Study the effect of Crystallization Factors on the Mechanical Properties of Semi - Crystalline Polymers for Transport Applications

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Abstract. Polyether ether ketone which combined with carbon fiber by 20% and 30% as reinforcement which purchased from a company Tangyin Sanyou Engineering Plastic Co. ltd/China. the degree of crystallization An significant role in semi-crystalline thermoplastics is played by (e.g. toughness, stiffness and solvent resistance). Primary aim of this work is to use density, DSC and FTIR to Research into the various induced degrees of crystallinity in PEEK composites Strengthened with carbon fiber (CF). In this research, three sheets were used: virgin poly ether ether ketone (PEEK), (PEEK+20 percent carbon fiber), and (PEEK+30 percent carbon fiber). the samples' mechanical and thermal properties produced ones were examined and compared in this study. The density test findings displayed a rise in crystallinity levels by (35.9, 54.4, 88.2) respectively, But a decrease in the degree of crystallinity when examining by DSC. The mechanical properties such as Tensile strength, Young's module and impact strength It showed an improvement in properties with an increase in the percentage of reinforcement with CF. In addition, FTIR for pure PEEK, (PEEK+ 20 percent CF) and (PEEK+30 percent CF) is found to induce minor shifting in peaks by adding 30 percent of carbon fibers and does not cause new peaks to appear and this suggests that there is no chemical reaction between the fibers and the PEEK matrix.

Keywords: PEEK, Crystallinity, Tensile Test, Impact Test

1. Introduction

A composite is a material of a structure consisting of two or more mixed ingredients that are not soluble in each other and are combined at a macroscopic stage. The reinforcing process is called one constituent and the matrix is called the one it is embedded in. Fibers, fragments, or flakes can be in the form of the reinforcing phase material. In general, the matrix phase materials are continuous [1]. In systems for industrial, naval and aerospace, composite materials are commonly used, where they are also subjected to loading for cyclic fatigue. Microstructure production composites for advanced high-performance have concentrated primarily on reaching high intensity and high modulus. Furthermore
such materials must. It can also absorb energy along with high strength and resist cyclic fatigue loads [2]. Crystallization takes place under very harsh conditions in most industrial conversion processes, usually at height cooling rates and with and below shear or extension flow, in many cases, strain. Therefore, when developing a polymer for certain applications, crystallization kinetics are of crucial importance to obtain from the morphology the desired properties formed via solidification [3]. The structural forming process of polymeric materials is dominated by crystallization, thus dominating the properties of the final polymer product[4]. Polymers with a basic structure of the cell unit and a relative large molecular order degree [5], are commonly correlated with the highest around crystallinity. The product of higher crystallinity a substance that is stronger more heat-stable, but also more delicate, and, while the Amorphous Ones areas have some resistance to elasticity and impact[6,7]. Today, a large variety of There are thermoplastics available and they are in popular use. PEEK and sulfide polyphenylene (PPS) are currently Most of the commonly recorded thermoplastic resins in the field of high performance thermoplastics. Since the majority of Semi-crystalline polymer morphology, high performance thermoplastics, crystallinity never levels reach around ninety percent. Since it has a powerful effect on chemical and mechanical characteristics, crystallinity in polymers of high performance is significant. Stiffness and tensile strength tend to be improved by crystallinity in general terms, whereas amorphous areas are more effective for energy absorption from impact. Many influences, including the form polymer and the circumstances for processing, decide the degree of crystallinity. During cooling from the melt state, polymer crystals form in the processing of a specific polymer type. In deciding the degree of crystallinity[8].There are many benefits of high-performance composites, including lighter weight, the ability to customize lay-ups for maximum strength and rigidity, increased fatigue life, corrosion resistance, and decreased costs of assembly attributable to less detailed fasteners and pieces with good design practices. The specific strength and specific high-strength modulus fiber composites, particularly carbon fibers, is higher than that of other similar aerospace metal alloys. This leads to higher weight savings, resulting in improved performance, higher payloads, longer range and savings in fuel9]. To be used in current aeronautical Project, strengthened Structural thermoplastic information components and assemblies are being organized. produced. The introduction of composites of thermoplastic matrix, which are presently considered as candidates For structures for primary aircraft, has acquired new attention in the thermoplastic polymer industry[10].

In 2004 M.C. Kuoa,b, et al studied Nano-sized SiO2 and Al2O3 particulate reinforced PEEK composites are being tested. Filled with alumina or silica nano-sized mensuration 15-30 nm to 2.5-10 wt. percent. Has been prepared at 4000C by vacuum hot press molding. X-ray diffraction, ddifferential scanning calorimetry, and thermos gravity analyzer have been tested for the composition through crystallinity degree checking PEEK resin and thermal stability with the addition of nanoparticles. Of 5-7.5 wt nanocomposites and it is noticed that the composites will result in a superior crystallinity fraction and temperature of degradation compared to the unfilled PEEK[11]. In 2012 Lanzhu Zhang 1, a, et al studied Analysis of PEEK composite mechanical properties . Composites of polyetheretherketone (PEEK) Shortened, reinforced with short fibers like short fibers of carbon (SCF), short fibers of glass (SGF) or polytetrafluoroethylene (PTFE) reinforced, graphite expanded and TiO2 nano material. The tensile elements efficiency (tensile strength and modulus) of PEEK composites rapidly rising as the weight content of short fibers increased. The tensile strength was first increased with the rise in PTFE content and then gradually decreased. However, during the shift in PTFE material, the tensile modulus remained constant [12].In 2014 R. Hemanthl, et al studied Impact on the mechanical properties with thermoplastic composites of fibers and fillers result in polytetrafluoroethylene (PTFE) composite filled with thermoplastic co polyester elastomer (TCE) and polyoxymethylene (POM), reinforced Short fiber glass with (SGF) and various shapes of micro fillers such as short carbon fiber (PTFE) (SCF). The results of testing of mechanical properties shows that short fiber glass fibers clearly improves the power of PTFE composites packed with TCE and POM and that different form ceramic fillers PTFE-filled tensile and bending properties of TCE composites, but that different shape micro fillers simultaneously exhibit a synergistic impact on the bending and
tensile properties of PTFE filled POM[13]. In 2020 Dong-Hyun Kim et al studied investigation inquiries of the hygroscopic and mechanical attributes of semi-crystalline polypropylene polymer through molecular dynamics and studies. Mechanical properties and characteristics of moisture absorption were investigated with regard to the degree of crystallinity via both experiments and molecular dynamics. From the XRD, DSC and tensile test, The crystal structure and crystallinity were evaluated, and the calculated crystallinity values were 46.5 percent and 50.1 percent for the regular and annealed samples. An rise in crystallinity was observed as a boost in stiffness and strength for the PP. T was found to cause lower moisture uptake due to higher crystallinity[14].

2. Experimental Part

2.1 Material

Three types of material sheets have been used in this work, supplied by Guangzhou Ideal Technology Co. Ltd/China. pure PEEK, PEEK + 20% CF and PEEK + 30% CF.

2.2 Density

A technique of immersion conforming to the norm Standard ISO 1183-1: 2019 calculates the density. specimen are dipped into the in a mixture water and moisturizing factor prior to weighting to avoid preventing the formation of bubbles in the Air on the large surfaces. For reproducibility, each one specimen will be weighted three times.

2.3 Mechanical and physical tests:

For most experiments and findings, three specimens were used, reflecting the average of three specimens examined. In accordance with ASTM D 638, tensile test samples were cut. This test was carried out using a tensile system (Bongshin model WDW-SE). The tensile device uses a load range (1-50KHN) with a speed range (0.1-50 mm/min). The specimen's form and measurements depend on the characteristics of the polymers in the tensile diagrams. Three specimens were tested using the most common tests to assess the impact resistance of plastics. Gant (HAMBURG), Model WP 400 style charpy Notch and un-notch specimens are manufactured in compliance with ASTM D 256-87-ISO 179.

2.4 Structural properties:

The structural study of pure PEEK and ternary blends of PEEK virgin, PEEK/20 % CF and PEEK 30 % CF was used to show the FTIR analysis. The sample is prepared as a powder mixed with transparent material KBr with a ratio of 1: 3 in IR spectroscopy. Then the mixture is well crushed to obtain homogeneous material and pressed into a disk to measure its form.

2.5 Differential Scanning Calorimetry

For each sample, differential scanning calorimetry - TA Instruments DSC, Q200 - is conducted to estimate Prediction the glass transition Tg, melting Tm, temperatures of hot crystallization Thc and the crystallinity Degree χc. Weighing Samples in hermetic aluminum pans, approximately 10 mg is encapsulated, heated up from 80°C to 380°C with a temperature slope of 10 K. min, then cooled from 380°C to 80 °C and finally heated under nitrogen flow of 50 mL/min from 80°C to 380°C. The temperature is maintained between each step for 1 min. each analyzed study is twice conducted.

3. Results and Discussions

3.1 Density Test

For all samples, the density is measured using the Archimedes equation. The density of pure PEEK is 1.33 g/cm-3. As PEEK is reinforced with carbon fiber with a different amount of weight, when reinforced by 20 % and 30 %, the density of PEEK will increase by 1.3375 g/cm-3 and 1.3838 g/cm-3 respectively. From equation (1), the degree of crystallinity χc is determined by understanding the theoretical density of the amorphous phase ρa and the crystalline phase ρc, respectively 1.263 g.- 3 and 1.400g.- 3 [15]. by considering Δρa and Δρc are theories values and tantamount to zero the absolute uncertainty is 4 per cent.

\[ \chi_c = \frac{\rho - \rho_a}{\rho_c - \rho_a} \]

(1)
Where Four percent is absolute uncertainty by considering \( \Delta \rho_a \), \( \Delta \rho \), The theoretical values showed a value equal to zero.

\( \chi_c = \) The degree of crystallinity.

\( \rho = \) The density of Calculated in the laboratory.

\( \rho_a = \) The amorphous phase density.

\( \rho_c = \) The Crystalline phase density.

Crystallization for PEEK without carbon fiber addition was found to be about (35.9 percent), then the degree of crystallization will reach about (54.4 percent) when adding 20 percent carbon fiber, and more than 20 percent will reach about (54.4 percent) when adding 30 percent carbon fiber (88.2 percent). as shown in table 1.

| Sample          | Density (g/cm\(^3\)) | Degree of Crystallization% |
|-----------------|-----------------------|-----------------------------|
| Pure PEEK       | 1.3122                | 35.9%                       |
| PEEK+20% CF     | 1.3375                | 54.4%                       |
| PEEK+30%CF      | 1.3838                | 88.2%                       |

Table (1) : Density and Calculated Crystallinity Degree by density for pure PEEK , PEEK+20% CF and PEEK+30%CF

3.2 DSC Test

![DSC Curves for PEEK and their composites](image-url)
Differential Scanning Calorimetry Characteristic temperatures, including the temperature of the glass, the temperature of melting and the temperature of hot crystallization, are measured by DSC for the sample as cleared in table 2.

The degree of crystallinity was calculated according to the following equation[16].

\[
\chi_c = \frac{\Delta H_{\text{exp}}}{\Delta H^*} \times W_f
\]

(2)

\(\chi_c\) = The degree of crystallinity.
\(\Delta H_{\text{exp}}\) = The experimental heat of fusion determined from DSC.
\(\Delta H^*\) = The heat of fusion of fully crystalline PEEK 130J/g.
\(W_f\) = The weight fraction of PEEK in the blend.

| Sample       | Tg(°C)   | Tm(°C)   | \(\Delta H\) (mJ) | \(\chi_c\)  |
|--------------|----------|----------|-------------------|-------------|
| Pure PEEK    | 141.03 °C| 346.35°C | 323.06 mJ, 53.84 J/g | 41.42 %     |
| PEEK+20%CF   | 135.79 °C| 346.90°C | 212.84 mJ, 35.47 J/g | 21.83 %     |
| PEEK+30%CF   | 120.41 °C| 346.61°C | 216.94 mJ, 36.16 J/g | 19.47 %     |

Table 2: DSC test for Pure PEEK, PEEK+20%CF, PEEK+30%CF

When comparing results the DSC test with Density test, When using the density test, we notice an increase in the degree of crystallinity with an increase in the percentage of reinforcement with carbon fiber, but when measuring the degree of crystallinity using DSC test We noticed a decrease in the degree of crystallinity with an increase in the percentage of reinforcement with carbon fibers.

because the method of preparing the sample does not clearly show the effect of the fiber, The samples used in this test are small, fine particles. which means that the sample is closer to the pure sample than the reinforced sample. Also the heat cycle is not ideal for the PEEK sample it should be a complete heating and cooling cycle.

3.3 FTIR Test

Results and Discussion for Fourier Transformation infrared FTIR analysis. FTIR spectroscopy is particularly attractive to determine the chemical functionalities in a material. It relies about the contact of infrared radiation with a sample's chemical functionalities. Stretching, contract and bend chemical bonds when an infrared (IR) beam reaches a sample, causing it to absorb IR radiation in a given wave number (cm\(^{-1}\)). The structure composition of poly ether ether Ketone is shown in Fig. (3,4,5) displays PEEK's infrared spectrum. The FTIR research findings that agreed with the results of earlier research were presented in this figure, Where it was characterized by PEEK. Benzene, ketone and aromatic ether bonds are the core classes of the PEEK molecule. The wavenumbers of carbon-hydrogen (=C-H in the Benzene ring) shaking of extension are 3035 and 3065 cm\(^{-1}\), the aromatic ring (C=C) are 1490 cm\(^{-1}\)and 1600 cm\(^{-1}\), the wavenumbers of ketone (C=O) is at 1653 cm\(^{-1}\)and aromatic ether bond (C-O-C) are present at 1050 cm\(^{-1}\)and 1227 cm\(^{-1}\)associated with carbon-oxygen-carbon stretching vibration. At wavenumbers 863, 841, and 700 cm\(^{-1}\) related to ring deformation distortion modes, and 1305, 1280, 965, and 952 cm\(^{-1}\) associated with PEEK crystallinity, ranging of wave numbers from 1200-1000 cm\(^{-1}\) correspond to CO, alcohol and ether stretches and C-H out-of-plane bending exchange patterns are seen below 900 cm\(^{-1}\). The FTIR analysis thus confirmations the Poly ether ether ketone structure as seen in Fig. (3),the FTIR analysis.
Figure 2: FTIR Test Show the IR spectrum of the pure polyether ether ketone and composite ((PEEK+ 20%CF) and (PEEK+ 30%CF) respectively.

This polymer composites have a very similar structure to the infrared spectrums of the pure PEEK polymer, and it cannot observe significant differences between IR spectrums, except the intensity for all characteristic peak of polymer nano composites ((PEEK+ 20%CF) and(PEEK+ 30%CF) respectively higher than their counterparts of base PEEK polymer.

3.4 Tensile results

This test compares the pure PEEK and PEEK composites' tensile properties (tensile strength at Split in break, Young's modulus (E) and percentage of Elongation at break) reinforced with different weight percentages of 20 Wt carbon fiber. Percentage, 30 wt. Percentage . Changing the proportion of the reinforcement weight. The tensile properties of composite substances under study are affected by many factors, such as the nature of the material for the matrix, type of reinforcement, volume fraction, and adherence between the matrix and the particles incorporated. The samples in the first part behave elastically from the above figures in the (stress-strain) curves (extension occurs in polymer chains without any bond rupture) and finally the behavior changes to plastic deformation (the deformation of polymeric material will lead to rupture in their bonding, and when the load stresses rise, growing cracks occur in polymer. The stress-strain curve of pure PEEK, 20wt. percent, 30wt. percent CF is represented in Figures 6, 7 and 8. From this figure, it can be noted that the increase in CF wt. The percentage contributes to an improvement in polymer composite tensile strength values, so the neat
PEEK transforms from (soft and strong) to (hard and strong) when the CF wt. percent in the composite exceeds 30wt. percent. As a function of CF wt. percent as shown in Figures (9) From Figs, the average data from the results of the tensile tests, (tensile strength at break (σ), Young's modulus (E), and failure elongation (ε)) Have been drawn. It appeared that the tensile strength and elastic modulus were increased with the weight proportion of CF rising. For composites strengthened with 20wt. percent CF, whose value reaches 124170 and tensile strength, for a composite sample strengthened with 30wt, the inclusion of CF in polymer composites has increased the tensile strength by 80%. CF percentage has increased by 85%, and their value reached 105830. The explanation for this outcome is owing to the successful bonding of the interface between the polymer matrix and carbon fibers, as well as the integration of strong fibers into the polymer matrix, resulting in limited polymer chain movement. This improves the stiffness of polymer composites, reduces plastic deformation and, for polymer composites, increases tensile strength and elastic modulus.

**Figure 3**: Curve of Stress-Strain for (A) Pure PEEK, (B) PEEK+20%CF, and (C) PEEK+30%CF
Figure 4: Show the Elastic modulus with Strengthening ratio for Pure PEEK, PEEK+20%CF, PEEK+30%CF.

3.5 Impact Test:
It is the materials which can resistance the fracture under stresses that are applied at high velocity. The samples are distorted during a short period so it's exposed to high strain rates. Figures (10), show the effect of weight ratio of carbon fiber, content on impact strength for PEEK. It can be observed from this figure, that impact strength of polymer composite has been increased with the addition of carbon fiber and reaching to the values (0.01675) KJ/m² at 20wt.% CF and reaching to the values (0.0218)KJ/m². When it was impact strength for PEEK without Carbone fiber about (0.0092)KJ/m².

Figure 5: Impact Strength of PEEK with different weight percentage of carbon fiber, for Pure PEEK, PEEK+20%CF, PEEK+30%CF.
With the addition of the chosen carbon fiber weight percentage, a remarkable change in the impact strength of the polymer composites can be seen. So, the effect strength values have improved by 45.1 percent when 20 percent of carbon fiber content is compared to pure PEEK, and it also rises by 57.85 when it includes 30 percent carbon fiber.

### 4. Conclusion

Investigating PEEK and PEEK reinforced carbon fiber's crystallization activity, provided insight into the effects of polymer matrix carbon fiber additions and their mechanical properties. Closer to the melt, at isothermal crystallization temperatures. Here, carbon fibers function as nucleation stress initiators and therefore increase the nucleation rate within the polymer and subsequent development. This shows that there could be a change in the crystalline growth of the polymer process, resulting in an increased degree of crystallinity, leading to an improvement in mechanical properties (Tensile strength, elastic modulus and impact strength). The effect of the increase in stiffness and the development of the fiber/matrix interface was this action. In addition, the polymer chains became more rigid, increasing degrees of crystallinity. The movement of polymer chains and the polymer chain packed together was impeded, which also resulted in the improvement of PEEK composites' mechanical properties.

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