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Fracture toughness analysis of O-POSS/PLA composites assessed by essential work of fracture method

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A B S T R A C T

Essential work of fracture (EWF) method was employed to investigate the effect of the octavinylisobutyl based polyhedral oligomeric silsesquioxane (O-POSS) addition in poly(lactic acid) (PLA) matrix on the fracture behavior of O-POSS/PLA composites. The 2 mm thick rectangular shaped PLA-matrix composites containing various weight ratios of O-POSS were injection molded after processing in a twin-screw extruder. Constant deformation rate tensile tests at room temperature were performed on double edge notched tensile (DENT) specimens with various ligament lengths. It was found that the addition of O-POSS to PLA improved the toughness. It was observed that a greater energy consumed after the maximum load reached on load–displacement curves for the composites. Optimum additive value was obtained at 7 wt% O-POSS.

1. Introduction

According to the recent report by Global Industry Analysts, the amount of annual plastic consumption is expected to be 297.5 million tons by 2015, which will result in a detrimental plastic waste problem [1]. Packaging materials have the highest impact in this figure. In this respect, utilization of biodegradable polymers such as poly(lactic acid), poly(ε-caprolactone) (PCL), polyhydroxybutyrate (PHB), etc as potential green packaging materials play an important role in overcoming this problem.

Due to its relatively better physical properties, compostability and full-scale commercial production from renewable resources like corn, potato and wheat, PLA is most widely used biodegradable polymers compared to the others in packaging applications. In order to improve the mechanical properties of PLA, one of the methods is to compound it with nanoparticles such as titanium dioxide (TiO_2), nanoclays, calcium carbonate, montmorillonite, attapulgite, silica, boehmite alumina, carbon nanotubes, polyhedral oligomeric silsesquioxane [2–8].

The polyhedral oligomeric silsesquioxanes (POSS) nanoparticles have high potential to reinforce, to toughen and to stabilize the polymers because of their flexible chemical and physical hybrid properties and relatively lower cost [9–13]. POSS are organic/inorganic hybrid materials with an empirical formula of $(RSiO_{1.5})_n$ where n is greater than 4 (generally 8). In addition, they have –Si–O– cage-like skeleton with organic side groups having reactive and/or non-reactive functionality. The organic side groups control the compatibility between POSS and polymers. Besides, the inorganic structure may provide polymers with molecular reinforcement, increased thermal stability, better flame resistance, etc. [14,15].

Only a limited number of studies are reported in the literature related to POSS reinforced PLA composites. Wang et al. prepared PLA-based biodegradable copolyester nanocomposites using POSS-NH_2 and POSS–PEG. They stated that the incorporation of POSS–PEG to the copolyester of poly(L-lactic acid) and poly(butylene terephthalate) (PLABT) matrix resulted in an increased tensile strength and Young's modulus. Besides, the elongation at break of PLABT/POSS–PEG nanocomposite significantly improved from 190% to 350% compared to pure PLABT [16]. In a recent work, Turan et al. investigated the effects of amine functionalized POSS on the mechanical and thermal properties and morphology of PLA and plasticized PLA. They demonstrated that the addition of 1–3% POSS particles to the PLA and plasticized PLA enhanced both the modulus and elongation at break values. On the other hand, mechanical properties of these composites decreased with further addition of POSS [17]. In another research conducted by Lee and Jeong, a series of POSS tethered polylactide (POSS–PLA) were synthesized via the ring-opening polymerization of L-lactide in the presence of 3-hydroxypropylheptaisobutyl-POSS, and then mixed with PLA. They found that the initial modulus and tensile strength of the PLA/POSS–PLA nanocomposites were improved with respect to neat PLA [18].

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The fracture event of ductile materials having large plastic deformation zone at the crack tip can be investigated by essential work of fracture (EWF) technique because of its experimental simplicity. According to this method fracture process zone is supposed to be divided into two regions. One of them is the inner region where the fracture process occurs, and the other one is the outer region where plastic deformation takes place. By this way, the total fracture work can be separated into two components: (i) essential work of fracture: the work spent in the inner fracture process zone, and (ii) non-essential work of fracture: the work spent in the plastic deformation zone [19–22].

In the current study, effects of POSS loading level on the fracture behavior of PLA/POSS composites were investigated by essential work of fracture (EWF) methodology for the first time in the literature. For this purpose, PLA and octaisobutyl-POSS (O-POSS) were compounded via melt blending method in a twin-screw compounder. The POSS content was varied as 1, 3, 7 and 10 wt% in the composites.

2. EWF theory

In EWF method, two different types of specimens, single edge notched (SENT) and double edge notched (DENT), having different ligament lengths are subjected to tensile tests. The eligibility of DENT specimen seen in Fig. 1 is due to its symmetrical geometry. This symmetry prevents the buckling of the sample under load. On the other hand, the handicap of DENT specimen is the difficulty of adjusting a same axis notch that can cause an unstable crack growth. Besides, the expected sharp load drop during testing can be obtained in DENT specimens, whereas it cannot be obtained in SENT even if the material is ductile enough [20,21,23].

Total energy dissipated in a notched specimen (W_f) consists of two components; (i) the energy absorbed in the inner fracture process zone (W_e), which is the resistance to crack initiation and (ii) the energy absorbed in the outer plastic deformation zone (W_p), which is the energy for activating the plastic deformation mechanisms that resists the crack propagation as shown in Fig. 1[24]. This can be mathematically expressed as given in the following equation:

$$W_f = W_e + W_p = w_e tL + \beta w_p L^2 \quad (1)$$

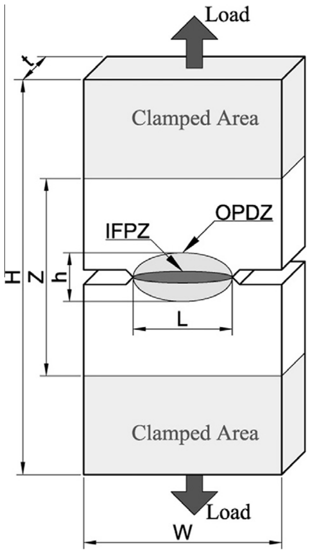

Fig. 1. Inner fracture process zone (IFPZ) and outer plastic deformation zone (OPDZ) in a double edge notched tension (DENT) specimen.

where t, L and β are specimen thickness (mm), ligament length (mm) and shape factor of the plastic zone, respectively. w_e and w_p are the essential and the non-essential work of fracture terms, respectively. Specific total work of fracture, w_f, can be obtained by dividing W_f by the fractured surface area, tL:

$$w_f = w_e + \beta w_p L \quad (2)$$

In other words, in plane stress-conditions for a given specimen thickness, variation of w_f versus L is linear and the intercept and the slope of this linear regression gives w_e and βw_p, respectively. By considering that, a load displacement curve consists of two regions. Then Eq. (2) can be converted to Eq. (3) by using an energy partitioning method defined by Karger-Kocsis [25]:

$$w_e = w_{e,y} + w_{e,nt} \quad \text{and} \quad \beta w_p = \beta_y w_{p,y} + \beta_{nt} w_{p,nt} \quad (3)$$

where w_{ey} and w_{ent} represent the yielding and the necking/tearing components of the specific essential work of fracture, respectively. The terms $\beta_y w_{p,y}$ and $\beta_{nt} w_{p,nt}$ represent yielding and the necking/tearing components of the specific non essential work of fracture, respectively.

To obtain crack opening displacement (COD) of the advancing crack tip, the linear dependence of the e_b with L can be plotted by using the following equation:

$$e_b = e_0 + e_p L \quad (4)$$

where e_b is extension at break, e_o is the extrapolated value of e_b at $L = 0$ representing the COD of the advancing crack tip and e_p is the plastic contribution to extension [20]. It is also possible to estimate w_e by using the e_0 value, which has been examined in several publications [26–28,40,42]. For this purpose a simple equation is used;

$$w_e = \lambda \sigma_y e_0 \quad (5)$$

where σ_y is the tensile yield stress and λ is a constant (taken as 0.67 for parabolic shapes).

In plane-stress conditions, fracture occurs independently from ligament length. That is why the net section stress term must be calculated to ensure this criteria. Net section stress can be written as given in the following equation:

$$\sigma_n = \frac{P_{\max}}{tL} \quad (6)$$

where P_{max} is the maximum load on load displacement curve.

3. Experimental

3.1. Materials

Poly(lactic acid) with the melt flow index of 10–30 g/10 min at 190 °C/2.16 kg was purchased from NaturePlast Company, France. Octaisobutyl-POSS (O-POSS) was purchased from Hybrid Plastics Company, USA. The chemical structure of O-POSS is shown in Fig. 2. The isobutyl groups on the POSS molecules are responsible from the solubility and compatibility. O-POSS is dissolvable in

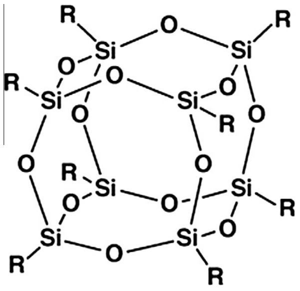

Fig. 2. The chemical structure of O-POSS (R: isobutyl).