

EFFECTS OF INTERFACIAL ADHESION ON DEFORMATION AND FRACTURE BEHAVIOUR OF COMPOSITES BASED ON POLYPROPYLENE AND GLASS BEADS

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ABSTRACT

In this study, the isotactic polypropylene, a semicrystalline polymer, was used as a matrix for composites containing 20% and 40% (by weight) of glass bead filler. Selected surface treatment was applied to obtain different adhesion between particles and polymer matrix. In addition to non-treated filler, filler treated with i) a release agent (labelled as NO adhesion) and ii) an adhesion promoter (labelled as GOOD adhesion) were incorporated into the matrix. The morphology, tensile mechanical and fracture behaviour (J -integral) were investigated. Morphology observation revealed a poor interfacial adhesion in the case of non-treated and “NO adhesion” samples represented with debonding of particles. In contrast, strong particle-matrix interactions were confirmed in “GOOD adhesion” samples. The presence of rigid filler particles increased the stiffness, while strain at break was decreased with the lowest value for the composites with strong interfacial adhesion. On the other hand, the higher rigidity and lower deformability decreased in fracture toughness.

Keywords: polypropylene, glass bead, tensile mechanical, J -integral.

1. INTRODUCTION

Particulate-filled polymer composites have a long history and consequently newcomers to the field usually expect to find an area of well-understood science with few intellectual challenges remaining [1]. The addition of fillers to polymer often creates new functional properties not possessed by the polymer matrix [1 - 4]. In general, fillers increase stiffness and heat deflection temperatures, decrease shrinkage and improve the appearance of composites [1]. Depending on the properties of particulate filler, they can also improve strength and/or toughness.

Polypropylene (PP) is a very versatile polymer. There are many ways in which the mechanical properties of PP can be modified to suit a wide variety of end-use applications.

Fillers, such as talc and calcium carbonate, are often used as extenders, thus reducing the final material cost. However, some improvement in stiffness and impact can be obtained with these materials. Solid glass microspheres are special type of filler that induces improved process ability and service performance in injection-molded polypropylene-matrix composites. Higher thermal conductivity, dimensional stability and small and well-distributed internal stress are three qualities of the glass microsphere-filled PP composites [3, 4].

Almost of research on PP/glass bead composites have focused on effect of particle size, filler loading and the filler-matrix adhesion on resulting mechanical behaviour. The maximum stress and strain to failure decrease with glass bead content and glass bead diameter [5]. Liang et al. [6-9] paid much attention on this system. The experimental results showed that glass beads play a role in inducing crazes and blocking the propagation of cracks to improve the toughness of filled PP composites, the notched Izod impact strength of the filled systems increased gently with increasing the volume fraction of the fillers when it was less than 15%, and then it decreased. The Young's modulus value was increased, while the tensile yield and tensile stress at break decreased with the increasing volume fraction of the filler. In these studies, the surface of glass beads was treated with silane coupling agent. By the using two silanes with different functional groups to modify the surface of glass particles, Thio et al. investigated [10] the effects of interfacial adhesion strength on the mechanical properties of particulate filled polypropylene composites. The tensile strength of the reinforced polypropylene increased with increasing adhesion strength. Impact toughness increased with weaker adhesion but the dependence became less pronounced as deformation rate was increased.

The general idea behind this study is to correlate structural parameters with emphasis on molecular mobility with resulting mechanical behaviour of particulate filled composites with thermoplastic matrix. The experimental model with different surface properties of glass bead was used as filler for isotactic polypropylene matrix, together with the multiscale approach using structure sensitive methods and mechanical testing were also applied in this work.

2. EXPERIMENTAL

2.1. Materials and specimens

Isotactic polypropylene Mosten TB 52.412 (Chemopetrol, Czech Republic) was used as a matrix in this study. Glass beads, average size ~ 20 μm , were used as filler.

Glass beads, fillers were modified with 1 % coupling agent vinyltriethoxy silane (Silquest A-151NT supplied by Momentive, Switzerland). Silane was added, under constant stirring, to aqueous solutions of the ethanol and water adjusted to a pH of 4 with acetic acid. The treatment solution was stirred constantly for 0.5 h to complete the hydrolyzing of silane. The filler particles were added to mixture. The slurries were stirred constantly for 2 h followed by tray drying at 80 °C for 2 h. The resulting glass beads were used as filler for polypropylene (PP). To obtain a GOOD adhesion between filler surface and polymer matrix, dicumylperoxide (Dicumyl peroxide 98% supplied by Sigma-Aldrich) at content of 0.15 % by weight of filler was added during this composite preparation as a catalyst for this process.

The preparation of mechanical test specimens was performed by injection-molded process. Polypropylene and glass beads were been compounded in the twin-screw compounder (extruder) Brabender and subsequently injection-molded into form of specimens (dog-bone).

2.2. Sample characterization and testing

The structure morphology was assessed by scanning electron microscope (SEM) taken on impact fracture cross-section of composites.

Tensile mechanical tests were carried out on Instron 5800 tensile tester at room temperature and cross-head speeds alternating of 1 mm/min and 50 mm/min. The following mechanical characteristics were derived from the stress-strain curves: Young modulus E , yield stress σ_y and strain at break ϵ_b . Reported values are averages of 10 individual measurements.

An instrumented Charpy impact tester Ceast Resil Impactor with 7.5J work capacity was used for the J -integral evaluation. Experimental parameters: notch depth, $a = 2$ mm ($a/W = 0.2$); support span, $s = 40$ mm ($s/W = 4$); pendulum hammer speed, $v_H = 1$ ms⁻¹. During impact tests the load (F) – deflection (f) diagrams were recorded. The total deformation energy up to the maximum impact load (A_G) was divided into elastic (A_{el}) and plastic (A_{pl}) parts. The values of the J -integral were determined by the following equation proposed by Sumpter and Turner [11]:

$$J_{id}^{ST} = \eta_{el} \frac{A_{el}}{B(W-a)} + \eta_{pl} \frac{A_{pl}}{B(W-a)} \frac{W-a_{eff}}{W-a}$$

where:

$$\eta_{el} = 0.5 + 5.5(a/W) - 5(a/W)^2,$$

$$\eta_{pl} = 2 - \frac{(1-a/W)(0.892 - 4.476a/W)}{1.125 + 0.892(a/W) - 2.238(a/W)^2}$$

and a_{eff} is the crack length at the onset of unstable crack propagation measured using a light microscope equipped with a metering table.

3. RESULTS AND DISCUSSION

3.1. Morphology observation

The introduction of inorganic filler into a polymer matrix results in a heterogeneous system. Adhesion between different materials is created by physical or chemical bonds between the adhesive and the substrate, and this depends on the selection of coupling agent. In studies of Liang et al., silane coupling agent was applied to modify the surface of glass beads, however, results were reported that the interfacial bonding between the matrix and the particles are weak. To obtain a strong interaction between glass bead particles and polypropylene matrix, vinyl silane was used to pre-treat glass bead and dicumylperoxide (DCP) was added during preparation of PP/glass bead composite.

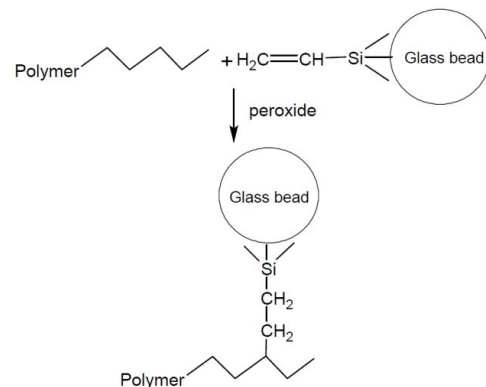


Figure 1. Reaction of polymer chain and silane treated glass bead with the presence of DCP.

Figure 2 presents structure morphology taken of the impact fracture cross section of PP/glass bead composites with 20 % of filler content. As revealed by SEM in the cases of non-treated and NO adhesion, there was a poor interfacial with the strong debonding of particles.

While in case of GOOD adhesion, a strong bonding achieved between glass bead particles and PP matrix, coated spheres adhere to the matrix.

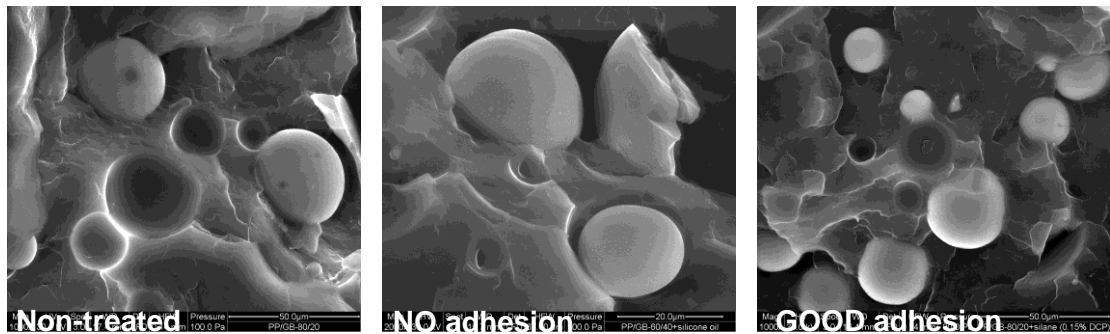


Figure 2. Degree of interfacial adhesion between glass bead and PP matrix.

3.2. Deformation behaviour

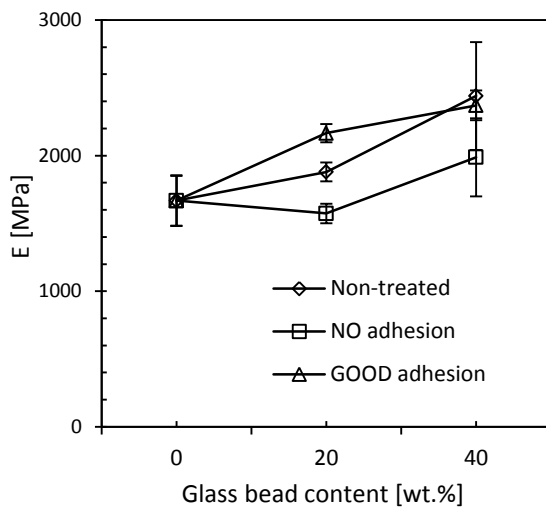


Figure 3. Young's modulus values of PP/Glass beads composites.

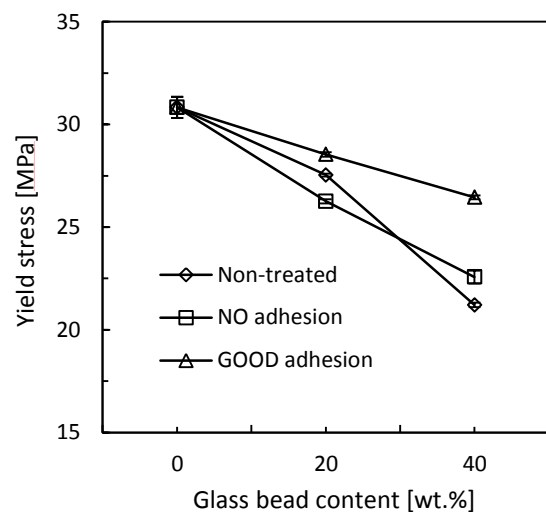


Figure 4. Yield stress of PP/Glass beads composites.

The effects of glass bead with different surface properties on the Young's modulus of filled polypropylene are presented in Figure 3. It can be observed that tensile moduli in all cases of composites increase with increasing filler loading. Generally, the addition of rigid particulate fillers increases stiffness, which is measured through Young modulus. This is due to the fact that fillers often exhibit higher stiffness compared matrix polymer. On the other hand, Young modulus is measured at the very beginning of a tensile test, where deformation is insufficient to cause particle-matrix debonding. However, obtained results indicated slightly change in value among cases of no-treated, NO adhesion and GOOD adhesion. This comes from the difference in adhesion between particles and polymer matrix with zero adhesion in case of NO adhesion and a strong adhesion in case of GOOD adhesion. The increasing in Young modulus of glass bead-filled composites indicates an increase in the rigidity of PP related to the restriction of the mobility in PP matrix due to the presence of fillers [12 - 14]. This mechanical restraint resulting from the enhanced surface interaction between two phases in composites. The similar trend also

found in other studies [9] that enhancement of the interfacial adhesion between the matrix and glass beads is helpful in improving the stiffness of filled PP composites.

Strength and toughness are very important for polymer composites used as structural materials. For particulate filled thermoplastic composites, it is generally believed that the interfacial adhesion between the filler particles and matrix is an important factor affecting strength and toughness of composites. On the other hand, yield stress gives information on filler-matrix interactions and consequently it is one of the preferred methods of composite testing [3]. In the case of a poor interaction (non-treated and NO adhesion) between the matrix and the filler, the interfacial layer cannot transfer stress was reflected by the lower yield stress value in comparison with a strong interaction in case of GOOD adhesion (Fig. 4). Therefore, one can assume that the strength of a particulate-filled composite is determined by the effective available area of load borne by the matrix as a result of the absence of the filler.

The higher yield stress values in case of GOOD adhesion in comparison with cases of non-treated and NO adhesion at the corresponding concentration reflect the interaction between glass bead particles and polypropylene matrix. On the other hand, it can be seen that in all cases, yield stress decreases with increasing filler loading. This is due to the fact that the concentration of the inclusions is the main factor affecting the yield strength of a filled polymer besides the interfacial adhesion between the fillers and matrix. The presence of glass beads has a weakening effect on the composite due to debonding. Weak adhesion and debonding reduce the volume fraction which can carry the applied load [3].

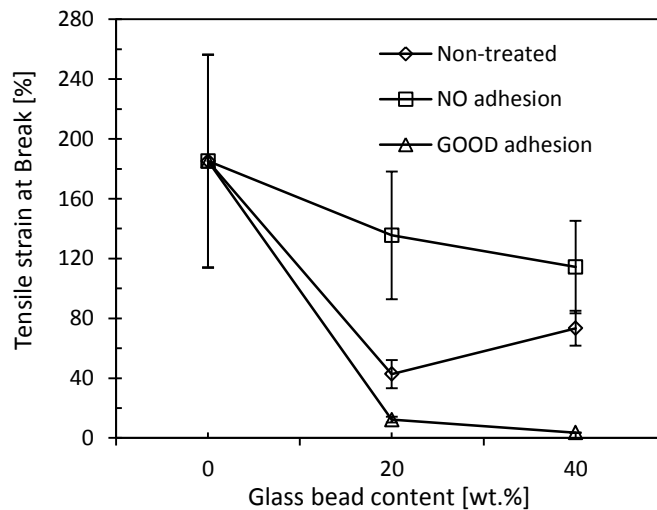


Figure 5. Tensile strain at break of PP/Glass beads composites.

Tensile strain at break is a parameter characterizing the extensibility of materials and it is usually inversely proportional to tensile strength which means that increasing the tensile strength of filled material usually contributes to a decrease in the strain at break. The strain at break value for composite of GOOD adhesion had a lowest strain at break value which corresponds with highest tensile strength value (Fig. 5).

3.3. Fracture behavior

J -integral was used to characterize the energy absorption of polymer materials at the initial stage of crack and the resistance for crack initiation. Figure 4 showed J_{ld} values of polypropylene and glass bead composites.

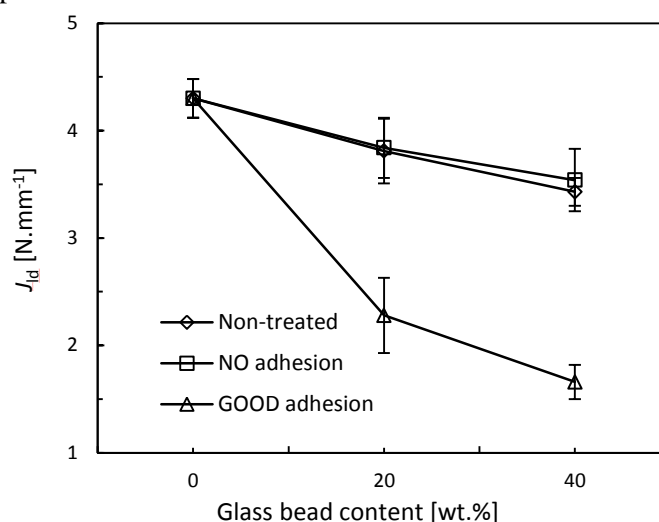


Figure 6. Fracture behaviour of PP/glass beads composites.

The fracture behavior of polymers is strongly affected by the addition of rigid particles. The incorporation of them into the polypropylene matrix leads to differences in the overall process of crack propagation and fracture. The process starts with the plastic deformation of the matrix ahead of the initial crack. The adsorption of polymer molecules on the filler surface through chemical bonds leads to the rigidity in structure of polymer chains. This leads to earlier crack initiation and propagation with dramatically decreasing of J -integral value in case of GOOD adhesion (Figure 6). Plastic deformation of the matrix polymer is the main energy absorbing process in impact [15] and this increases when the interaction between particles and polymer matrix is lowered in case of non-treated and NO adhesion.

4. CONCLUSIONS

The presence of rigid filler particles together with a strong interaction with polypropylene matrix lead to a system with higher rigidity, thus increasing stiffness of composites. Tensile yield stress decrease as a function filler content, however, this decreasing was compensated by interfacial adhesion between filler particles and polymer matrix. Tensile stress is increased with an increase of the adhesion. The higher rigidity and lower deformability leads to earlier crack initiation and propagation with decreasing in fracture toughness.

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TÓM TẮT

ẢNH HƯỞNG CỦA ĐỘ KẾT DÍNH GIỮA CÁC PHA ĐẾN TÍNH CHẤT BIẾN DẠNG VÀ PHÁ HỦY CỦA VẬT LIỆU TRÊN CƠ SỞ POLYPROPYLEN VÀ HẠT THỦY TINH

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Trong nghiên cứu này, isotactic polypropylen – polyme bán tính thể, đã được sử dụng làm chất nền cho vật liệu chứa 20 % và 40 % (theo khối lượng) hạt thủy tinh. Quá trình xử lý bề mặt chất độn được ứng dụng để có được những tương tác khác nhau giữa các hạt chất độn và chất nền polyme. Bên cạnh chất độn không được xử lý bề mặt, chất độn được xử lý với i) tác nhân loại

bỏ liên kết (kí hiệu là NO adhesion) và ii) tác nhân thúc đẩy liên kết (kí hiệu là GOOD adhesion) đã được đưa vào trong chất nền. Hình thái, tính chất cơ giãn dài và tính chất phá hủy (được xác định qua tích phân J) của vật liệu đã được xác định. Quan sát hình thái bề mặt gãy của vật liệu cho thấy sự tương tác pha yếu trong các trường hợp chất độn không được xử lí bề mặt và mẫu vật liệu NO adhesion. Ngược lại, tương tác pha mạnh được quan sát thấy trong trường hợp của mẫu vật liệu GOOD adhesion. Sự xuất hiện của các hạt chất độn cứng nhắc đã làm tăng độ cứng trong khi độ biến dạng ở điểm đứt giảm xuống với giá trị lớn nhất trong trường hợp của mẫu vật liệu có tương tác pha mạnh. Mặt khác, độ cứng nhắc cao hơn cũng như khả năng biến dạng thấp hơn đã dẫn đến sự suy giảm của độ bền phá hủy của mẫu vật liệu.

Từ khóa: polypropylen, hạt thủy tinh, tính chất cơ, tích phân J .