

Manufacture and Mechanical Properties of PET-Based Composites Reinforced with Zinc Particles

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Abstract: This work analyzes the mechanical behavior of new composite materials with polymeric matrix, made from recycled polyethylene terephthalate (r-PET), reinforced with 10, 20, 30 and 40 wt% Zn metal particles, processed under isothermal sintering at constant temperature (256°C) and time (15 min) conditions. The r-PET/Zn composite material samples were obtained by a powder traditional technique, namely, ball-milling, uniaxial dye-pressing to obtain pre-forms followed by isothermal sintering. The observations through optical microscopy of the overall morphologies that resulted after sintering the samples studied, were compared against the r-PET-control sample without reinforcement, processed under the same conditions. From the results, it was found that the metal particles were distributed uniformly in the matrix; further, increasing amounts of metal particles tended to improve the mechanical behavior resulting in a stronger material, as was the case of the two materials with higher metal contents (30 and 40 wt% Zn).

Keywords: PET, Mechanical Properties, Zinc Reinforcements, Recycled Polymer

1. Introduction

At present, the plastic known as PET (Polyethylene Terephthalate), is one of the most important commercial polymers that constitutes around 70% of all synthetic polymers produced [1]. México is the second largest consumer of bottled soft drinks, according to the annual report of ECOCE, which is an organization in Mexico that groups the main companies manufacturing PET bottles. Furthermore, there seems inexact knowledge in México of the final destination of the recycled materials, whether they are reprocessed as flakes, fibers, strapping tapes or miscellaneous containers. However, the lack of socially conceived measures and facilities for the population to dispose of the PET containers, has given rise to significant environmental impacts.

Therefore, government authorities are quite concerned with (1) the consumption of natural resources such as oil, (2) the toxicity associated with their manufacture, use and reprocessing, and (3) the environmental impact arising from unregulated disposal of plastics [1]. In spite of numerous market possibilities and diversification, and that the PET bottles are fully recyclable, México only recycles about 20% of the plastic, while Japan recycles the 40%, Europe 33% and USA 23% [2].

There are several ways of recycling PET, however, the choice method that enables cost reductions is basically mechanical [3], where the particles obtained can be used to produce strip, packaging materials [2], granules of recycled PET used to manufacture partially oriented yarn and filaments [3], that can also be exported as raw material to highly dynamic emerging markets in China, Taiwan and India [4],

where the range of recycled PET (r-PET) products processed appear to be broader. Moreover, the recycled polymer can be reinforced with different kinds of materials like ceramic, metal even polymer, where processing techniques like PIM (powder injection molding) are applied in order to attain a broader range of properties and be used for either traditional or newer applications. This technique allows combination of particle-reinforced thermoplastic injection molding with sintering in order to obtain different materials. However, no evidence has been found of implementing the well-known powder technique, from conventional powder metallurgy [5], with solid state diffusion, applied to metallic and ceramic materials, where the finely ground compacted particles are mixed and sintered to join their contacting surfaces [6].

Many studies have recently been made in relation to polymer matrix composites, to be used in engineering applications due to their low density and high resistance. The great variety of thermoplastic matrices allows to experiment with different combinations in the manufacture of composite materials to reduce costs and increase specific properties [7]. Among the materials most sought for use as a polymer matrix is PET, due to the large amount of waste of this type of material generated every day around the world. Which has originated its application in different industries such as automotive [8], electronics [9-10] and construction [11-14].

On the other hand, zinc is a malleable metal, good conductor of heat and electricity with density of 7.133 g/cm^3 , and particularly low melting point of 419.58°C , Occupies the 25th place in order of abundance, also has a hexagonal crystal structure which gives it ductility and resistance. Taking the above mentioned antecedents it can suggest the manufacture of a composite material with polymer matrix PET-based reinforced with zinc particles. The objective of this work is to manufacture a PET-Based composite reinforced with zinc particles by means of isothermal sintering process, and to characterize mechanically the new material.

2. Experimental

The materials used to carry out this study were: sieved recycled PET (r-PET) powders with maximum particle size of $420 \mu\text{m}$ and zinc metal powder with maximum particle size of $1\text{-}5 \mu\text{m}$ (QuimiNet, 99.7 % of purity). Both constituents were mechanically crushed and subsequently poured into an α -alumina container of a ball mill, using stabilized zirconia elements in the 1:15 ratio, varying the proportion of metal, 10, 20, 30 and 40 wt % Zn, and processed for 3h in the ball mill (labmill - 3000), at a speed of 200 rpm [15].

The obtained powders were compressed in an uniaxial hydraulic press at a pressure of 350 MPa, using steel dies in order to obtain dimensionally appropriate specimens for determination of some physical properties, like: density, percent porosity, hardness and microstructure. The samples employed were 20 mm O. D. cylindrical specimens having 2 g of the powder mix. For mechanical testing, two test procedures were considered suitable, namely, bending and impact tests on rectangular $10 \times 10 \times 70 \text{ mm}$ specimens, in

accordance with the standards ASTM D 790 [16, 17] and ASTM D 256 [16, 18], respectively. For the analysis of fracture, the specimens were $70 \times 10 \times 4.8 \text{ mm}$ manufactured according to standard ASTM E399 [16, 19]. Apart from the impact and bending specimens, those required for fracture and the impact test had a notch at the center of their body at an angle of 45° . For the compression test, cylindrical specimens were prepared 10 mm diameter by 10 mm height according to standard ASTM D 695 [16, 20]. Subsequently, all test pieces were isothermally sintered at 256°C for 15 minutes using an electric muffle furnace Lindberg, model 51894 that reaches a maximum temperature of 1100°C . All samples were sintered varying the reinforcing metal content, calling each compound by its composition.

3. Results and Discussion

3.1. Density

This was obtained by the Archimedes method and the results are plotted in Figure 1, from which it becomes straightforward that as the metal content in the composite samples increases, their density increases too. This is expected because the density of the metal reinforcement (7.133 g/cm^3) is greater than that of the polymer matrix (1.36 g/cm^3).

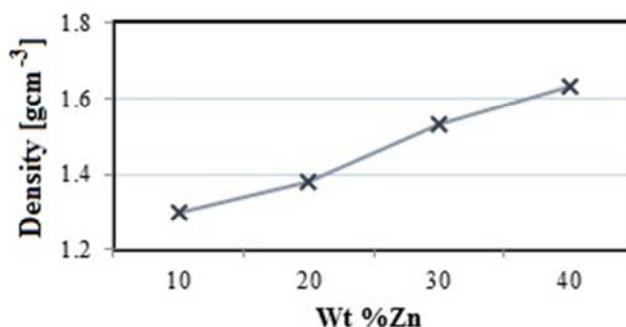


Figure 1. Comparison of the values of maximum density in the studied composites.

3.2. Percent Porosity

In order to get the porosity percent a statistical method was applied. On the optical micrograph grid of each sample, nodes that matched with the pores of the material were counted, getting the results displayed by Figure 2. Inherent to the production process, the specimens present a quantity of porosity that tends to decrease as the metal content increases in the samples. However, at the beginning of the sintering process the samples undergo a significant expansion, especially those with lower metal content. Notwithstanding, when the samples reached the temperature conditions and with increasing residence time, the specimens tend to shrink again, although empty spaces are formed in the polymer particles unions. However, the metal particles did not appear to be affected in this same sense because of the inherent metal stability during the sintering process. Therefore, the composites with lower metal content attained greater porosity.

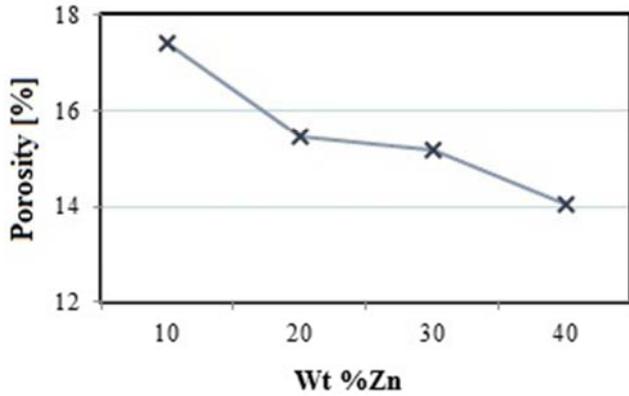


Figure 2. Comparison of the values of maximum porosity percent in the studied composites.

3.3. Hardness

The results shown in Figure 3, were obtained with a hardness meter mod. TH210, Shore D scale. Used for thermoplastic materials. Comparing the four studied composites with the control, unreinforced polymer, it can be seen the significant hardness increase for all samples with metal reinforcement. However, the difference among the composites is small, because to begin with, the metal particles are expected to exert a large influence on this property relative to the control sample, though thereafter, the difference in the other composites is levelled out; the composites with the higher zinc content, seem to have softened very slightly.

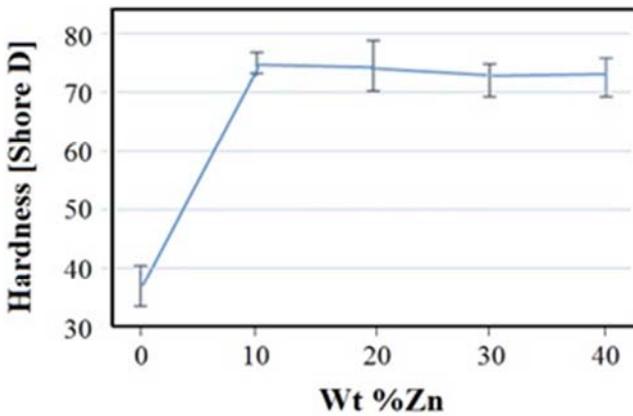


Figure 3. Comparison of the hardness results from the studied composites.

3.4. Bending

For the three point bending test, an United universal testing machine, mod SSTM - 1 was used, at 5 mm / min rate, that yielded the results plotted in Figure 4, in which one can see that the resistance of the three materials with greater metal content is substantially higher than that reported for the control material, approximately 40%. Considering the best results obtained from this test, it becomes clear that the reinforcing metal additions increase the materials resistance, through absorbing a portion of the plastic deformation energy associated, which helps rise their flexural strength, especially for the 3 composites with greater metal content.

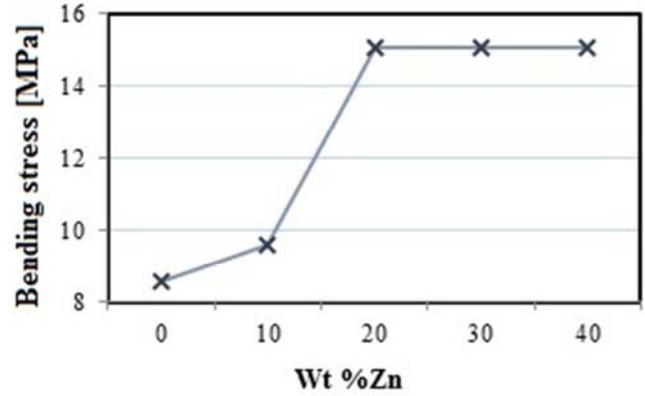


Figure 4. Comparison of the maximum values of bending stress in the studied composites.

Figure 5. Presents the percent deflection results obtained from the bending test. As expected, the percent deflection increased in the samples containing the greatest reinforcing metal content, which implies that the deformation increase is associated with the material toughness, so the ductility of the metal contributes to improve resistance, allowing greater deformation prior to fracture.

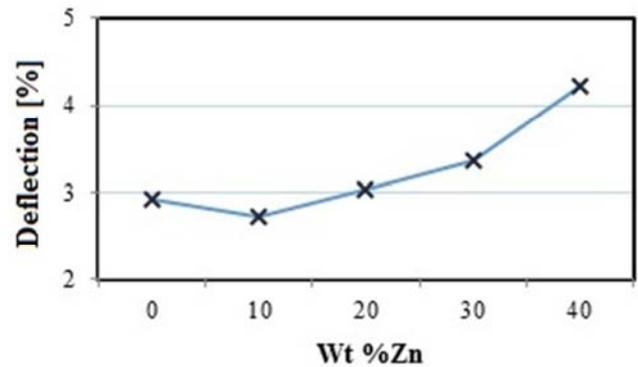


Figure 5. Percent deflection of the studied composites obtained from the bending test.

3.5. Compression

This test was performed using an universal Monsanto machine, applying load of 125 kg and 6 mm min⁻¹ deformation rate, that led to obtaining the engineering stress values, which subsequently were converted by means of equation 1 into real stress [21], the final results obtained are plotted in Figure 6.

$$\sigma_R = F/A_0 (1-e) \tag{1}$$

Where:

- σ_R : True Stress [MPa]
- F: Test force applied [N]
- A_0 : Specimen cross-section [m²]
- E: Engineering deformation

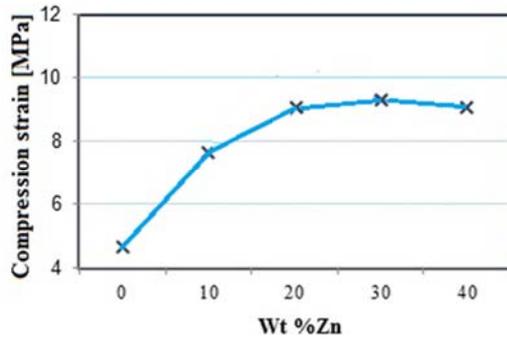


Figure 6. Comparison of the values of maximum compressive stress in the studied composites.

It is plain that the materials resistance is favorably influenced by the metal reinforcement, however, after adding a certain amount of metal, it can be possible to appreciate a decreasing trend as though the metal had absorbed some of the deformation energy more or less directly, as if the matrix contribution in transmitting the deformation energy seems to be less important than that at work by the excess metal aggregates, which form an increasingly important network, the connectivity of which altered the composite configuration, its role therefore, particularly in relation to the compression test was to absorb part of the energy associated to the load applied.

3.6. Impact

This type of test was performed using an Izod Tinius Olsen machine, model 892; the results are plotted in Figure 7. Observing the results of the test allows appreciation of the favorable function that the metal reinforcement exerts on increasing the material resistance, which must be associated with dissipating within the composite a fraction of the energy generated at impact moment by the zinc aggregates.

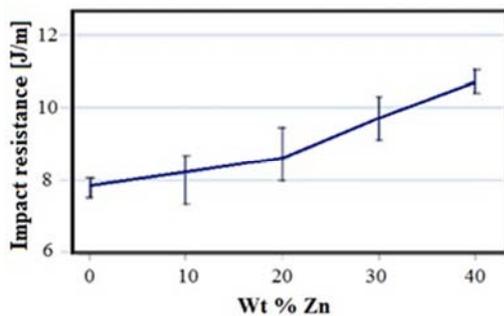


Figure 7. Comparison of the Izod impact resistance values obtained for the studied composites.

3.7. Tenacity

The stress intensity factor K was theoretically calculated, first sizing the notches made in each specimen (opening, depth, angle and radius) by a profile projector Mitutoyo mod. PH - 3500 and subsequently testing the specimens in 3 - point bending jig, in a universal machine Instron mod. 5500R applying a displacement rate of 0.5 mm min^{-1} .

Based on the Peterson's model, encoding the geometry of the specimen [22] and applying equations 2 to 8 [23], they

were obtained K_{tn} (Concentration factor of elastic stresses), σ_{max} (stress root hub) and σ_{nom} (nominal stress).

$$K_{tn} = C_1 + C_2 (a/W) + C_3 (a/W)^2 + C_4 (a/W)^3 \quad (2)$$

In the case where $2.0 \leq a/r \leq 20$, the following equations apply:

$$C_1 = 2.966 + 0.5021 a/r - 0.009 (a/r)^2 \quad (3)$$

$$C_2 = -6.475 - 1.126 a/r + 0.019 (a/r)^2 \quad (4)$$

$$C_3 = 8.023 + 1.2531 a/r - 0.020 (a/r)^2 \quad (5)$$

$$C_4 = -3.572 - 0.634 a/r + 0.010 (a/r)^2 \quad (6)$$

$$\sigma_{nom} = 3PS / 2Bd^2 \quad (7)$$

$$\sigma_{max} = K_{tn} X \sigma_{nom} \quad (8)$$

Where:

W: Height of the test specimen [m]

P: Applied force [N]

S: Span between the supports [m]

a: Crack depth [m]

r: Notch curvature radius [m]

B: Specimen thickness [m]

d = W - a [m]

Using equation 9, the K_{IC} was obtained by the Irwin model [22].

$$K_{IC} = \beta \sigma (\pi a)^{1/2} \quad (9)$$

Where:

β : Geometric factor, obtained from tables, using the geometry of the specimen (in this case 1.13)

σ : Reference to the maximum stress to crack, it was estimated

a: Crack depth.

The K_{IC} results obtained were used to generate the plot in Figure 8. Looking at the results in figure 8 it can be noted that the value of K_{IC} tends to grow from a metal content of 30%. Although the metal absorbs a portion of energy prior to fracture, rigid behavior of these polymeric materials limits the stress resistance. Anyway, for the sample with greater metallic reinforcement content (40% Zn) the improved fracture toughness compared to the sample without Zn addition was approximately 40%, which can be considered positive in terms of material fracture toughness improvement.

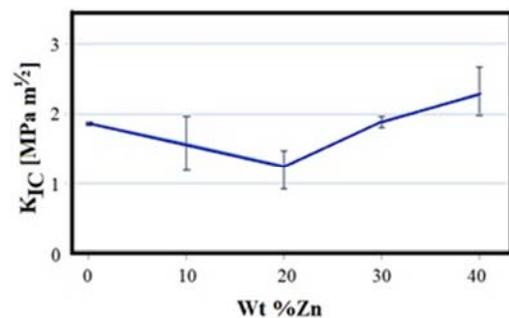


Figure 8. Comparison of the theoretical values of K_{IC} in the studied composites.

3.8. Released Energy

The energy criterion postulated by Griffith states that the fracture in a cracked body will come when the speed of conversion of energy available is greater than a critical value, this like a property of the material. Where G (energy released during the fracture) value is related to the stress intensity factor K , for a linear solid - elastic. So that G relates the stress intensity with the modulus of elasticity as can be seen in equation 10 [22].

$$G = K^2 / E \quad (10)$$

Where:

K : Stress intensity factor

E : Elasticity modulus

Thus the values obtained with Equation 10, for each composite, are shown in Figure 9. There is a relationship between the results of the stress intensity value (K_{IC}) and the energy released upon fracture. From the compounds with 30% metal reinforcing it is possible to appreciate an increase in fracture toughness resistance compared to the control material. It indicates that the increase in zinc content helps store certain amount of released energy while fracture occurs. This behavior is translated in a greater capacity to absorb stresses in the composite when it is working under the action of mechanical stress.

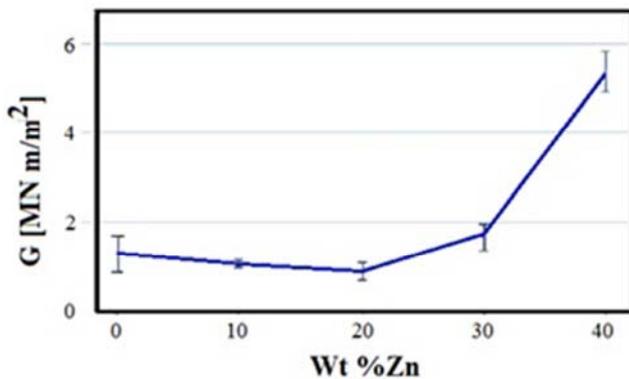


Figure 9. Values of the energy released during the fracture of the studied composites.

3.9. Scanning Electron Microscopy

In order to perceive the manner in which the reinforcement is distributed throughout the composite, electron microscopy characterization was performed with a microscope XL30 Phillips ESEM, using backscattered electrons (BSE). Figure 10 (a-d) present the contrast difference due to the chemical composition of the composites, as established by this technique.

From the micrographs in Figure 10 (a-d), it is possible to note a relatively uniform distribution of some compact aggregates, somewhat flattened through previous cold work, within a polymer matrix; the metal reinforcement tended to conglomerate due to their relative ductility, although

coalescence of metal particles increase with increasing metal contents. The relative homogeneity helps to have more uniform material properties, while the elliptical shape of the coalesced particles contributes both to reduce stresses in the matrix as well as to reduce the presence of stress concentrators that may reduce the strength of the materials studied.

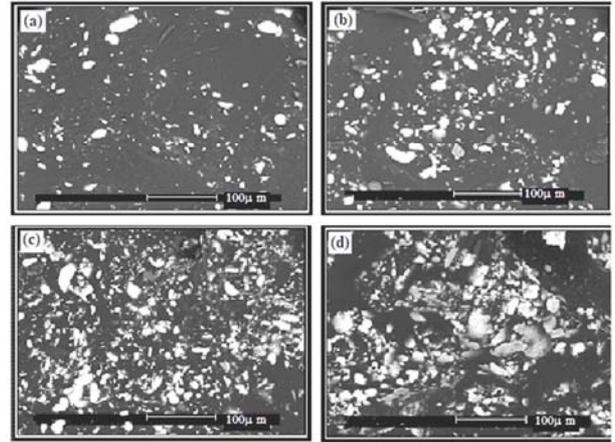


Figure 10. Scanning electron micrographs of *r*-PET/Zn composites. (a) 10% Zn sample, (b) 20% Zn sample, (c) 30% Zn sample, (d) 40% Zn simple.

4. Conclusions

- Al_2O_3 -based composites can effectively be produced by inducing fine dispersions of silver particles, through a combination of experimental techniques, such as; mechanical milling and pressureless sintering (in an argon-atmosphere).
- The refined and homogeneous incorporation of silver in a ceramic matrix (Al_2O_3) improves its fracture toughness. Alternatively, increments in sintering temperature are reflected as enhancements of the density and consequently of the fracture toughness of the same one.
- From the fracture toughness measurements and microstructure observations, it can be commented that the toughening mechanism in Al_2O_3/Ag composites is due to plastic deformation of the metallic phase, which forms crack-bridging ligaments.

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