

Development of lightweight high-performance polymeric composites with functionalized nanotubes

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ABSTRACT: In this article, we highlight the various properties of an ultralightweight poly(ether ketone) (PEK) composite. In this study, special emphases were laid on the preparation of low-density, high-performance polymeric foams with foaming agents and activators. PEK, foamed PEK, and carbon nanotube (CNT)-reinforced foamed PEK composites were considered for this study. The density of the polymer decreased with the reinforcement of the foaming agent. We also noted that with the reinforcement of the modified CNT in the foamed PEK, there were marginal increases in the density and hardness of the composites. We also noted that the mechanical properties of the CNT-reinforced foamed PEK was on par with those of basic PEK. Thermogravimetric analysis gave us a clear indication that the thermal stability of the composites was not affected by the reinforcing foaming agent and nanoparticles. Scanning electron microscopy and transmission electron microscopy clearly indicated the formation of foams and also the dispersion of nanoparticles in the composite structure. We also observed that because of the reinforcement of multiwalled CNTs in the composite, there was an improvement in the hardness of the composite. An increase in the specific strength was observed in the foamed PEK composites. The CNT-reinforced foamed PEK showed a marginal decrease in the specific strength without a compromise in the impact strength. The impact strength of the CNT-reinforced foamed PEK composite was found to be similar to that of the basic PEK. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43471.

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INTRODUCTION

There is a huge demand for lighter components with improved specific properties and functionalities in high-performance polymeric composites for aerospace and packaging applications. Polymeric composites are mainly of interest in structural application for aviation and space applications.¹ Poly(ether ketone) (PEK) is a semicrystalline polymer that exhibits a glass-transition temperature of 152 °C and a melting temperature of 372 °C. This property of PEK enables it to be used as a desired matrix material for high-temperature applications. Recently, there has been an increase in the demand for advanced high-performance thermoplastics for composite structures.² PEK-based carbon-fiber-reinforced thermoplastic composites offer greater advantages for building advanced structural components for spacecraft applications because of its high strength, stiffness, and thermal and dimensional stability. PEK is a melt-processable polymeric material that possesses exceptional thermal and mechanical properties along with a resistance to

corrosive environments. In the poly(aryl ether ketone) family of polymers, poly(ether ether ketone) has already been shown to be much more attractive for applications with its light weight, high stiffness, high thermal stability, and excellent impact properties. Because of the superior properties of PEK, it is bound to have more applications in high-temperature and lightweight applications.

Recently, great interest has been raised in the development of low-weight, polymer-based composites by means of foaming in integration with multifunctional fillers.³ Foaming agents replace the parent molecules with a multiscale system (foam) and thereby create a porous or reduced-density structure. An activator or initiator is required to initiate proper foaming action of the foaming agent toward the polymeric molecules; this aids in the manufacturing of the essential amount of foam.^{4,5}

It is certain that although the density of the material is reduced, there will be some variations in the properties of the parent material. To compensate for these fluctuating properties, such

Table I. Barrel Temperatures Setup in the Extruder

1st zone	2nd zone	3rd zone	4th zone	5th zone	6th zone	Die head
380 °C	385 °C	390 °C	395 °C	400 °C	400 °C	400 °C

as those in the strength, hardness, and thermal stability, nanofiller reinforcements have been used for both PEK and foamed PEK agents to ensure the retention of properties in the composite. In this context, carbon nanotubes (CNTs) appear to be the foundation for an effective reinforcement because of their exceptional one-dimensional structures and outstanding thermomechanical properties.⁶ However, it is difficult to disperse CNTs into the polymeric matrix because of their large aspect ratio and chemical inertness.⁷ Therefore, through the functionalization of the CNTs, both the dispersion quality of CNTs and the interfacial bonding between CNTs and the polymer can be enhanced. Many studies on the use of single-wall CNTs and multiwalled nanotubes as reinforcements for polymeric composite materials have been found to improve the properties of the material.^{8–10} Several chemical functionalization methods have been suggested for multiwalled carbon nanotubes (MWCNTs).^{11–13} In this study, we used covalently functionalized MWCNTs.

Werner *et al.*¹⁴ developed a carbon nanofiber-reinforced polyether ether ketone foam with an injection-molding technique. This was the principle breakthrough in the field of high-performance foamed polymeric composites. Saatchi⁴ foamed high-temperature thermoplastic polymers with blowing agents, including sodium borohydride (NaBH₄) and magnesium hydroxide [Mg(OH)₂], as activators.

Research on PEK-based nanocomposites with a special emphasis on both carbon-based nanofillers, such as nanotubes or nanofibers, and inorganic nanoparticles have been performed in the past.²⁰

On the basis of these considerations, in this investigation, we focused on developing foamed polymeric composite structures with higher specific strengths; therefore, special emphasis was given to lowering the density without significantly compromising on the mechanical and thermal properties of the material. These kind of materials could be of significant use in packaging industries, reducing the weight of the packing and also reducing the cost. The polymeric matrix used for this study was PEK. Studies were conducted on three types of compositions:

1. The basic PEK material.
2. A composite mixture of PEK and foaming agent (activator).
3. A composite mixture of PEK, foaming agent, and covalently functionalized MWCNT reinforcements.

EXPERIMENTAL

Materials

Commercial PEK (grade 1400G, trade name G-PAEK; Gharda Chemicals, Ltd., India) was used as the polymer. The foaming agents, including NaBH₄ and activator Mg(OH)₂, were purchased

from Sigma-Aldrich. COOH-modified MWCNTs, with diameters ranging from 20 to 30 nm, was supplied by Nanoshel.

Procedure for Composite Preparation

PEK powders were extruded in a Steer extruder and were compression-molded in a Bharani 500-ton instrument.

In the case of the foamed PEK, a mixture was generated by the reinforcement of 0.1 wt % NaBH₄ and 0.3 wt % Mg(OH)₂ with PEK powder (99.6 wt %). For the uniform dispersion of the foaming agent in the polymer powder, the mixture was mixed in a high-speed compounding mixer at a rotational speed of 5000 rpm for 10 min. The mixture was fed into a twin-screw extruder; this was followed by compression molding. The pellets from the twin-screw extruder were spread evenly in the female mold. The temperature of the mold was maintained at 390 °C. The male mold was used for generating a constant pressure of 310 Bar.

In the CNT-reinforced foamed PEK, a mixture of 0.1 wt % NaBH₄, 0.3 wt % Mg(OH)₂, 0.5 wt % modified CNTs, and 99.1 wt % PEK was mixed in a high-speed compounding mixer at a rotational speed of 5000 rpm for 10 min. The mixture was then fed into the twin-screw extruder to enhance the dispersion. The pellets were then compression-molded.

Extrusion

The three specimens were pelletized with a Steer Alpha 25 Lab series twin-screw extruder. The screw speed was maintained at 400 rpm. The nominal torque/shaft was set at 40 Nm. The barrel temperatures for different zones are listed in Table I.

In the time span of 10 min, 500 g of the mixture was inserted into the extruder through the hopper. The size of the pellets was 1.8 mm.

Specific Gravity

The density was calculated with a Shimadzu Aux 220 analytical balance according to ASTM D 792. The density and specific gravity were calculated as follows:

$$\text{Specific gravity} = \frac{a}{(a+w)-b}$$

where a is the mass of the specimen in air, b is the mass of the specimen and sinker (if used) in water, and w is the mass of the totally immersed sinker when it was used and the partially immersed wire:

$$\text{Density (g/cm}^3\text{)} = \text{Specific gravity} \times 0.9976$$

The densities of the foamed PEK and CNT-reinforced foamed PEK were measured with the water-displacement method. The specimens were primarily weighed with the balance and then submerged in a graduated cylindrical containing distilled water at 23 °C. The displaced water was used to determine the density of the specimens. The ratio of the mass in air to the change in volume of water provided the density.

Table II. Density and Percentage Reduction of the Three Specimens

Specimen	Composition	Density (g/cc)	Reduction (%)
1	PEK	1.3	0
2	PEK plus foaming agent and activator (specimen 2)	0.47	63.85
3	PEK plus foaming agent, activator, and MWCNTs (specimen 3)	0.7	46.15

Morphological Study

The morphological analysis of the composites was performed with scanning electron microscopy (SEM). SEM studies were carried out with JEOL/EO (JSM-6490) at an accelerating voltage of 20 kV. SEM was performed to determine the presence of foams in the composite. The specimens were first submerged in liquid nitrogen and then cryogenically cut to study the morphology.

Transmission electron microscopy (TEM) was performed with a HT7700 120 kV high-contrast electron microscope with an acceleration of 100 kV and a magnification of 200,000 \times . This was a powerful instrument for understanding the dispersion of CNTs in the composites. The polymeric composite samples were cryogenically fractured to study the presence of nanoparticles in the composites.

Thermogravimetric Analysis (TGA)

The thermal stability of the specimens was determined with a TA SDT Q600 instrument (TA Instruments). The samples were heated from 25 to 700 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C/min under a nitrogen atmosphere.

Tensile Testing of the Composites

The polymeric composite samples were tested for tensile and compression strengths in a Zwick Roell instrument. The tensile tests were performed through the maintenance of a cross-slide displacement of 5 mm/min. Seven specimens were tested, and the mean values with the standard deviations are reported. The test was performed as per the specification of ASTM D 638.

Shore Hardness and Microhardness Testing of the Composites

To determine the flexibility of polymers, in general, two types of hardness tests are carried out. Generally, the Shore A scale is used for softer rubbers/plastics, and Shore D is used for harder ones. In case of the high-performance thermoplastic polymers, the Shore D scale is used. We measured the Shore D values for all of the samples with the indentation method and determined the penetrating depth of a indenter with a Shore hardness meter (Hardmatic Mitutoyo, 321JAA283).¹⁵ An average of seven measurements in different positions were taken under one indentation time (5 s).

The Vickers microhardness was obtained with a Matsuzawa microhardness tester (MXT-70) with a constant load of 980.665 N and a dwell time of 15 s. An average of six microhardness measurements was made in various different positions for each specimen.

Impact Test of the Composites

Izod impact testing was carried out at room temperature with a notched specimen with specifications from ASTM D 256. The specimen dimensions were 64 \times 12.7 \times 3.2 mm³ with a notch of 0.3 mm. The release angle of the pendulum was 150 $^{\circ}$. Seven specimens were tested, and the mean values with the standard deviations are reported.

RESULTS

Density of the Composites

The density was measured to determine the change in the density of the polymeric sample after the reinforcement of the foaming agent and nanoparticles. Tables II and III give information on the densities of the PEK composites.

The reduction in density (weight reduction) was obtained by the action of foaming agents, which replaced PEK molecules with foam multiscale structures. Along with the foaming agent, COOH–MWCNT was also used to upgrade the specific properties, such as the hardness. CNT-reinforced foamed PEK also showed a decrease in the density because of the presence of foam. We also noted that when the ratio of reinforcement was increased after a certain value, the change in density was not noticeable. Hence, 0.1% foaming agent with 0.3% activator was fixed as the optimum composition for density reduction on the basis of trial and error.

Cellular lightweight fiber-reinforced composites were developed by the reinforcement of carbon dioxide into a thermoplastic matrix reinforced with continuous fibers. Studies were performed on conventional and cellular-reinforced polyethylene (2,6-naphthalate) and glass fibers. The presence of microcells reduced the apparent density of the structure and also led to a significant enhancement in the impact properties of the polymeric composite. The structural and functional performances were enhanced further by the reinforcement of the nanofiller (expanded graphite) dispersed in the matrix.¹⁹

We also noted that for a 60% reduction in density, 2–4% pyromellitic acid was required as the foaming agent. However, the production of pyromellitic acid is a tedious process as such,

Table III. Density with Various Foaming Agent Compositions

Composition	Density (g/cc)
PEK + 0.1% NaBH ₄ + 0.3% Mg(OH) ₂	0.47
PEK + 0.2% NaBH ₄ + 0.6% Mg(OH) ₂	0.54
PEK + 0.3% NaBH ₄ + 0.9% Mg(OH) ₂	0.6

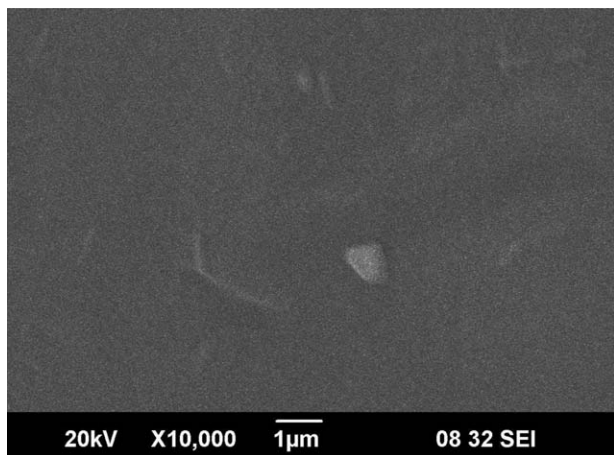


Figure 1. SEM image of basic PEK (specimen 1).

and consequently, a larger quantity is required for proper foaming. Therefore, we concluded that sodium borohydride with merely 0.1 wt % was the optimum foaming agent.¹⁷

Morphology Studies

Figures 1–3 show the SEM micrographs of the basic PEK and foamed PEK. From the SEM micrographs shown in Figure 1, we clearly observed that the surface of the polymer was relatively smooth. In the case of the foamed PEK and CNT-reinforced foamed PEK, it was evident from Figures 2 and 3 that the pores or foam was present on the composite specimen. However, in the case of the nanoreinforced foamed PEK, CNT dispersion was not visible because the size of the CNTs was 30 nm.

The state-of-the-art literatures reveal that foamed articles show a porosity of 65–70%.^{13–15} It has been reported that this porosity is noticeable with SEM.¹⁶ The influence of wood-flour-reinforced phenolic foams on the density, mechanical properties, and morphology of the composites was studied. We observed that the incorporation of 1.5 wt % wood flour into

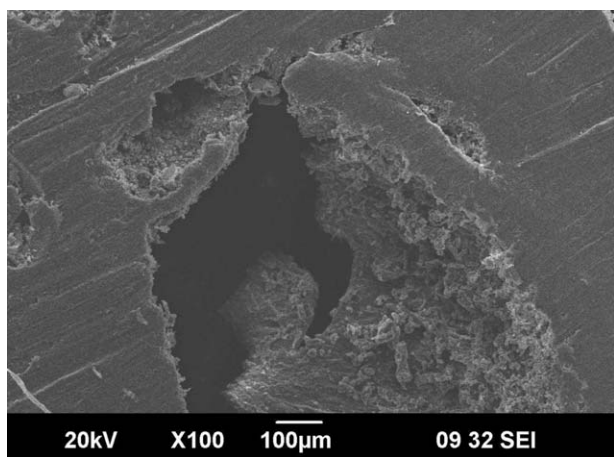


Figure 2. SEM image of the PEK and foaming agent composite (specimen 2).

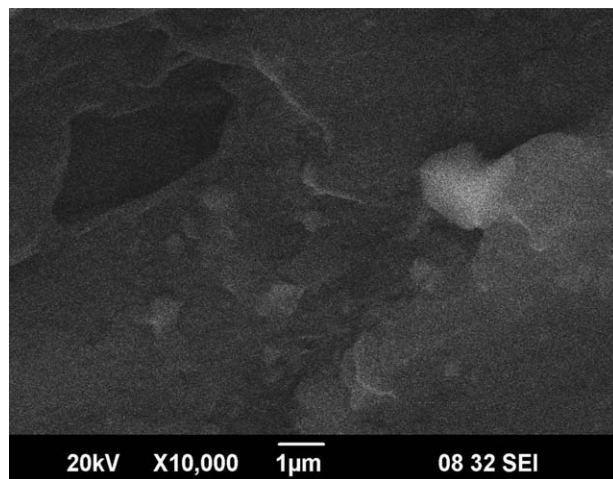


Figure 3. SEM image of the PEK, foaming agent, and MWCNTs (specimen 3).

the phenolic foams resulted in an increase in the compressive modulus and strength up to 130 and 154% in comparison to the unreinforced foam. The SEM micrographs clearly indicated the presence of porosity in the structure of the composites.¹⁸

To determine the dispersion of the modified CNTs in the polymeric composites, composite samples were analyzed under TEM. Figures 4 and 5 show the TEM images of the polymeric composite samples. These clearly indicated the uniform dispersion of CNTs in the foamed composites.

TGA for the Composites

TGA studies were performed for specimens, including the PEK, foamed PEK, and CNT-reinforced foamed PEK.

The decomposition temperature of NaBH_4 was 520°C , and the decomposition temperature of $\text{Mg}(\text{OH})_2$ was 360°C . The resulting decomposition temperature of a 1:3 blend of $\text{NaBH}_4/\text{Mg}(\text{OH})_2$ appeared to be 405°C , as shown in Figure 6. The decomposition temperatures of both specimens 1 (PEK) and 3

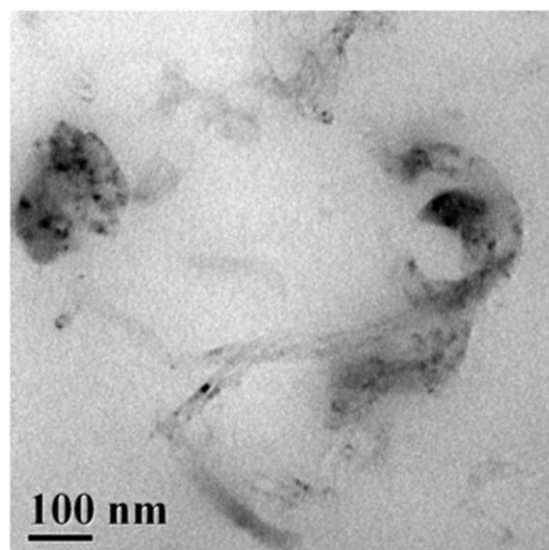


Figure 4. TEM image of the PEK foamed composites.

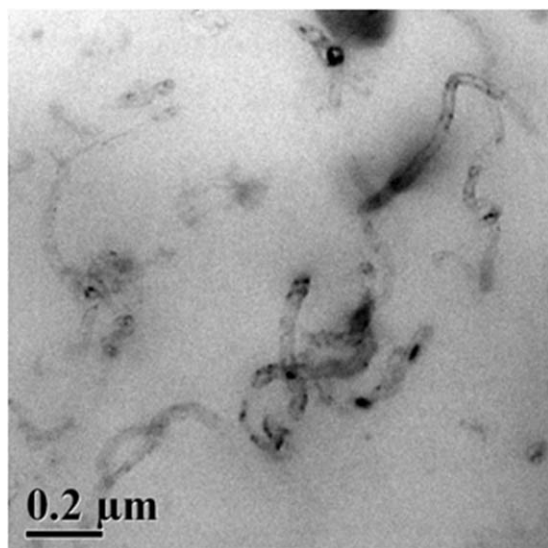


Figure 5. TEM image of the PEK composites.

(CNT-reinforced foamed PEK) were almost similar at 555 °C; however, that of specimen 2 was 485 °C, as shown in Figure 6. TGA was used to investigate the effect of the foaming agents and functionalized MWCNTs on the thermal properties of the resulting composite.

The TGA graphs of the new nanocomposite materials and unfilled sample were more thermally stable and could be recommended for high-temperature applications. All three curves exhibited similar percentages in the weight loss profiles. However, as NaBH_4 was used as a foaming agent, and the melting point of NaBH_4 was 400 °C. Consequently, the mass loss was a little higher when the foaming agent was introduced.

No significant difference in the thermal properties was observed in the polymeric composites with different compositions. This gave a clear indication that the reinforcement of the functionalized multi wall carbon nano tubes (f-MWCNTs) and foaming agents retained the thermal behavior; hence, this would make it useful for high-temperature applications. Apparently, insignificant changes in the TGA plots were observed; this may have

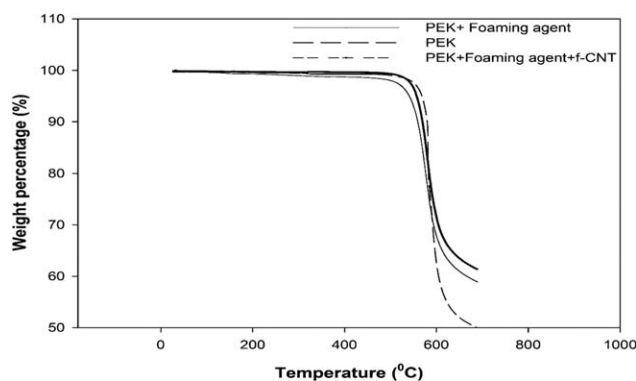


Figure 6. Weight percentage versus the temperature (°C) for three specimens under a nitrogen atmosphere.

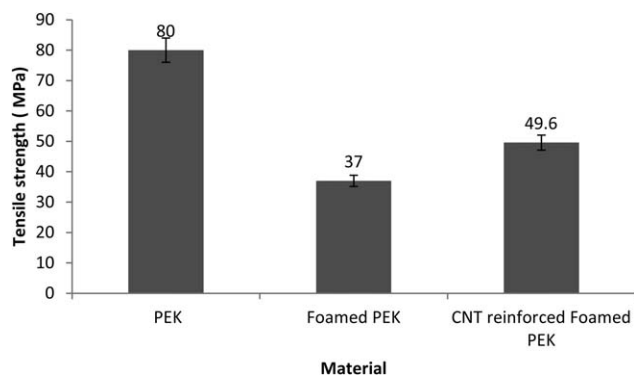


Figure 7. Tensile strength of the CNT/PEK composites.

been due to the small amount of nanoparticles and foaming agent used as a reinforcement.

Mechanical Testing (Tensile Testing)

The tensile strengths of the polymeric composites are shown in Figure 7. We observed that the tensile strength of the foamed PEK decreased in comparison to that of the basic PEK because of the presence of the porous structure. Therefore, the reinforcement of CNTs in the foamed PEK was necessary for it to regain its strength up to certain extent as the stress line across the CNTs may have been useful to absorb the requisite stress. Hence, the strength increased.

In this context, the fiberlike structure of the CNTs and their low density, high aspect ratio, and high mechanical properties make them a potential material as a reinforcement in composite materials. This was evident from the supertough composite fibers fabricated by Dalton *et al.*²¹

The specific strengths of the polymeric samples were also calculated, as shown in Figure 8. We noted that the specific strengths of the foamed PEK and CNT-reinforced foamed PEK were higher than that of the basic PEK, despite the fact that the basic PEK showed a higher tensile strength.

It was clear from Figure 8 that the specific strength of the foamed PEK was significantly high. This may have been due to the decrease in the density because of the presence of the foaming agent. The reinforcement of nanoparticles increased the density, and this further decreased the specific strength.

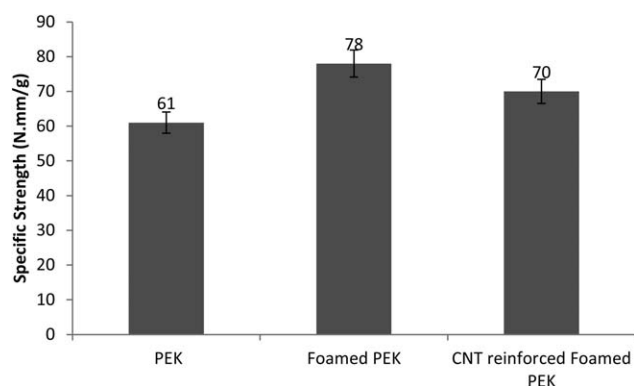


Figure 8. Specific strength of the CNT/PEK composites.

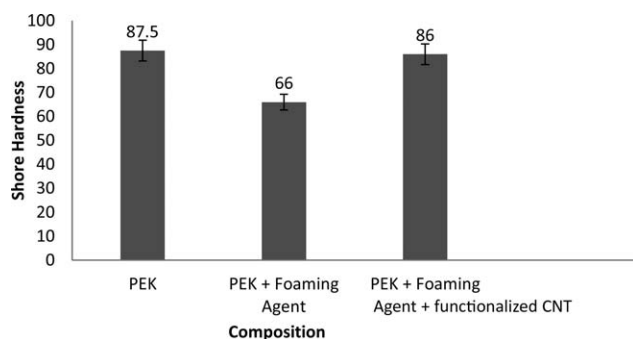


Figure 9. Shore hardness of the three specimens.

Shore Hardness

The maximum Shore hardness value was achieved for the unfilled PEK material followed by the MWCNT nanocomposite, as shown in Figure 9. The composite with foaming agent alone appeared to have a lower hardness value; this was due to the hydrogen molecules being created and replaced by the foam multiscale structures.

Generally, in the case of softer rubbers/plastics, the Shore A scale is used. However, in the case of harder plastics, the Shore D scale is used. In this study, because high-performance polymers were used, the Shore D scale was used for the hardness measurement. There was a reduction in the Shore hardness with the dispersion of the foaming agents. This was mainly due to the increase in the porosity created by the foaming agents, and therefore, the weight decreased. However, with the incorporation of the functionalized MWCNTs, the hardness of the composite was amplified compared to that of the unfilled PEK. This was mainly due to the improvement in the interfacial interaction between the matrix and the nanotubes because of the functionalization of the MWCNTs.

The reduction in the hardness may have been due to the foaming action, which mostly replaced the PEK molecules; they, thereby, lost the parent material properties. However, with the reinforcement of f-MWCNTs into the composite, the hardness increased to 86. This value was almost comparable to that of the unfilled PEK; that is, with reinforcement, it was able to attain hardness. The hardness of the polymer depended on the following factors: (1) the number of crosslinks, (2) the molecular weight of the polymer, and (3) the degree of crystallinity. In this case, the number of crosslinks was more appropriate.

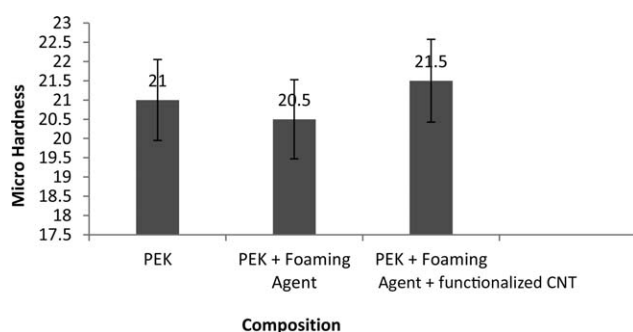


Figure 10. Microhardness of the three specimens.

Table IV. Impact Strength Values

Composition	Impact strength (J/m)
PEK	13
PEK plus foaming agent	10.7
PEK plus foaming agent, activator, and MWCNTs (specimen 3)	12.5

The nanocomposite showed a higher microhardness than the basic PEK; this was due to the effect of functionalization and resulted in better dispersion and interaction between the filler and the polymer matrix. Figure 10 shows the microhardness of the polymeric samples.

The Vickers microhardness resulted in a very small decrease in the foamed PEK compared to the basic PEK. The enhancement in the hardness of the functionalized MWCNT-reinforced foamed PEK when compared to the foaming-agent-reinforced PEK was due to the functionalized sites of the MWCNTs. The presence of MWCNTs may have resulted in the formation of crosslinks; hence, this enhanced the interfacial bonding with PEK.

It was possible that the functionalized sites of the f-MWCNTs were able to form crosslinks with the thermoplastic matrix and, therefore, enhanced the hardness of the polymer. Therefore, we concluded from the hardness test that the f-MWCNTs played a better role with respect to reinforcement.

Impact Testing of the Composites

The unfilled PEK specimen showed an impact strength of 13 J/m, as shown in Table IV. The MWCNT composite showed an impact energy similar to that of unfilled PEK. We concluded that the reinforcement of MWCNTs, even merely up to 0.5%, was found to be effective because the crosslinking of the polymers by the covalently functionalized MWCNTs essentially helped attain an impact strength even in lightweight material.

The impact strength of the PEK and PEK composites with the foaming agent, activator, and f-MWCNT showed no significant difference; this was probably because of the action of crosslinking, obtained similarly to that in the case of the hardness.¹⁶ The linkage was able to hold all of the molecules together with the nanotubes and increased the strength. If there had been a little greater increase in the quantity of nanotubes, the strength would have increased much more than the obtained value. Therefore, this investigation concluded with a high note in that the mechanical properties, in particular the specific strength, were increased by the incorporation of an appropriate foaming agent.

CONCLUSIONS

High-performance polymers, such as composite-based PEK matrixes, reinforced with foaming agents are able to produce lightweight composites. We found that the best composition with respect to foaming for the ultra-high-performance thermoplastic polymer was 0.1% NaBH₄ and 0.3% Mg(OH)₂ with a

1:3 ratio. The morphological analysis of the two composite specimens clearly showed the presence of foams in the composite and also revealed information about the dispersion of CNTs in the composites. The thermal stabilities of the two composites were almost similar compared to that of the unfilled PEK. We also noted that the specific strength of the foamed PEK was significantly high; however, the tensile strength of the CNT-reinforced PEK was relatively higher. The hardness of the composite increased because of the presence of covalently functionalized MWCNTs in the composite. Because of the porous structure in the foamed PEK, we expected to have significant applications in aviation, space, and defense because PEK is a high-temperature-resistant polymer.

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