

Fabrication of advanced poly(etheretherketone)/clay nanocomposites and their properties

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ABSTRACT

High performance polymer nanocomposites based on poly(etheretherketone) (PEEK) as matrix and modified clay as reinforcement were fabricated using hot pressing at 380 °C and 45 MPa. The clay was varied from 0 to 5 wt%. Nanocomposites were characterized by X-ray diffraction (XRD), Vickers hardness tester, high resistivity meter, and impedance analyzer to get information about morphology, microhardness, electrical conductivity and dielectric properties of nanocomposites, respectively. The experimental density was very close to the theoretical density. XRD showed exfoliation of clay up to 3 wt% and intercalation for 5 wt% nanocomposite. The water absorption decreased by 38 % at 1 wt% clay content. The microhardness increased up to 12 % for 2 wt% clay nanocomposite. Electrical conductivity was increased two orders of magnitude higher than pure PEEK. Dielectric constant was increased slightly with increasing clay content. The significant improvement in properties at lower clay loading might be attributed to the exfoliation of clay in the matrix. Copyright © 2010 VBRI press.

Keywords: Polymer-matrix nanocomposites; microhardness; conductivity; dielectric property.



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Introduction

Montmorillonite clay (MMT) particles are crystalline materials which consists of stacked platelets with thickness 1 nm, diameter from 10 to 1000 nm, and the spacing between platelets less than 1 nm [1]. An interaction between the clay particles and the polymer matrix has been improved by using organically modified MMT clay [2-3]. Impermeable nature and larger aspect ratio (100-1000) of clay layers decreases significantly (up to 50%) the permeability of the polymers for gases like oxygen, hydrogen, carbon dioxide and water. Due to an excellent barrier property, polymer/clay nanocomposites are used for the food packing industry [4-7].

The mechanical properties of clay filled epoxy [8-9], polypropylene (PP) [10-11] and nylon 6 [12] nanocomposites were increased significantly. An increase in impact strength was attributed to the strong interaction between the clay and the polymer matrix. However, a poor interaction between the polyethylene (PE) and the clay layers results in decreased impact strength of nanocomposites [13]. The addition of clay in polymer matrix also improves dimensional stability [14-16] and thermal stability [17-18] of nanocomposites. Page et al. [19] studied mobility and relaxation mechanism of the polyimide (PI)/clay nanocomposites using dielectric relaxation spectroscopy. Dielectric strength of polyimide/clay nanocomposites increased with increasing

clay content. However, above 3 wt% clay it decreased due to the formation of clay aggregates [3]. Similarly, Jiang et al. [4] investigated that the increase in leakage-current density of 3 NH₂-silicate filled polyimide nanocomposites with exposure time was sharply retarded compared to pure polyimide. It is interesting to see that a small loading of clay has shown interesting improvement in mechanical, thermal and electrical properties of various polymers such as PS [2], PI [3, 19], epoxy [8], nylon 11 [9, 11], PP [10], nylon 6 [12], PE [13], PVDF [15] and PET [18]. These nanocomposites have been processed by melt mixing, solution casting and in-situ polymerization techniques with low processing temperatures (< 250 °C). At such low processing temperatures the degradation of alkyl ammonium salt which is used to modify clay is negligible during processing. Recently, Zou et al. have studied poly(p-phenylene sulfide)/clay nanocomposites prepared by melt mixing at 300°C [20].

To the best of our knowledge, clay filled poly(etheretherketone) (PEEK) was not studied so far. Therefore, in present work, we have selected PEEK as a matrix. It is a high performance semi-crystalline polymer which exhibits high melting (335°C), glass transition (143°C) and continuous use temperature (250°C). Moreover, it has outstanding thermal, mechanical and electrical properties which make it an attractive material for automotive applications particularly in journal bearings and piston rings [21-22]. However, its cost is comparatively higher than other polymers. In view of above, modified clay was selected as reinforcement in the PEEK matrix and a systematic study on morphology, mechanical, thermal, dielectric and water resistance properties of PEEK/clay nanocomposites was carried out. We found significant increase in microhardness and resistance to moisture absorption at smaller clay content. Compared to pure PEEK a low dissipation factor, which is desired in electronic packaging applications, was also found for nanocomposites.

Experimental

Materials

The commercial PEEK (Grade 5300PF) donated by Gharda Chemicals Ltd. India under the trade name GATONE™ PEEK was used as matrix. The modified clay Cloisite20A (C20A) with density of 1.77 g/cc was obtained from Southern Clay Co. Ltd. The d-spacing of its (001) plane determined from X-ray diffraction (XRD) is 21.5 Å. An ethanol purchased from Changshu Yanguan Chemicals, China was used as a medium for homogenizing PEEK and clay particles.

Fabrication of nanocomposites

Both pure PEEK and clay powders were dried in a vacuum oven at 150 °C for 3 h. The dried clay powder was suspended in an absolute ethanol using sonication bath for 1 h. Then, appropriate quantity of dried PEEK powder was added slowly into clay/ethanol suspension and sonicated for 20 minutes. The mixture of PEEK/clay/ethanol was stirred at 80 °C for 3 h using high speed stirrer to remove

ethanol. The resultant powder was dried in a vacuum oven at 150°C for 12 h for complete drying. The required weight of the mixed powder was filled in a tool steel die to make the sample of 13 mm in diameter. Die is heated from room temperature to 380 °C at an average heating rate of 3 °C/min under pressure of 45 MPa. The dwell time was 20 minutes. After this, samples were cooled with average cooling rate of 7°C/min to a temperature of 100 °C and samples were ejected and polished. Nanocomposites containing 0, 1, 2, 3 and 5 wt% clay in the matrix were fabricated and characterized.

Characterization

Theoretical density of the composites was calculated using a rule of mixtures (ROM) with density of clay 1.77 g/ and of PEEK 1.30 g/cc (of compacted sample). For theoretical density (ρ_{th}), it was assumed that there were no voids and no loss of clay powder during processing. The ROM can be expressed by $\rho_{th} = \rho_m V_m + \rho_f V_f$, where, V_m is the volume fraction of the matrix and V_f is the volume fraction of the filler. The ρ_m and ρ_f are the density of matrix and filler, respectively. The experimental density was determined by using Archimedes's Principle. XRD pattern of pure PEEK compact, clay powder and nanocomposites containing 1, 2, and 3 wt% clay was recorded on Philips X'Pert PANalytical PW 3040/60. Ni filtered Cu α radiation ($\lambda = 1.54 \text{ \AA}$) generated at 40 kV and 30 mA was used for angle (2θ) ranging from 3 to 30°. The scan step size and time per step was 0.017° and 5 s respectively. The microhardness of well polished samples was measured using Vickers hardness tester (Future Tech Corp FM-700, Tokyo, Japan) at a constant load of 100 gm and dwell time of 15 seconds. Average values of six readings were reported as the microhardness of samples. Water absorption resistance of nanocomposites was carried out at 30 °C. Samples were dried in a vacuum oven (- 500 mm Hg) at 150 °C for 24 h. The dried nanocomposites were placed in distilled water for a total immersion period of 2 and 7 days. The weights of the immersed samples were measured using electronic balance to an accuracy of 0.1 mg. Before weighing the specimens were wiped using a tissue paper. The relative weight gain was expressed as a percentage of initial weight. The dielectric constant was obtained from the measurement of capacitance (C) using Wayne Kerr Electronics precision impedance analyzer [6515B, UK] at frequencies varying from 10 KHz to 15 MHz at 30°C. The dielectric constant (ϵ) was evaluated by the relation $\epsilon = Ct/\epsilon_0 S$, S is the surface area and t is the thickness of the dielectric material. The ϵ_0 is the permittivity of the free space ($8.854 \times 10^{-12} \text{ F/m}$). The dissipation factor was measured directly from the instrument. Silver conductive paste was applied on both sides of the sample before measuring dielectric constant and electrical conductivity of the samples. The volume resistance of samples was determined by using high resistance meter (Keithley 6517B). Then, the volume resistivity was measured by the relation $\rho = R(A/L)$, ρ is resistivity in Ω/cm , R is resistance in ohms, L is the thickness in cm and A is the cross sectional area (cm^2) of sample. The electrical conductivity was reported as the reciprocal of the volume resistivity.

Results and discussion

Density of nanocomposites

Fig. 1 shows correlation between the theoretical and the experimental density of the nanocomposites as a function of clay content. Density of PEEK and clay was considered 1.30 g/cc and 1.77 g/cc, respectively. The density of nanocomposites increases with increasing clay content. The experimental density of the nanocomposites containing up to 3 wt% clay is very close to that of theoretical density. This shows that these samples are almost porosity free and dense. However, experimental density of 5 wt% clay nanocomposite is slightly lowered than the theoretical density. This might be attributed to the agglomeration of clay particles in the PEEK matrix. During hot pressing the infiltration of PEEK resin, due to very high melt viscosity is difficult through the clay agglomerates. Hence, this results in porosity in the sample.

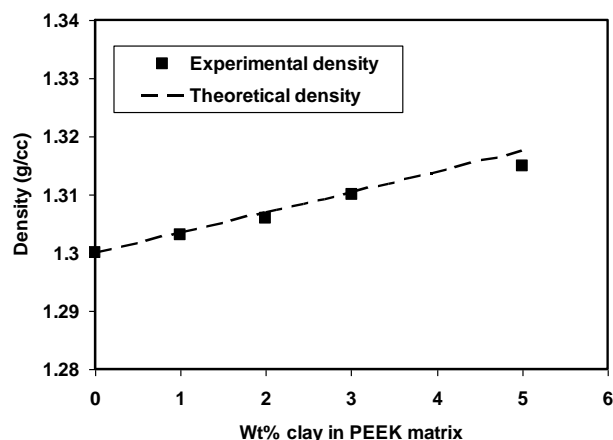


Fig. 1. Theoretical and experimental density of PEEK/clay nanocomposites.

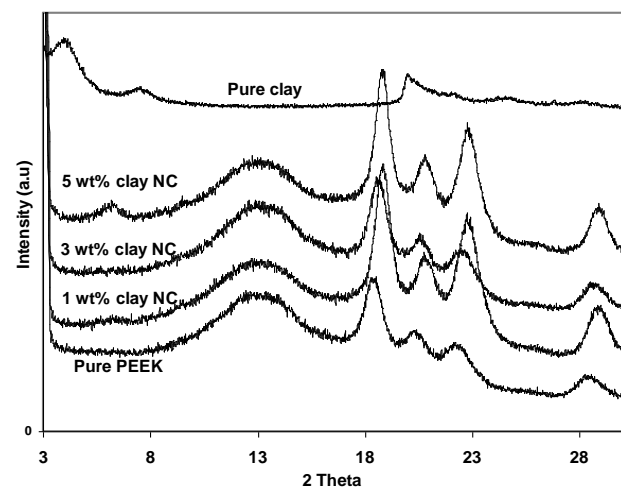


Fig. 2. XRD pattern of pure PEEK, clay powder and nanocomposites (NCs).

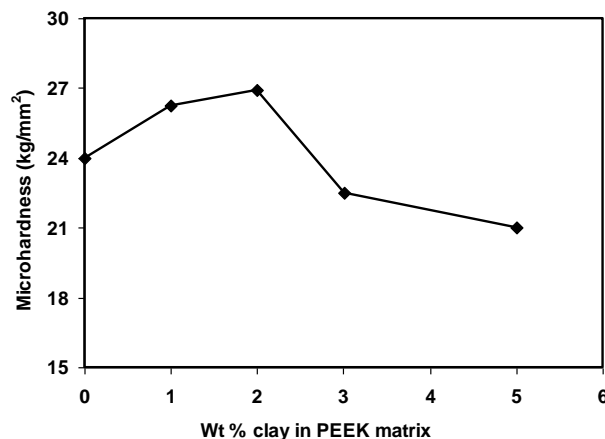


Fig. 3. Microhardness as a function of clay of nanocomposites.

X-Ray diffraction (XRD)

The XRD pattern of pure PEEK compact, clay powder and nanocomposites containing 1, 3, and 5 wt% clay is shown in Fig. 2. The PEEK crystallize primarily in the form-I with orthorhombic crystal structure showing diffraction peaks positions (2θ) at 18.7° , 20.8° , 22.9° , and 28.9° , which correspond to diffraction planes of (110), (111), (200), and (211), respectively. The XRD pattern of clay shows diffraction peaks at 4.05° and 7.55° which corresponds to d-spacing of 2.19 nm and 1.19 nm, respectively. It can be seen that there is no diffraction peak of clay constituent in 1 and 3 wt% clay nanocomposites. This indicates that either the d-spacing of the intercalated clay layers are larger than 2.94 nm ($2\theta < 3^\circ$) or they are exfoliated (i.e., clay layers loss order structure and are separated/dispersed) in the PEEK matrix. When the clay content is increased to 5 wt%, only one diffraction peak of clay appears at $2\theta = 6.3^\circ$ which corresponds to d-spacing of 1.42 nm. This d-spacing is between $d = 2.19$ nm for a highly expanded clay layers and $d = 1.19$ nm for less expanded clay layers. The increased d-spacing (> 1.19) may be attributed to the intercalation of PEEK chain into the clay layers during processing. The lower angle ($2\theta = 4.05^\circ$) diffraction peak of pure clay was found absent indicating that the peak was shifted to less than 3° which could not be observed due to lower limit of XRD. The probability of decrease in d-spacing from 2.19 nm to 1.42 nm due to degradation of the alkyl ammonium salt (modifier of clay) during processing cannot be ignored [20].

Vickers microhardness

Fig. 3 shows the microhardness of PEEK/clay nanocomposites as a function of clay content. Microhardness increased with increasing clay content. It increased from 24 kg/mm^2 for pure PEEK to 26.3 kg/mm^2 for 2 % clay nanocomposite. The increased hardness may be attributed to the higher hardness of the silicate clay than that of PEEK matrix and its exfoliated clay content. However, on further increasing clay content a decrease in microhardness was observed, i.e., it decreased to 21 kg/mm^2 for 5 % clay nanocomposite. This trend is similar to that of reported for epoxy/clay [8], nylon 11/clay [9] and PEEK/ Al_2O_3 [21] nanocomposite. The decrease in

hardness for higher clay nanocomposites may be attributed to the formation of aggregates which in turn could not resist penetration of indenter.

Water absorption resistance

The % water absorption of PEEK and its nanocomposites is shown in **Fig. 4**. It can be seen from **Fig. 4** that water absorption of pure PEEK is 0.23 %. Water absorption of polymer is high because water molecules can easily diffuse through the polymer chain. It is reduced to 0.14 % and 0.17 % for 1 wt% and 2 wt% nanocomposite, respectively. In nanocomposites, presence of clay layers force the water molecules to travel through tortuous path and hence, results in decreased water absorption [1, 4]. On further increasing clay above 3 wt%, clay layers form aggregates/porosities as shown in **Fig. 1**. These porosities might be the reasons of increasing water absorption at higher clay content.

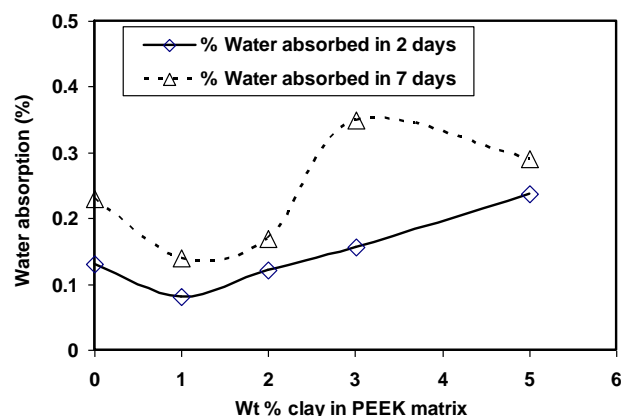


Fig. 4. Water absorption of PEEK/clay nanocomposites.

Electrical properties

Fig. 5a and **b** show the dielectric constant of the PEEK/clay nanocomposites as a function of logarithm of frequency and clay content, respectively. It can be seen clearly from **Fig. 5a** that the dielectric constant of nanocomposites is weakly dependent on frequency from 10 KHz to 15 MHz. **Fig. 5b** shows that the dielectric constant of pure PEEK is 3.38. It increased with increasing clay content up to 3 wt%. Thereafter, it did not increase significantly. However, it is still slightly higher than that of pure PEEK. The increased dielectric constant is due to the higher dielectric constant of clay 16.9 (at 10 KHz) [23] than that of pure PEEK matrix. A similar trend in dielectric constant was investigated for clay filled poly(vinyl alcohol)/poly(ethylene oxide) blend [24], epoxy [25] and polyimide [3] nanocomposites. In case of 5 wt% clay nanocomposite, dielectric constant is slightly smaller than that of 3 wt% nanocomposite. It is probably due to the presence of porosity as confirmed from density. The dielectric constant of the air is 1 and hence, the effective dielectric constant of the nanocomposites with higher clay loading decreases.

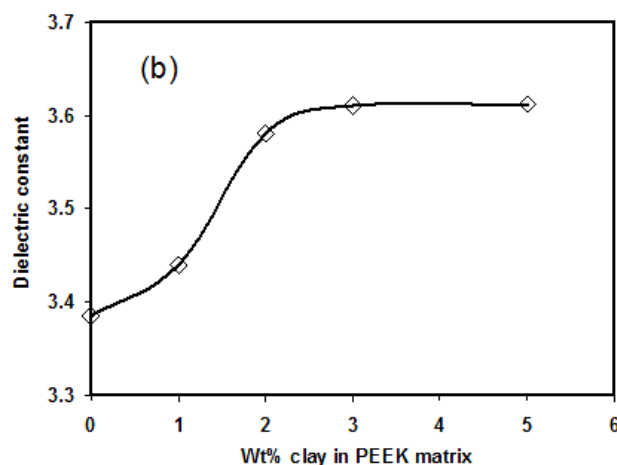
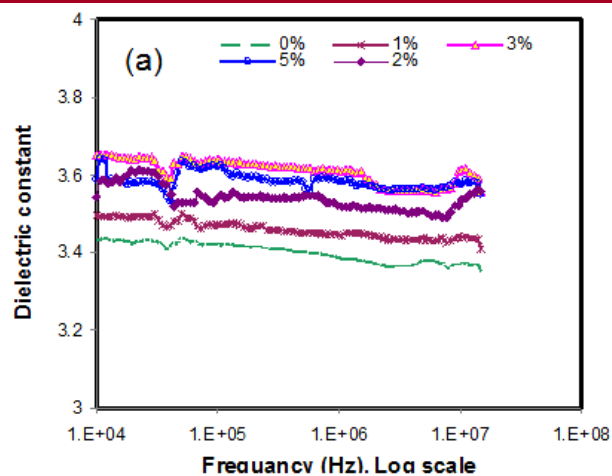


Fig. 5. Dielectric properties of PEEK/clay nanocomposites as a function of (a) frequency and (b) weight % clay in PEEK matrix (at 1MHz).

Fig. 6a and **b** show the dissipation factor ($\tan \delta$) of the nanocomposites as a function of logarithm of frequency and clay content, respectively. The $\tan \delta$ measured at 1 MHz for pure PEEK was 0.009. It decreased with increasing clay content, i.e., to 0.0063 for 1 wt% and to 0.0045 for 2 wt% clay nanocomposites. However, it increased to 0.005 and 0.006 for 3 wt% and 5 wt% clay nanocomposite, respectively. The dissipation factor was increased at higher frequencies due to the charge mobility at the higher frequencies according to Kanipatisas et al. [25].

Fig. 7 shows the volume electrical conductivity of nanocomposites as a function of clay content. It increased slightly with increasing clay content up to 2 wt% clay. However, above 3 wt% clay, due to the aggregates/porosities in the nanocomposites, it gets saturation. According to Lu et al. [23] the electrical conductivity of clay is 13.8×10^{-9} S/cm. Due to the higher electrical conductivity of the clay, the conductivity of nanocomposites increased about two orders of magnitude higher, i.e., from 6.9×10^{-14} S/cm for pure PEEK to 2.4×10^{-12} S/cm and to 4.5×10^{-12} S/cm for 3 wt% and 5 wt% clay nanocomposites, respectively. Similar trend was reported for polypyrrole/MMT nanocomposites [26].

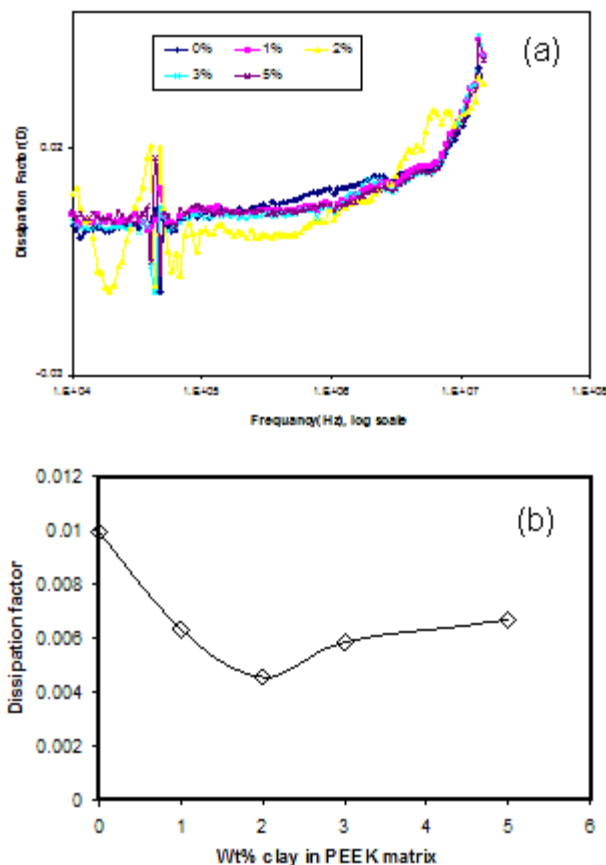


Fig. 6. Dissipation factor of PEEK/Clay nanocomposite as a function of (a) frequency and (b) weight % clay in PEEK matrix (at 1MHz).

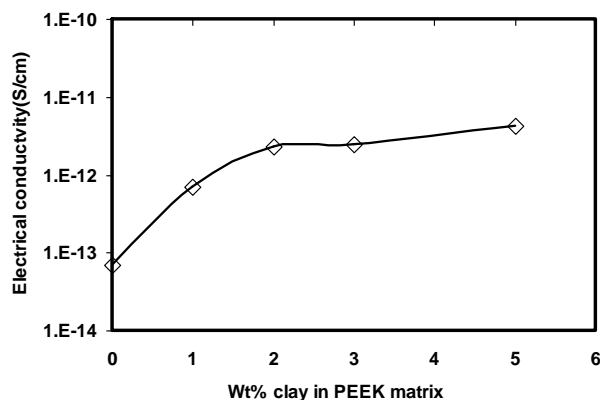


Fig. 7. Electrical conductivity of PEEK/clay nanocomposites.

Conclusion

High performance PEEK/clay nanocomposites were successfully fabricated by suspension method followed by hot pressing. XRD showed exfoliated structure for PEEK/clay nanocomposites with low clay content and intercalated structure for 5 wt% clay nanocomposite. A significant increase in microhardness and water absorption resistance was achieved for the nanocomposites with exfoliated structure. However, due to the agglomeration of clay particles both microhardness and water resistance were decreased at higher clay content. Electrical conductivity of nanocomposites was increased two orders

of magnitude higher than pure PEEK. The Dielectric constant was increased slightly with increasing clay content. The dissipation factor (at 1 MHz) of the nanocomposites was decreased from 0.009 for pure PEEK to 0.0045 for 2 wt% clay nanocomposites.

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