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Physico-chemical analysis of semi-crystalline PEEK in aliphatic and aromatic solvents

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ABSTRACT

Polyether ether ketone (PEEK) is a semi-crystalline thermoplastic polymer having excellent mechanical and thermal properties. Exposure of this polymer to aliphatic and aromatic solvents can lead to degradation or swelling of the polymeric material. The present work described the plasticization and stability analysis of semi-crystalline PEEK under different aromatic and aliphatic solvent environment. A variety of solvents (acetone, benzene, benzyl alcohol, chloroform, methanol, and toluene), based on their Hildebrand's Solubility Parameter, were chosen for investigation. The physico-chemical characteristics of virgin and treated polymeric samples were investigated using Gas Chromatography–Mass Spectrometry (GC–MS), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The results indicated that the solvent exposure did not significantly affect the thermal behavior and chemical structure of the polymer. However, it seems that certain components of the polymer were leached into the solvent phase as revealed by the GC–MS analysis. The present study identified PEEK as a potentially suitable polymer for the applications where high resistance to aliphatic and aromatic solvents is needed.

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Introduction

Polyether ether ketone (PEEK) is a speciality thermoplastic polymer with an excellent combination of favorable attributes such as high strength-to-weight ratio (1), resistance to chemical and biological attack (2,3), excellent thermal stability (4), high glass transition (5), and melting temperatures (6). Due to these exciting properties, PEEK has been reported for wide range of applications including automotive and aerospace industries (7), energy and power generation (8), biomedical applications (9,10), and insulating materials (11). Besides, the comparatively higher melting and glass transition temperatures make PEEK an excellent choice for high-temperature applications such as sealing system of nuclear reactors (12).

Most frequent applications of polymeric materials entail the interaction of the polymeric surface with potentially harsh environments, such as cleaning solutions, lubricating oils, solvents, and detergents. In aggressive offshore oil/gas industrial applications where polymers are usually utilized as gaskets and seals, the prolonged liquid contact offers enormous risk to the effective performance of the polymeric parts (13). The polymeric

surface can become dissolved, plasticized, or softened, if exposed to such harsh environments for a longer period of time. In certain applications, chemicals, either alone or in combination with other parameters, attack or absorb into the polymer matrix to bring about changes in physical and chemical properties of the polymer (14). Such changes deteriorate the surface mechanical characteristics and eventually the optical properties of the polymer. Therefore, it is extremely important to apprehend the solvent interaction with polymer and to identify the potential physico-chemical changes in polymer as a result of such interactions.

Stober et al. (15) studied the effect of water, low-density aviation hydraulic test fluid (Skydrol), and methylene chloride environments on the plasticization and crystallization behavior of PEEK. The results showed the resistance of PEEK towards the investigated solvents. However, interaction of PEEK with methylene chloride led to two significant effects: plasticization phenomenon and crystallization of partially crystallized polymeric films.

Iqbal et al. (16) studied the surface plasticization of semi-crystalline PEEK in different solvent environments

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using nano-hardness method. The hardness experiments were conducted on the neat and the solvent immersed polymeric surfaces. It was observed that semi-crystalline PEEK exhibited a significantly inert behavior to ordinary organic solvents but water and chlorinated organic solvents triggered deterioration in the surface mechanical properties. Recently, we reported the influence of acetone environment, as a function of different exposure times, on the nano-mechanical properties of PEEK using nano-indentation method (17). The results showed that the nano-mechanical properties of PEEK displayed a decreasing trend as a function of increasing exposure times to the acetone environment, which was linked with the swelling/softening of polymeric network. These studies were focused on the effect of different solvents on the nano-mechanical surface properties of PEEK. Therefore, the current study covers the influence of these solvents on the physico-chemical characteristics of PEEK including thermal and structural behavior.

In the present work, an attempt has been made to corroborate the impact for the exposure of range of industrial aliphatic and aromatic solvents (acetone, benzene, benzyl alcohol, chloroform, methanol, and toluene) on the physico-chemical and thermal behavioral of semi-crystalline PEEK using Gas Chromatography–Mass Spectrometry (GC–MS), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Fourier Transform Infrared Spectroscopy (FTIR) techniques. These solvents were selected based on their respective Hildebrand Solubility Parameter, which is defined as the square root of the cohesive energy density divided by the molar volume (18). Indeed, the use of this solubility parameter has a long history and it is a manifestation of the relative solvency behavior of a liquid. Furthermore, these solvents were selected to see their effect on bulk properties, instead of nano-mechanical properties as reported earlier (16,17).

Experimental

Commercially available semi-crystalline PEEK sheet, with 1.2 mm thickness, was purchased from Goodfellows, Cambridge. Laboratory grade solvents including acetone, benzene, benzyl alcohol, chloroform, methanol, and toluene were obtained from Sigma Aldrich. All chemicals were of analytical grade and used as received.

PEEK sample was immersed in the individual selected solvent in sealed containers at room temperature (25°C) for a period of 8 weeks prior to the characterization. Subsequently, TGA analysis of air-dried PEEK samples was performed on TA instrument in the temperature range of 25–900°C with constant heating rate of 10°C/min under N₂ flow of 100 mL/min.

A TA instrument calorimeter calibrated with ISO 9000 was used for the DSC analysis. Analysis was performed in the presence of nitrogen in an aluminum sample holder and the temperature was varied from 25°C to 900°C with a heating rate of 10°C/min using 4–5 mg polymeric sample. An empty sample holder was used as an inert reference.

FTIR analysis of untreated and solvent-immersed samples was conducted on PerkinElmer by using diamond-attenuated total reflectance. All spectra were measured from 650 to 3800 cm⁻¹ at a resolution of 2 cm⁻¹. A separate background spectrum was eliminated from each measurement.

For GC–MS analysis, separation was accomplished using a constant flow of 1.2 mL/min through an Agilent HP-5MS column prior to Electron Impact Ionisation with a source temperature of 473 K at 75 eV. Initially, the oven temperature was controlled at 308 K and maintained isothermally for 7 min. Following that, temperature was increased to 573 K at 13.25 K/min under dynamic mode, and was held constant at this value for 15 min.

Results and Discussion

Thermogravimetric Analysis (TGA)

Thermal resistance of solvent treated PEEK samples was observed as a function of temperature by using TGA. Figure 1 presents weight percentage as a function of temperature for virgin PEEK and PEEK immersed in selected solvents. All the samples exhibited similar trend up to 550°C except PEEK samples treated with chloroform, methanol, and benzyl alcohol. It could clearly be perceived that at around 150°C, these samples showed first decomposition stage, that was a very fast step, while for the range of 550–600°C, all the samples showed decomposition stage which seems to be slower than first step. This was second decomposition stage for chloroform, methanol, and benzyl alcohol-treated PEEK samples. After this temperature, again constant behavior is observed up to 900°C with different residual weight for each sample. Similar results for the thermal analysis of modified PEEK samples obtained by nitration, amination, and carbonyl reduction have also reported in the literature (19,20).

Another way to express TGA result is Derivative Thermogravimetric (DTG) analysis, rate of mass loss as a function of temperature, as shown in Figure 2. A rapid increase in derivative was associated with the weight loss of the sample. Analysis of DTG curve showed that the degradation rate for all the samples was same except benzyl alcohol and chloroform-treated PEEK up to 580°C. It means that both benzyl alcohol

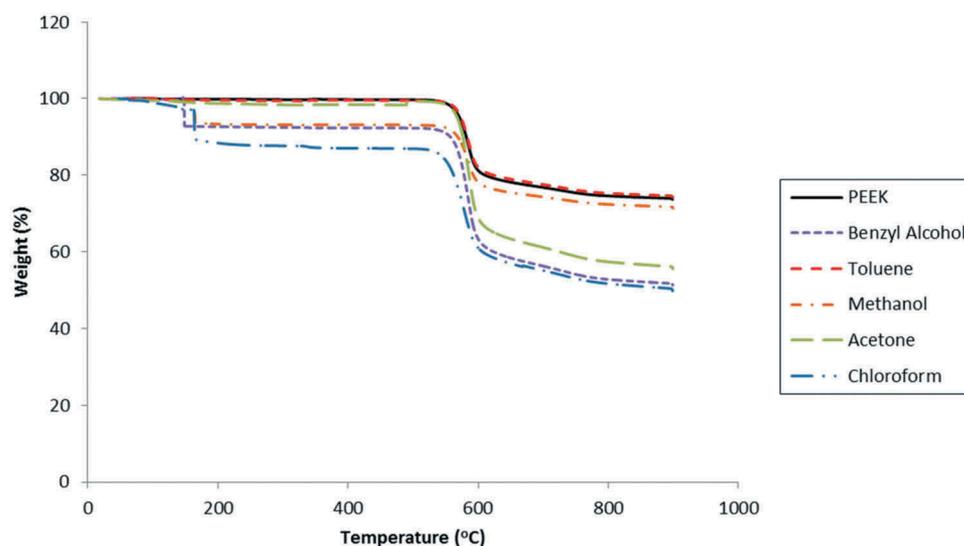


Figure 1. TGA curves for virgin PEEK, and PEEK immersed in benzyl alcohol, toluene, methanol, acetone, and chloroform up to 900°C with 10°C/min.

and chloroform-treated PEEK have higher degradation rate than all other samples. At 585°C, degradation rate for benzyl alcohol was 9% and 6% for chloroform as compared to untreated PEEK. After this temperature, the rate loss of the mass became almost constant. Al Lafi et al. (21) reported similar results for the PEEK samples irradiated with ions (H^+ and He^{2+}). This behavior has also been observed by Di Vona et al. (22) for the thermal analysis of the sulfonated PEEK samples.

Differential Scanning Calorimetry (DSC)

Degree of crystallinity of solvent-treated polymeric samples was observed by using DSC. Figure 3 showed

the relation between temperature and heat flow of virgin PEEK and the acetone, benzyl alcohol, chloroform, methanol, and toluene-treated PEEK samples. By increasing temperature, amount of heat for all the samples gradually increased until almost 400°C and then it started to decrease. This behavior indicated that the investigated polymer was stable up to 400°C under studied conditions. Similar trend for all the samples was observed, however, at two temperatures, 343°C and 580°C, instability in values was observed. A small peak at 343°C was linked with the melting point of the polymer (6). At 580°C, there was an abrupt change in heating values of all samples including pure PEEK. The results revealed that there was no change in the melting

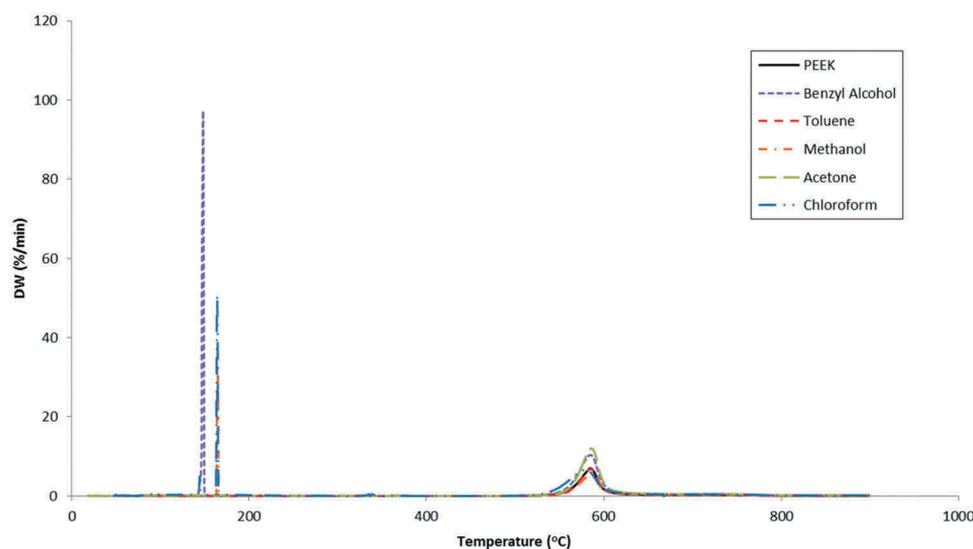


Figure 2. Derivative Thermogravimetric curves for virgin PEEK and PEEK immersed in benzyl alcohol, toluene, methanol, acetone, and chloroform up to 900°C with 10°C/min.

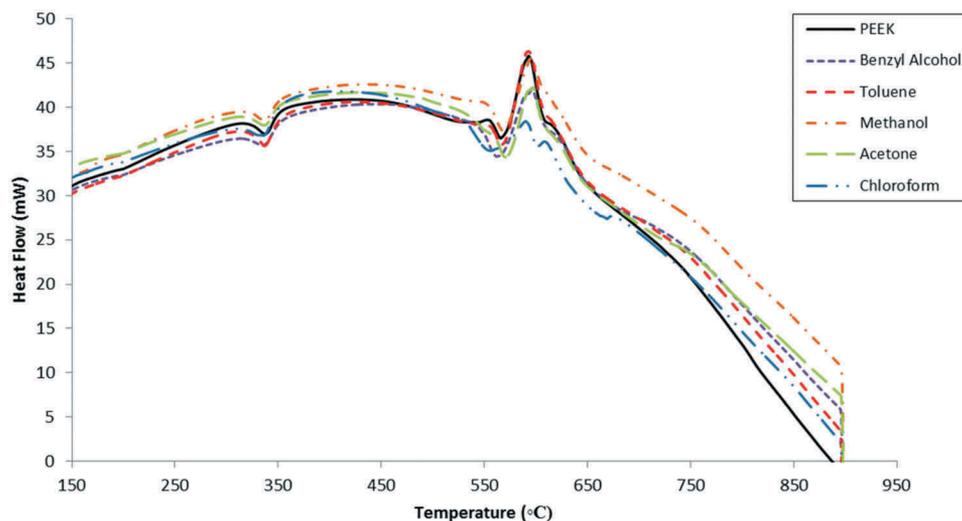


Figure 3. DSC scans for virgin PEEK, and PEEK immersed in benzyl alcohol, toluene, chloroform, methanol, and acetone up to 900°C.

point of the polymeric sample after solvent treatment; however, rate of decomposition of solvent interacted PEEK was different for each treated sample.

In the study of Mohammed et al. (14), the analysis of PEEK, subjected to sour gases under high pressures and temperatures, was reported. Various analytical techniques including differential scanning calorimetry, dynamic mechanical thermal analysis, and tensile tests were used to investigate the changes during aging process. A decrease in the glass transition temperature and bending modulus was observed, which was linked with the surface plasticization phenomenon. Furthermore, similar results from the DSC analysis were also observed for hydroxylated PEEK-OH samples (23).

The percentage crystallinity of virgin PEEK sample and solvent-treated PEEK samples was calculated by using the following equation (24):

$$\% \text{ crystallinity} = \alpha = 4 \frac{\Delta H_m - \Delta H_{rec}}{\Delta H_{\text{pure crystalline}}} \quad (1)$$

where ΔH_m is the change in melting enthalpy, ΔH_{rec} is the change in recrystallization enthalpy, and $\Delta H_{\text{pure crystalline}}$ is the change in enthalpy of pure semi-crystalline material. Table 1 showed the % crystallinity of each sample based on 10°C/min heating rate as calculated from the above equation.

Percentage crystallinity of virgin semi-crystalline PEEK sample was found to be $38 \pm 2\%$, whereas a slight change in percentage crystallinity was observed for each solvent immersed sample. Toluene, benzyl alcohol, and methanol-treated PEEK showed some solvent-induced crystallization, while this solvent-induced crystallization was absent in the case of acetone-treated PEEK and this behavior is similar to the already reported

Table 1. Percentage crystallinity of virgin and solvent-treated PEEK samples.

Sample	% Crystallinity
Virgin PEEK	$38 \pm 2\%$
Toluene-treated PEEK	$42 \pm 2\%$
Benzyl alcohol-treated PEEK	$39 \pm 2\%$
Acetone-treated PEEK	$38 \pm 2\%$
Chloroform-treated PEEK	$37 \pm 2\%$
Methanol-treated PEEK	$39 \pm 2\%$

results in the literature (25). The PEEK sample immersed in chloroform has indicated a slight decrease in the crystalline content. This might be due to plasticization of the polymer from the solvent which may be due to similar Hilderbrand Solubility Index of the polymer and the solvent (25).

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was also performed to identify the functional groups present in the samples. Nguyen and Ishida (26,27) reported the FTIR spectra of PEEK films and assigned the witnessed vibrational modes for crystalline and amorphous phases. Figure 4 showed the FTIR results of virgin semi-crystalline PEEK sample in the form of absorbance as a function of wavenumber. Different peaks were observed at specific wavelengths representing particular functional groups. From $500\text{--}700 \text{ cm}^{-1}$, three peaks were evident indicating aromatics group. Ether group, having less intensity, was analyzed at 1100 cm^{-1} . A pair of peaks, observed around 1500 and 1600 cm^{-1} , possibly depicted the presence of aromatic ring. A peak in the region of 1700 cm^{-1} might be related to the ketone ring (C = O). In the range of $2800\text{--}3100 \text{ cm}^{-1}$, two less intense peaks were possibly due to C-H stretch vibrations.

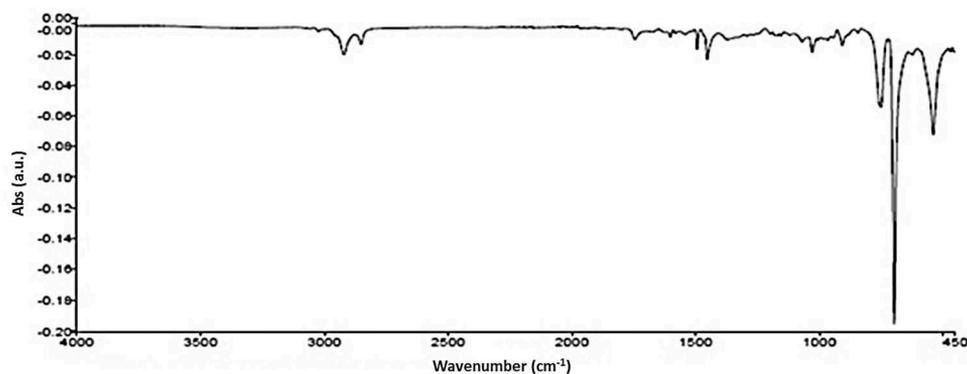


Figure 4. Virgin PEEK spectra by using FTIR with four scans.

Figure 5 showed the FTIR spectra of PEEK sample immersed in acetone. No change in the chemical composition of acetone-treated polymeric sample was observed as neither any new peak appeared in the spectra nor any existing peak disappeared. Therefore, by analyzing, it was evident that the acetone-treated PEEK sample was not chemically degraded but during $1000\text{--}1700\text{ cm}^{-1}$, it can be perceived that there were some changes in the shape of peak from the originally present peak. In fact, this change was neither showing any sort of decomposition nor it was related to any attachment of additional functional group with the polymer structure; however, this might be due to some noise present during experimentation. From this fact, it can be concluded that PEEK can be used as a material of construction of equipment which are designed to operate in these fluid environments. Similar behavior was also observed for all other solvent-treated PEEK samples. Similar FTIR spectrum has also been reported in the literature for sulfonated PEEK and Hyaluronic Acid-coated PEEK samples (28,29). The interaction of PEEK with the organic solvent, tetrachloroethane, was also found to impart significant effects on the physical and chemical properties of PEEK (30).

Gas Chromatography–Mass Spectroscopy (GC–MS)

GC–MS analysis was also conducted to identify the leached out components from treated polymer samples. Virgin and treated PEEK samples were used in the analysis to compare the changes occurred as a result of PEEK–solvent interactions. It can be easily seen from Figure 6 that a peak was observed for benzene-treated PEEK sample, not for virgin sample, which was attributed to the identification of a new component, *N*-Phenyl-naphthalen-1-amine (molecular formula $\text{C}_{16}\text{H}_{13}\text{N}$) and molecular weight 219 g/mol). Similar behavior was also observed for the other treated polymeric samples (31–33).

Conclusion

PEEK is an excellent thermoplastic polymer widely used in aerospace and biomedical applications. In this study, the changes in morphological and thermal stability of PEEK sample, when treated with different aromatic and aliphatic solvents, were investigated. FTIR analysis confirmed that no surface reduction or morphological change in the studied polymer

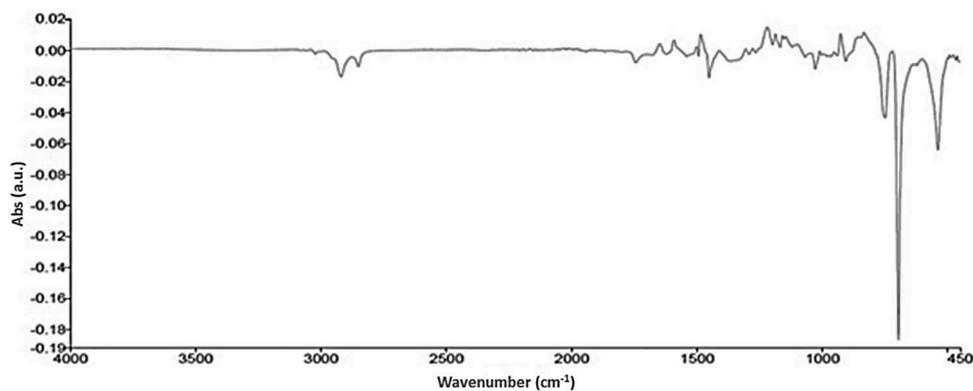


Figure 5. Spectra of acetone-treated PEEK sample by using FTIR with four scans.

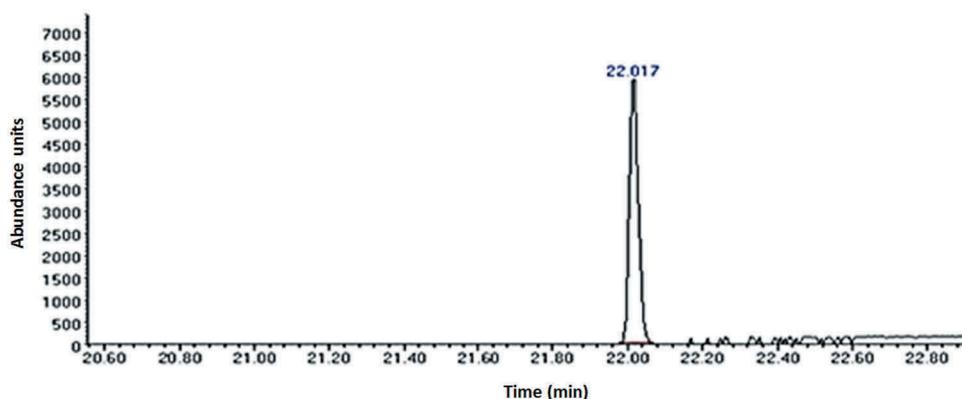


Figure 6. GC-MS spectrum of the benzene-treated PEEK, solution of n-hexane (one drop), and benzene 1 ml.

was caused by these solvents. Moreover, benzyl alcohol, methanol, and chloroform showed the significant impact on the thermal stability of PEEK as evident from TGA analysis. However, crystallinity of polymer was found to be unaffected by the presence of considered solvents. GC-MS analysis detected a component *N*-Phenyl-naphthalen-1-amine ($C_{16}H_{13}N$) with molecular weight 219 g/mol as one of the decomposition products. In the premises of these findings, it can be concluded that semi-crystalline PEEK showed considerable stability under harsh chemicals and dynamic thermal environment.

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