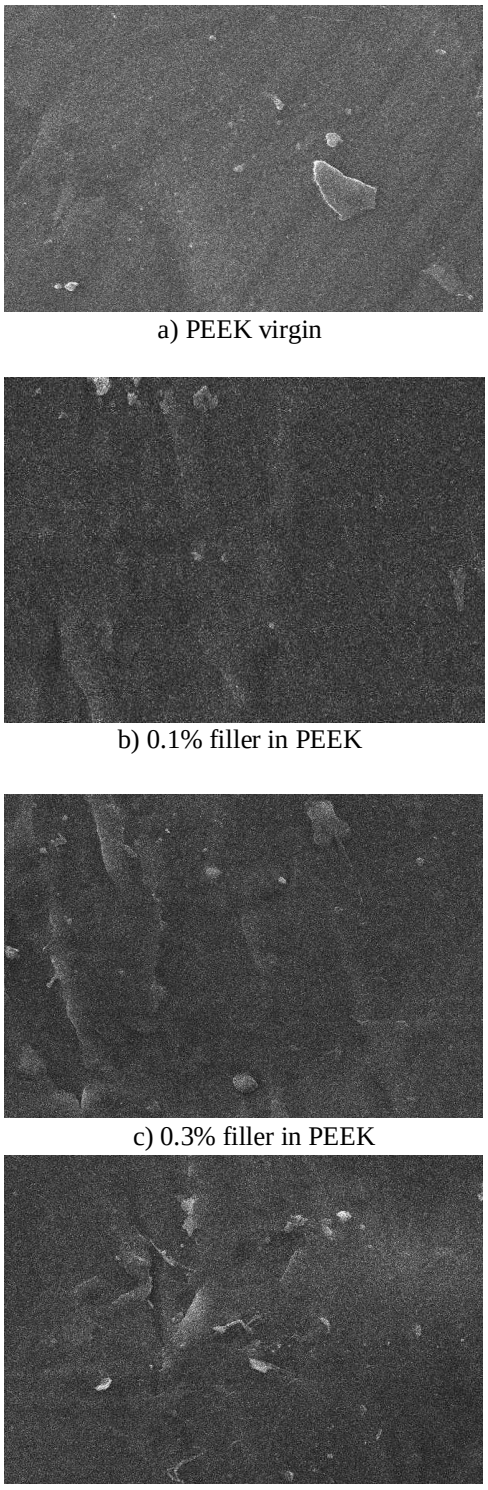
Composition		Flexural strength, MPa (PEEK Flexural Strength – 144.82 MPa)	Flexural Modulus, MPa (PEEK Flexural Modulus – 3698.42 MPa)
PEEK, gm	Filler %	PCS coated MWCNT	
500	0.1	154.76	3816.38
500	0.3	165.24	3988.52
500	0.5	159.64	3845.91

Table 3.4: Izod Impact & HDT of PEEK with Inorganic polymer coated MWCNT composite

Composition		Izod Impact, J/m (PEEK Izod Impact – 90.2 J/m)	Heat Deflection Temperature (HDT), Deg C (PEEK HDT – 156.3 Deg C)
PEEK, gm	Filler %	PCS coated MWCNT	PCS coated MWCNT
500	0.1	99	161.3
500	0.3	104	166.2
500	0.5	100	162.4

3.2 Morphological properties

SEM micrographs were shown in Figure 3.1 (a, b, c, d) for the virgin PEEK 0.1, 0.3 & 0.5% PCS coated MWCNT fillers in PEEK matrix. The scanning micrograph shows the homogeneously dispersion of filler in to polymer matrix. It is due to the coating of PCS in to MWCNT due to this elastomeric phase improved the dispersion in to polymer matrix.



a) PEEK virgin

b) 0.1% filler in PEEK

c) 0.3% filler in PEEK

d) 0.5% filler in PEEK

Fig 3.1 Morphological properties of PEEK/ PCS coated MWCNT

IV. CONCLUSIONS

Various compositing of PEEK/ Polycarbosilane coated MWCNT were blended with twin screw extruder and

analysed for mechanical, thermal and morphological properties. Mechanical and thermal properties of the nanocomposites were increased with the increasing the loading of nano clay up to 0.3 %. This was also confirmed through SEM microghaph. The thermal properties also shown the significant improvement with the incorporation of polycarbosilane coated MWCNT.

REFERENCES

[1] Kemmish D. (2010) 'Update on the technology and applications of poly-aryletherketones'. iSmithers.

[2] Patel P, Hull TR, McCabe RW, Flath D, Grasmeder J, Percy M. (2010) Polymer Degrad Stab. Vol 95, pp. 709.

[3] Jenkins M. (2001), Polymer Vol 42, pp.1981-86.

[4] Tseng YC, Woo EM. (1998), Macromol Rapid Commun Vol 19, pp.215-8.

[5] Hudson SD, Davis DD, Lovinger AJ, (1992) Macromolecules Vol 25, pp.1759-65.

[6] Q, Wang. Q. Xue, H. Liu, W. shen, J. Xu. (1996) 'The effect of particle size of nanometer ZrO_2 on the tribological behaviour of PEEK' Wear Vol 198 pp.216-219.

[7] M.Sumer, H. Unal, A. Mimaroglu. (2008) 'Evaluation of tribological behaviour of PEEK and glass fiber reinforced PEEK composites under dry sliding and water lubricated conditions' Wear, Vol 265, pp.1061-1065.

[8] Z. Zhang, C.Breidt, L. Chang, K. Freidrich. (2004) 'Wear of PEEK composites releted to their mechanical performances' Tribolog International, Vol 37, pp.271-277.

[9] Diez- Pascual AM et al. (2010) 'High performance PEEK/corbon nanotubes composites compatibilized with polysulphones, I- structure and thermal properties' Carbon, Vol 48, No.12 pp. 3485-99.

[10] Diez- Pascual AM et al. (2010) 'High performance PEEK/corbon nanotubes composites compatibilized with polysulphones, II-mechanical and electrical properties' Carbon, Vol 48 No.12 pp.3500-11.

[11] Yu M-F, Files BS, Arepalli S, Ruoff RS. (2000) 'Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties' Phys. Rev. Lett. Vol 84 No.24 pp.5552-5.

[12] Salvetat J-P, Bonard J-M, Thomson NH, Kulik AJ, Forro F,Benoit W, et al. 'Mechanical properties of carbon nanotubes' Appl phys A Vol 69 pp.255-60.

[13] Thostenson ET, Ren Z, Chou T-W. (2001) 'Advances in the science and technology of carbon nanotubes and their composites' a review, compos Sci Technol Vol 61pp.1899-912.

[14] Thostenson ET, Li C, Chou T-W. (2005) 'Nano composites in context' Compos Sci Technol Vol 65 pp.491-516.

[15] Coleman JN, Khan U, Blau WJ, Gun'ko YK. (2006) 'small but strong: a review of the mechanical properties of carbon nanotube-polymer composites' Carbon Vol 44 pp.1624-52.

[16] Pham JQ, Mitchell CA, Bahr JL, Tour JM, Krishanamoorti R, Greeen PF. (2003) 'Glass transition of polymer/single-walled carbon nanotube composite films' Polym Sci Vol 41 pp.3339-45.

[17] Cochet M, Maser WK, Benito AM, Callejas MA, Martinez MT, Benito JM, et al. (2001) 'Synthesis of a new polyaniline/nanotube composite: "in situ" polymerization and charge transfer through site-selective interaction' Chem Commun pp.1450-1.

[18] Naffakh M, Gomez MA, Ellis G, Macro C. (2003) 'Thermal properties, structure and morphology of PEEK/thermotropic liquid crystalline polymer blends' Polym Int Vol 52 No.12 pp.1876-86.

[19] Hsiung CM, Cakmak M, White JL.(1990) 'Crystallization phenomenon in the injection moulding of poly ether ether ketone and ite influence on mechanical properties' Polym Eng Sci Vol 30 No.16 pp.967-80.

[20] Jonas A, Kegras R. (1991) 'Thermal stability and crystallization of poly (aryl) ether ether ketone' Polymer Vol 32 No.15 pp.2691-706.

[21] Werner P, verdejo R, Wollecke R, Alsadt V, Sandler J, Shaffer MSP. (2005) 'Carbon nanofibers allow foaming of semi crystalline poly (ether ether ketone)'Adv Matter Vol 17, pp.2864-9.

[22] Deng F, Ogasawara T, Takada N. (2007) 'Experimental charecterization of poly b) 0.1% filler in PEEK (ether ether ketone)/ multi-wall carbon nano tube composites' Key Eng Mater Vol 334 No,335 pp.271-4.

[23] Song L, Zhang H, Zhang Z, Xie S. (2007) 'Processing and performance improvements of SWNT paper reinforced PEEK nanocomposites' Composites A. Vol 38 No.2 pp.388-92.

[24] Lin Jin, Jerry Ball, Tim Bremner, Hung-Jue Sue. (2014) 'Crystallization behaviour and morphological characterization of poly (ether ether ketone)' Polymer Vol 55 pp.5255-5265.

[25] Cong Gao, Shuling Zhang, Xiujie li, Shisheng Zhu, Zhenhua Jiang. (2014) 'Synthesis of poly (ether ether ketone) - block- polyimide copolymer and its compatibilization for poly (ether ether ketone)/thermoplastic polyimide blends' Polmer Vol 55 pp.119-125.

[26] F.D. Rzatki, D.V.D. Barboza, R.M. Schroeder, G.M. de O, Barra, C. Binder, A.N. Klein, J.D.B. de Mello. (2014) 'Effect of surface finishing, temperature and chemical ageing on the tribological behaviour of a poly ether ether ketone composite/52100 pair' Wear Vol 12 pp.035.

[27] Yongseon Hwang, Myeongjin Kim, Jooheon Kim. (2013) 'Improvement of the mechanical properties and thermal conductivity of poly (ether-ether-ketone) with the addition of graphene oxide- carbon nanotube hybrid fillers' Composites: Part A Vol 55 pp.195-202.

[28] Behnam Ashrafi, Ana M. Diez-Pascual, Leon Johnson, Marc Genest, Simon Hind, Yadienka Martinez- Rubi, Jose M. Gonzalez- Dominguez, M. Teresa Martinez, Benoit Simard, Marian A, Gomez-Fatou, Andrew Johnston. (2012) 'Processing and properties of PEEK/glass fiber laminates: Effect of addition of single-walled carbon nanotubes' Composites: Part A Vol 43 pp.1267-1279.

[29] T.K. Mishra, Ashish Kumar, Vishal Verma, K.N. Pandey, Vijay Kumar. (2012) 'PEEK composites reinforced with zirconia nanofiller'. Composites Science and Technology, Vol 72 pp. 1627-1631.