The Influence of Annealing on the Crystallization and Tribological Behavior of MWNT/PEEK Nanocomposites

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In this study, annealing influence on crystallization and scratch behavior of neat and multi-wall carbon nanotube (MWNT) reinforced poly(ether ether ketone) (PEEK) nanocomposites have been investigated. Crystallization behavior of normal and annealed samples was investigated by using differential scanning calorimeter (DSC). Scratch behavior of normal and annealed samples was investigated by using micro scratch tester. In DSC analysis, it was detected that, melting enthalpy of annealed neat PEEK was increased sharply when compared to neat PEEK. Melting enthalpies of annealed PEEK nanocomposites prepared with addition of up to 1 wt% MWNT were increased with a decreased trend. However, nanocomposites with higher contents of MWNTs (>1 wt%) were dramatically affected by annealing process and melting enthalpy decreased sharply. Friction coefficient values of ‘annealed MWNT reinforced PEEK composites’ were found to be lower than ‘normal PEEK composites.’ Annealing process affects scratch hardness of both annealed and MWNT reinforced PEEK. Annealed nanocomposites with various MWNT concentrations showed higher scratch hardness values than normal PEEK nanocomposites.

INTRODUCTION

Due to the superior mechanical properties, thermal stability, and chemical resistance, poly(ether ether ketone) (PEEK) has been widely used in aerospace, automotive, and chemical industries [1–4]. Therefore, there are many studies interested in improving the properties of PEEK by using carbon, graphite, glass, and aramid fibers or micro/nano particles. Beside this, carbon nanotubes are excellent candidate nanofillers for polymers on account of their unique mechanical and physical properties [5–7]. Lots of efforts have been devoted further for improving the properties of PEEK via incorporation with carbon nanotubes. Bangarusampath et al. [8] interpreted that increasing nanotube content provides increase of the storage modulus of the PEEK nanocomposite melt. Ogasawara et al. concluded that the stress–strain behavior of PEEK is almost linear up to 1.5% strain, the stress strain curves of carbon nanotube (CNT) reinforced PEEK composites exhibit considerable nonlinear and hysteresis behaviors from the extremely low strain (<0.1%) under both tensile and compressive loading [9].

It is well known that crystallization behavior plays a crucial role in the properties of semi-crystalline polymers and therefore it is necessary to pay attention to this issue. In literature, there are a few studies which deal with the crystallization behavior of CNT reinforced PEEK composites. Díez-Pascual et al. [4] interpreted that differential scanning calorimetry (DSC) showed a decrease in the crystallization temperature with increasing single-wall carbon nanotube (SWNT) content, whilst no significant changes were observed in the melting of the composites. In another study, it is reported that CNTs improved mechanical properties and promoted the crystallization rate of PEEK as a result of heterogeneous nucleation [3].

Annealing effects on the microstructure and morphology of polymer materials have been a subject of major technological and scientific interest for a number of years [10]. Annealing has been performed to polymers for improving their crystalline order [11]. There are many studies about annealing influence on the crystallization behavior of neat polymers [4, 11, 12]. However, there relatively few reports dealt with the influence of annealing on the multi-wall carbon nanotube (MWNT) reinforced PEEK nanocomposites. Also to our knowledge, in these studies there is little information about multi-melting behavior of annealed PEEK and MWNT/PEEK nanocomposites. Therefore, one of the aim of this study is to examine and explain annealing influence on the neat and MWNT reinforced PEEK nanocomposites.

In recent years, scratch resistance has become an important performance requirement of polymers for applications where surface aesthetics is essential such as interior...
EXPERIMENTAL DETAILS

**Materials**

The high temperature, semi-crystalline matrix (PEEK) supported from the company Evonik Industries, Germany is with the commercial name of Vestakeep 2000UFP20. The density is 1.30 g/cm³ and the average particle size is approximately 20 μm. MWNTs Nanocyl®-7000, used in this study were supported from Nanocyl Co., Belgium. According to the datasheet, they were produced via the catalytic carbon vapor deposition (CCVD) process. The average length was 1.5 μm, the average outer diameter was 9.5 nm, the carbon purity was 90%, and surface area was about 250–300 m²/g. The polymer, provided as fine powder, was dried at 110°C for 6 h to remove their moisture and stored in a dry environment before mixing.

**Preparation of MWNT/PEEK Composites**

The melt blending of PEEK with a weight percentage of 0, 0.5, 1, 3, and 5 wt% of MWNTs was conducted using a DSM Xplore 15 ml twin-screw micro-compounder. Compounding was carried out at a screw speed of 100 rpm with the maximum barrel temperature set at 380°C. The melted mixture of neat and MWNT reinforced PEEK material was then injected into the mold which is at 175°C under 12 bar. Following this procedure to ensure a maximized and more importantly a uniform degree of crystallinity of the polymer matrix, all PEEK-based specimens were annealed at 260°C for 4 h between metal plates. Injection molded samples were cut into rectangular shapes with the dimension of 30 mm × 10 mm × 2 mm for the scratch tests.

**Experimental Procedure**

**DSC Characterization.** For DSC measurements, samples were prepared by shaving approximately 10 mg from the injected samples and sealed in aluminum pans. The crystallization and melting behavior of the normal and annealed nanocomposites were investigated by TA Instruments DSC Q200 differential scanning calorimeter, operating under a nitrogen gas flow. DSC measurements were carried out at a heating rate of 10°C/min from 25°C to 400°C.

**Scratch Test.** In the study, the scratch resistance of the prepared samples was examined by “CSM Micro Scratch Tester,” Rockwell S-218 type indenter having a spherical diamond and a contact radius of 200 μm was used. The samples were fixed on a leveling platform attached to a displacement stage and normal load was applied by placing dead-weights on the indenter holder. In order to eliminate the surface roughness effect and the effect of variation in skin thickness, the indenter is performed a pre-scratch under the load of 0.03 N. Mechanically induced surface damage in the form of a scratch was introduced on the surface of the samples using loads at 10 N. The scratch velocity was chosen at a range of 30 mm/min and the length of scratch was 10 mm. Each sample was tested three times and the average values were taken. During the experiments, the scratch behavior of normal and annealed PEEK with various MWNTs is inspected as a function of scratch hardness and coefficient of friction.
RESULTS AND DISCUSSION

Effects of MWNT Addition and Annealing on the Crystallinity of the PEEK Nanocomposites

The effects of carbon nanotube addition and annealing on the crystallinity of the PEEK were investigated by DSC measurements. Fig. 2 illustrates DSC thermogram of manufactured neat PEEK which is exposed to heating of 10°C/min. It is observed that melting peak occurred at 343.88°C and melting enthalpy analyzed as 47.30 J/g. Thermogram shows that there is a shoulder occurring at approximately 260°C and it could be attributed to some imperfect crystals occurred during manufacturing of PEEK samples.

It is known that nanotubes had an effect on the crystallization behavior of PEEK [3]. Beside this it is also known that annealing could increase the crystallinity [4]. Both the MWNT addition and annealing effects on the melting enthalpies of PEEK materials have been investigated by DSC. Analyzed results are shown in Fig. 3. It is clear that for normal samples; there is a melting enthalpy increment up to 1 wt% MWNT addition.

Nucleation ability of PEEK is obvious at low MWNT contents. In other words, the amount of nucleation sites had a percolation threshold that could not further produce increment in the crystallization with the increasing loadings of nanotubes. With the higher MWNT contents after 1 wt%, melting enthalpy values were decreased remarkably. According to this situation, 1 wt% MWNT addition is seen as critical threshold for PEEK polymer matrix as similar with other studies dealing with various properties of different polymers reinforced with carbon nanotubes [19–21]. Actually, a formation of MWNTs network has a profound effect on the crystallization behavior of PEEK matrix. It should be noted that there are two types of MWNT effects on the crystallization of composites. As the content of MWNTs is low, MWNTs are supposed to be uniformly dispersed in the polymer and function as heterogeneous nucleation agent, evidenced as increment of melting enthalpy. On the other hand, when the content of MWNTs is high and above the percolation threshold (>1 wt%), less uniformly dispersed and more entangled bundles of MWNTs may hinder the diffusion of polymer chains during crystallization, resulting in decreased melting enthalpy.

It was suggested that annealing process for polymers should be made between glass transition and melting temperature. And also it was reported that the crystal phase mass fraction was increased with the annealing temperatures approaching the melting temperature [12]. This report is in agreement with our results that; annealing neat PEEK at 260°C increased the crystal phase and the melting enthalpy of the polymer matrix as seen in Fig. 4. Melting enthalpy was increased sharply to 55.29 J/g; the apparent melting temperature remained almost unchanged (344.07°C) by annealing the neat PEEK at 260°C.

FIG. 2. DSC curve of manufactured neat PEEK (heating at 10°C/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIG. 3. Melting enthalpies of normal and annealed MWNT/PEEK composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIG. 4. DSC curve of neat PEEK sample annealed at 260°C (heating at 10°C/min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
Melting enthalpy increment was decreased slowly with the annealing process of 0–1 wt% MWNT/PEEK nanocomposites. This decrement in melting enthalpy could be attributed to the unfolding chains of imperfect PEEK crystals by high temperature annealing. With higher MWNT contents (>1 wt%) the melting enthalpy values decreased sharply due to the annealing process as same as normal MWNT/PEEK nanocomposites as seen in Fig. 3. Additionally, it could be said that a formation of MWNT network has a negative effect on crystallization behavior of annealed PEEK nanocomposites.

Scratch Behavior of Normal and Annealed PEEK Nanocomposites

Depending on the research plan given in Fig. 1, consequences of scratching of normal and annealed (260°C) PEEK samples with various MWNT concentrations have been reported in the second part of the study. Coefficient of friction and scratch hardness results of normal and annealed nanocomposites were correlated with MWNT concentration.

Zig-zag nature of the worn track is caused by the stick–slip motion of the indenter on the MWNT reinforced PEEK surface. In stick process, there is no relative removal between the indenter and nanocomposite surface due to the adhesion force. Accordingly, the surface presents a higher tangent deformation and hence material accumulates ahead of the sliding indenter. Once the stress applied on the polymer surface exceeds the necessary critical stress [22], the slip stage is initiated and exists until the stress decreases to below the critical stress, when the indenter and the nanocomposite surface stick again. Friction plays a critical role at scratching, influencing all scratch quantities to some degree. When scratch experiment was performed, two quantities of normal and tangential forces ($F_{\text{norm}}$ and $F_{\text{tan}}$, respectively) were acquired. The ratio of $F_{\text{norm}}/F_{\text{tan}}$ was in a standard manner defined as the apparent coefficient of friction [23]. Therefore, the coefficient of friction indicates the resistance of the material to the indenter penetration in the tangential direction [24–26]. Fig. 5 shows the evolution of friction coefficients as a function of MWNT concentrations in normal and annealed PEEK samples.

From Fig. 5, it is observed that friction coefficient values of normal and annealed nanocomposite samples decrease sharply up to 1 wt% MWNT concentration. Due to extremely low frictional properties of nanotubes, it is possible to explain that decreased friction could be worn off MWNTs acting as a lubricant, much like powder graphite lubricants. However, the MWNTs also change the wear behavior and possibly the adhesion of water molecules to the particular surface [27]. Beside this, for both nanocomposite samples the coefficient of friction values begin to increase again when MWNT concentration exceeds 1 wt%. Similar to Ref. [17, 28], it is attributed that MWNT begin to conglomerate in the PEEK polymer. On the other hand, the coefficient of friction values decrease with annealing for all MWNT concentrations. By annealing; the crystallinity of nanocomposite samples is improved compared to normal nanocomposite samples.

Scratch hardness investigation can also be used to determine the material’s resistance to scratch deformation. Scratch hardness, which is also a measure of the scratch resistance, was calculated using [29, 30]:

$$
H = \frac{4F_n}{\pi w^2}
$$

where $H$ is the scratch hardness in N/mm², $F_n$ is the scratch load in N, and $w$ is the residual scratch width. “$x$” is a parameter that assumes a value of 1 for purely elastic contact and 2 when the contact is plastic. Other types of material behavior involving visco-elastic and visco-plastic contacts will have a value for the parameter $x$ between 1 and 2 [31]. In the present study, $x$ is assumed to be 1. It may be noted that Eq. 1 involving scratch width is sensitive to the nature of the material. There is a direct relationship between the scratch width and scratch hardness.

Materials with higher scratch hardness are expected to exhibit higher scratch resistance to scratch damage. Average scratch width of normal and annealed nanocomposite samples is given in Table 1. From Table 1, it is easily

<table>
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<tr>
<th>MWNT content (wt%)</th>
<th>Scratch width (µm)</th>
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<tbody>
<tr>
<td></td>
<td>Normal samples</td>
</tr>
<tr>
<td>0</td>
<td>248,027</td>
</tr>
<tr>
<td>0.5</td>
<td>243,074</td>
</tr>
<tr>
<td>1</td>
<td>240,777</td>
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<tr>
<td>3</td>
<td>239,070</td>
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<td>5</td>
<td>236,600</td>
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proved that scratch width of scratch groove is decreased with higher MWNT concentrations. Due to higher concentrations of MWNT particles which are settled in PEEK matrix, the spherical indenter penetrates the surface of nano-composite shallower and causes the scratch width much lower than PEEK matrix. The greater the value of scratch width, the greater is the susceptibility to enhanced plastic deformation. By this way, surface morphology of PEEK matrix is improved with higher MWNT concentrations. On the other hand, it is observed that for each MWNT concentration scratch widths of annealed nanocomposites are lower than normal samples. According to the calculated scratch width of normal and annealed nanocomposites, Fig. 6 represents the calculated average scratch hardness of two different nanocomposite materials due to various MWNT concentrations. It is observed from Fig. 6 that for each MWNT concentration scratch widths of annealed nanocomposites are lower than normal samples. According to the calculated scratch width of normal and annealed nanocomposites, Fig. 6 represents the calculated average scratch hardness of two different nanocomposite materials due to various MWNT concentrations. It is observed from Fig. 6 that scratch hardness values of each nanocomposite material are increased in higher MWNT concentrations. It is analyzed that the presence of hard carbon nanotube particles in PEEK matrix affects the scratch width. Due to lower scratch width, both nanocomposite materials exhibit higher scratch hardness. During the course of scratch, MWNT dispersed uniformly which could be released from the PEEK matrix and transferred to the interface between the nanocomposites and the spherical indenter. Thus MWNT may serve as spacers preventing the close touch between the indenter and the nanocomposites, which slows the wear rate and improves the scratch hardness. This is because the MWNTs may form mechanical interlocking within the matrix and allow the transfer of the effective load from the matrix to the MWNT as similar to Ref. 32. Beside this, it is determined that scratch hardness is affected due to annealing. The scratch hardness values of annealed nanocomposites with various MWNT concentrations are higher than normal nanocomposite samples. It can be asserted that annealing has improved the mechanical interlocking between PEEK matrix and carbon nanotubes.

CONCLUSION

In this study, effects of MWNT addition and annealing on the crystallinity of PEEK were investigated by DSC analysis. DSC analysis showed that:

- Melting enthalpy increases on addition of 1 wt% MWNT. Yet, adding MWNT more than 1 wt% to PEEK negatively effects melting enthalpy and causes a decrease.
- Melting enthalpy of annealed neat PEEK is increased sharply when compared to neat PEEK. However this increment is decreased slowly up to 1 wt% MWNT addition into PEEK. PEEK with higher contents of MWNT (>1 wt%) dramatically affected by annealing process.

Effects of MWNT addition and annealing on the scratch behavior of PEEK were investigated by micro scratch tester. Test results showed that:

- Friction coefficient values of normal and annealed MWNT reinforced nanocomposites decrease sharply on addition of 1 wt% MWNT. But, coefficient of friction values begin to increase by adding more MWNT (>1 wt%) into PEEK. On the other hand, when the MWNT reinforced PEEK composite was annealed, the coefficient of friction values were decreased in all concentrations.
- Scratch hardness values of MWNT reinforced PEEK composites are increased in higher MWNT concentrations. Moreover, it is determined that annealing process affects scratch hardness of scratch hardness of MWNT/PEEK nanocomposites. Annealed nanocomposites with various MWNT concentrations showed higher scratch hardness values than normal PEEK nanocomposites.

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REFERENCES