Ionic liquid modified PEEK-MWCNTs nanocomposites with enhanced thermomechanical properties

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Abstract. Polyetheretherketone (PEEK) is a stable semi-crystalline thermoplastic polymer with excellent thermal and chemical properties and is used in many applications, especially as a biomaterial. However, poor mechanical properties: mismatching of elastic modulus to human bone retards the use of PEEK as a biomaterial for bone implant material. In the present study, ionic liquid (IL) modified multiwalled carbon nanotubes were used to prepare PEEK nanocomposites via internal mixer and compression molding processes. The morphologies, thermal and mechanical properties of the prepared nanocomposites were evaluated. Uniform and excellent distribution of MWCNTs into PEEK was achieved by optical microscopy. The thermogravimetric study showed that the decomposition temperature of the composites was boosted 7 % ± 0.9 as compared to those of PEEK composites prepared without IL. Moreover, the elastic modulus of the PEEK nanocomposites was improved by ionic liquid modified MWCNTs into the PEEK. Thus, the prepared PEEK nanocomposites have the potential to be used for fabricating bone implants.

Keywords: PEEK, MWCNTs, IL, Melt blending, Thermomechanical properties

1. Introduction

Polyetheretherketone is a high-performance polymer with an aromatic backbone that shows excellent thermal and chemical stability. Being one of the best thermoplastics with highest processing conditions; melting point 343 ℃ and glass transition temperature 143 ℃, it is widely used in electronics, aerospace, industry, and many other applications especially in biomedical applications as an implant material. PEEK provides additional advantages including the potential to be sterilized repeatedly and readily shaped when used in biomedical applications [1, 2]. However, low mechanical strength and mismatch of elastic
modulus restrain its use in biomedical applications [3]. To improve the required properties, various nanofillers such as carbon nanofibers [4] and montmorillonite (MMT) [5] have been utilized due to their low density, lightweight, and easy processability. Polymer/CNTs composites have got the interest of the science and engineering community due to their excellent thermomechanical properties [6]. The large aspect ratio (>1000) and low mass density of CNTs provide remarkable performance when CNTs/polymer nanocomposites are prepared [7, 8].

Several studies have been reported on polymer/CNTs nanocomposites by different research societies. Cao at al. fabricated PEEK/MWCNTs/BG nanocomposites through compounding and injection molding processes. It was showed that thermomechanical properties of the ternary biocomposites were remarkably enhanced to those of without MWCNTs composites [3]. PEEK hybrid composites were prepared by reinforcing inorganic multiwalled carbon nanotubes and bioactive glass. It was found that the nanocomposites had substantially increased the crystallization properties and tensile strength [9]. Similar behaviour has been observed by Huang et al. for PVDF/CNTs nanocomposites [10]. Nevertheless, excellent distribution and deagglomeration of CNTs into polymer matrices are still challenging due to their high aspect ratio as well as π-π stacking [11].

Among the noncovalent modifiers, Ionic liquids are the green solvents [12] at room temperature and have low toxicity, nonvolatile, high thermal stability, chemical stability, and melting point below 100 ℃. Such properties of the ILs have given great attention to the researchers. Therefore, they provide a simple procedure for the preparation of organic-inorganic composites in ILs or composites based on ILs/polymers [13, 13]. Recently, a novel poly (urethane-ionic liquid)/multi-walled carbon nanotubes (PUIL/MWCNT) composites were fabricated with greatly well-settled MWCNTs into the polymer due to the π-interactions between the imidazolium and MWCNTs [14]. Sharma et al. [15] worked on the dispersion of MWCNTs into PVDF with ionic liquid [EMIM][TF2N]. It indicated the non-covalent interactions between PVDF and IL, resulted in the excellent distribution of MWCNTs. Non-covalent interactions between IL and PVDF have been observed and resulted in the homogeneous dispersion of MWCNTs. In another study, PVDF nanocomposites were fabricated by adding ionic liquid coated CNTs via melt compounding. The findings showed clearly that IL@CNTs displayed improved dispersion and increased crystallinity [16].

To date, no study has been reported for the excellent dispersion of MWCNTs into PEEK by IL. Thus, the current research aims to investigate the effect of IL-modified MWCNTs on the morphological and thermomechanical characteristics of PEEK nanocomposites.

2. Materials and Methods

2.1 Materials

PEEK polymer and bioactive glass powder (BG) were obtained from Huaian RuanKe Engineering Plastics Trade Co., Ltd., China. IL, [EMIM][Ac] (1-ethyl-3-methylimidazolium Acetate, 98 % purity), purchased from Sigma Aldrich, Germany and multi-walled carbon nanotubes (MWCNTs) were received under the trade name Ugent Tech SDN BHD, Malaysia with a diameter of around 15 nm and length of around 5 μm. All the materials were used as received without further treatment.
2.2 Preparation of PEEK/MWCNTs/BG/IL nanocomposites

1 g of MWCNTs were physically mixed with IL (0-2.5 %) by agate mortar followed by the hot plate at 180 °C and 200 rpm for 2 h to prepare IL modified MWCNTs. The mass ratio between MWCNTs and IL ranges from 1:0 to 1:2.5. The nanocomposites were prepared by direct mixing of PEEK (12 g) and BG (1.5 g) powder to IL modified MWCNTs in internal mixer at 350 ℃ for 3 min and followed by compression molding at 350 ℃ for 10 min to prepare nanocomposites sheets. Table 1 indicates the compositions of the prepared composites.

| Sample Name | PEEK (g) | BG (g) | MWCNTs (g) | IL (%) |
|-------------|---------|-------|------------|-------|
| PBMIL₀      | 12      | 1.5   | 1          | 0     |
| PBMIL₀.₅    | 12      | 1.5   | 1          | 0.5   |
| PBMIL₁      | 12      | 1.5   | 1          | 1.0   |
| PBMIL₁.₅    | 12      | 1.5   | 1          | 1.5   |
| PBMIL₂      | 12      | 1.5   | 1          | 2.0   |
| PBMIL₂.₅    | 12      | 1.5   | 1          | 2.5   |

2.3 Characterization

2.3.1 Optical Microscopy

Dinolite microscope (AD4113ZT Dino-lite) was used to calculate the size of MWCNTs aggregates in the prepared nanocomposites at 50 mm magnification.

2.3.2 Thermogravimetric Analysis

The decomposition temperature of all the samples was determined by the thermogravimetric analyzer (TGA Q600; TA, USA). The prepared samples were vacuum dried overnight at 100 °C and heated up to 900 °C at 10 °C/min in a nitrogen environment.
2.3.3 Nano-indentation

Nanoindenter (supplied by Zwick/Roell, USA) was used to calculate the elastic modulus of the prepared nanocomposites at Poisson ratio 0.5 by using QCMS modulus-hardness method.

3. Results and Discussion

The dispersion of MWCNTs into PEEK was evaluated by the Dinolite microscope and shown in Figure 1. The average size of MWCNTs agglomerates was 0.357 mm in PBMIL₀ as demonstrated in Figure 1a. Whereas, when IL modified MWCNTs were used, uniform and excellent distribution of MWCNTs into PEEK polymer was observed and the size of MWCNTs aggregates was also reduced as shown in figure 1 (b-f). This refers to the strong interfacial interactions between the imidazolium cation and π-electrons of MWCNTs. [17-19]. A similar study has been reported for the uniform dispersion of MWCNTs into PVDF by IL [10].

The weight loss and decomposition temperature of the fabricated PEEK nanocomposites with different amounts of IL are shown in Figure 2. The decomposition temperature of PBMIL₀ was recorded as 590 °C which was boosted to 601 °C and 629 °C for PBMIL₀.₅ and PBMIL₁ respectively. This increase in the decomposition temperature shows high compatibility between IL and the polymer matrices. Polystyrene (PS) and MWCNTs based nanocomposites were prepared by melt mixing procedure for enhanced thermal properties. It was evident that IL modified MWCNTs were precisely distributed into the polystyrene and the thermal stability curve was shifted to higher decomposition temperature [20]. When loading of IL is more than 1%, the decomposition temperature of the composites was reduced due to the plasticizing effect caused by the IL. J. Abraham et al. also observed a similar trend for SBR nanocomposites [21].
Figure 1. Optical micrographs of PEEK nanocomposites at 50 mm.

Figure 2. TGA curves of the prepared PEEK nanocomposites at 10℃/min.
Figure 3 shows the elastic modulus of PEEK nanocomposites as a function of contact depth. For PBMIL\textsubscript{0}, the elastic modulus was 5.39 GPa which was shifted to 7.05 GPa for PBMIL\textsubscript{0.5}. At the same time, maximum elastic modulus values were obtained for PBMIL\textsubscript{1}. This refers to the strong interactions, uniform distribution, and enhanced compatibility between the MWCNTs and PEEK matrix. When the composition of IL is more than 1%, the obtained values are less than that of PBMIL\textsubscript{1}. This decline may be ascribed to the plasticization of IL in PEEK nanocomposites [21]. All the values are calculated and compared with human bone. Thus, the environmentally friendly approach and the prepared PEEK nanocomposites have the potential to use as human bone implants.

![Figure 3. The elastic modulus for PEEK nanocomposites at contact depth (70 µm)](image)

4. Conclusion

The morphological and thermomechanical properties of the ionic liquid modified PEEK/MWCNTs/BG nanocomposites have been investigated. Excellent and uniform distribution of MWCNTs into the PEEK was evaluated and confirmed by optical microscopy. The decomposition temperature and thermal stability of PBMIL\textsubscript{1} were significantly higher than those of other PEEK nanocomposites. Due to the exact match of the elastic modulus values to human bone, the nanoindentation tests revealed that the fabricated PEEK nanocomposites can be used as a replacement for bone implants. The present findings show that IL can be used as an effective and environmentally friendly reagent for the preparation of PEEK based nanocomposites with promising biomedical applications.
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