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Predictive Models of Ethylene-Vinyl Acetate (EVA) Copolymers with Powdered Zn Fillers

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Summary: Metallic Zn filler was used to increase the electrical properties of ethylene-vinyl acetate copolymer (EVA). Other properties were also modified such as mechanical and thermal behavior. It is possible to predict the behaviour of EVA-Zn system by using different models.

Keywords: composites; electrical properties; fillers; mechanical properties

Introduction

Ethylene vinyl-acetate copolymers (EVA) are broadly used in the industry (toys, footwear,...) due to a good combination of mechanical properties (elasticity) and easy processing. There are many and varied materials that can be incorporated to these copolymers with certain purposes: coloration, stabilization, foaming...

There are many works devoted to the development of polymers with good electrical properties for use in the production, for example, of composite electrodes[1-2]. The incorporation of metallic fillers represents an interesting procedure to modify the electrical properties of polymers [3].

We have worked on the development of composite electrodes that use EVA as matrix with the incorporation of powdered metallic Zn as filler. Mechanical and thermal properties have been studied to establish the features and the range of use of this material.

On the other hand, we have worked on the development of predictive models that help us to predict the properties of these materials. The use of general theories such as percolation theory has given excellent results in the prediction of electrical properties of conductive polymers.

We have made the use of this theory to the mechanical and thermal properties in order to establish the limitations of the theory and optimize the proposed models. Determination of

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percolation thresholds of the different properties can help us to establish the validity of this theory.

Experimental

Materials

i) EVA copolymer. We have used EVA ALCUDIA ® PA-420 supplied by REPSOL CHEMICAL, INC. in pellet form, which has been subjected to a pulverization process in order to make easier the mixture with metallic Zn powder. This it is characterized for its flexibility and it is specially suitable for injection moulding. It contains an antioxidant as additive.

ii) Zn powder. Fine powder of metallic Zn supplied by MERCK has been used. EVA and Zn powders were mixed by a dry mixing process with vibration to improve the homogeneity of the mixture.

Sample preparation

Plates with dimensions of 120x60x4 mm were obtained with different amounts of Zn powder (10, 20, 30, 40, 50, 60, 62.5, 65, 70, 72.5, 75% Zn by weight) by means of the use of a hot plate press. These plates were prepared with a constant pressure of 10 kg/cm^2 during 180 s at 120 °C and later a cooling process to 40 °C for 600 s was applied.

Methods and characterization techniques

We have prepared samples according to the procedure established in ISO-527. Tensile tests of specimen were carried out in a universal test machine IBERTEST ELIB 30 (S.A.E. Ibertest, Madrid, Spain) at 10 mm/min.

Thermogravimetric analysis of EVA copolymer was carried out in a METTLER TOLEDO TGA-SDTA 381e (Mettler Toledo Inc., Schwerzenbach, Switzerland) in order to determine the content of vinyl acetate in the copolymer. Samples were treated under the following conditions : flow of N_2 (20 ml/min), weight of the sample (8-10 mg), ramp of temperature (30-700 °C at 10 °C/min). To determine the best processing conditions, calorimetric studies of different compositions have been carried out with a METTLER TOLEDO DSC STAR-2000 (Mettler Toledo Inc., Schwerzenbach, Switzerland). Samples were treated under the following conditions : flow of N_2 (50 ml/min), weight of the sample (5-10 mg), ramp of temperature (30 – 450 °C at 10 °C min).

Results and Discussion

Characterization of EVA-Zn system

Thermogravimetric analysis allows to determine the percentage of vinyl acetate in the EVA copolymer (Figure 1). It is possible to determine this content because degradation of EVA copolymers occurs in two steps. The first one is attributed to vinyl acetate phase degradation. This content results to be approximately of 20 %wt. It is important to know the percentage of vinyl acetate because of its polar behavior which can contribute together with Zn powder to change the electrical properties. This content is the typical for applications in toys and footwear industry.

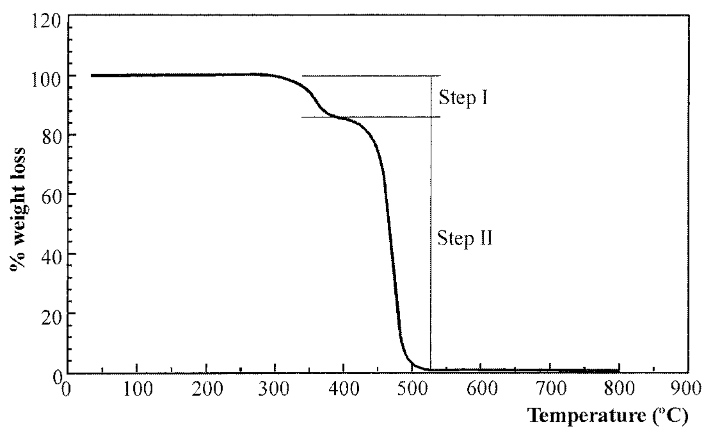

Figure 1. Thermogravimetric curve of EVA ALCUDIA ® PA-420. [I] Removing of volatiles generated in the degradation of the vinyl acetate, (mainly acetic acid). [II] Degradation of carbon chain residue.

The different DSC curves allow to identify the most suitable temperatures for processing by means of a hot plate press without EVA degradation (Figure 2). Since EVA degradation processes start at relatively low temperature (around 220 °C), it is necessary to process the mixtures at lower temperatures.

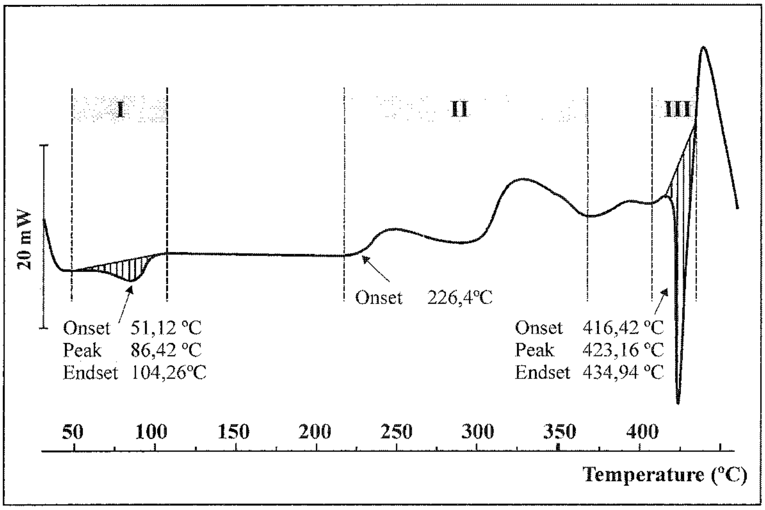

Figure 2. DSC thermogram of EVA with 50%wt Zn. [I] Melting of the crystalline phase of EVA, [II] Degradation process of EVA, [III] Melting point of Zn.

Mechanical properties of EVA/Zn system vary considerably with Zn content[3]. We observe an important reduction in mechanical ductile properties (Figure 3) such as elongation at break since Zn powder can act as a stress concentrator which plays an important role during the fracture process. This situation must be considered in order to use these composites at industrial level where a good balance between ductile and resistant properties is needed.

Similar behavior can be found in the evolution of the tensile strength (Figure 4) since the presence of Zn promotes the fracture due to the low interaction with the EVA matrix. This low interaction is related to the presence of polar groups in EVA chains which can interact with metallic Zn powder. Nevertheless, these interactions are very weak and do not contribute to improve adhesion between the two phases.

This lack of interaction in the interphase is responsible of the fracture process since there is not a continuous phase to transmit loads. Zn filler, which is quite resistant and promotes important changes in electrical properties, reduces considerably the mechanical ductile properties.

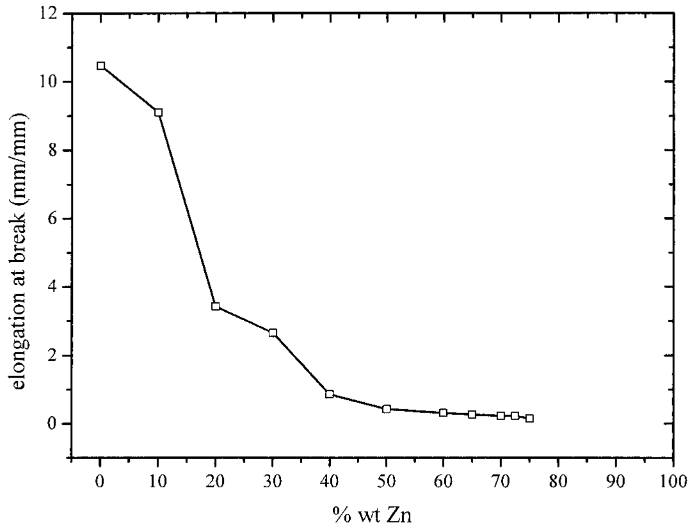

Figure 3. Variation of elongation at break of EVA-Zn system with different percentage of Zn.

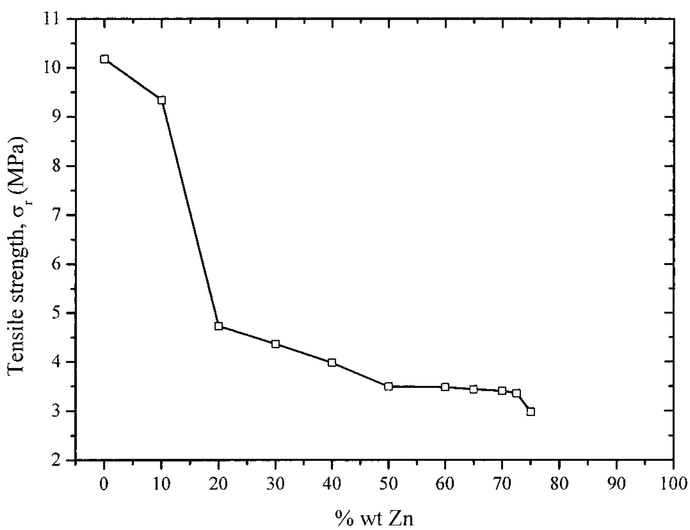

Figure 4. Variation of tensile strength of EVA-Zn system with different percentage of Zn.

Nevertheless, stiffness is increased by increasing the Zn loading in the mixture as indicated by the variation of Young modulus (calculated as tangent modulus) of the EVA-Zn system (Figure 5). Typical values of Young modulus of EVA copolymers are considerably increased to values similar to other commodities.

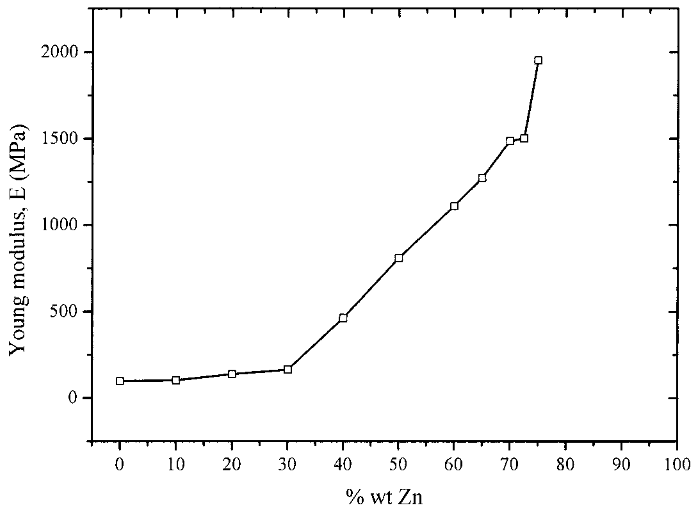

Figure 5. Variation of Young modulus of EVA-Zn system different percentage of Zn.

Prediction of behaviour

Due to the importance that fillers are acquiring in the preparation of composites, it is interesting to predict their behavior in order to optimize the formulations.[4-5]

There are many theories that can help us to establish the mechanical performance of the composites. Some of these theories are similar to those used to determine the performance of materials reinforced with different types of fibres. Many of these models consider different fractions of the material working in series or in parallel. Parallel fractions contribute to composite stiffnes while series fractions play an important rol in the fracture process since adhesion between phases must be considered.[6-7]

Percolation theory, which is of general use and applicable to all kind of multiphase systems, is one of the most interesting to study for prediction of the behavior of composites. When using this theory it is important to determine the type of net that better fits the behavior of the material (Figure 6) (square, triangular, hexagonal, cubic,...) since each one presents different percolation thresholds, necessary to predict the stiffness of the system.

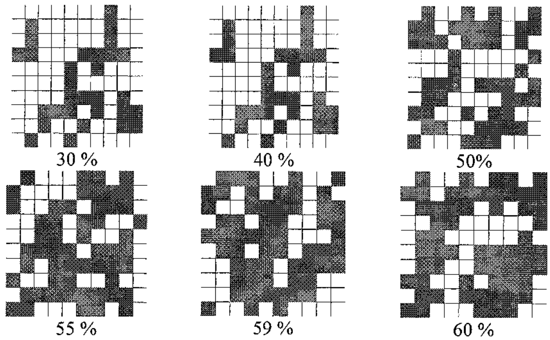

Figure 6. Percolation simulation for a square net (percolation threshold =0,59).

Percolation threshold based on mechanical properties is close to 0,16. This value can be obtained from the observation of the variation of the characteristics of the system. Electrical properties give similar results[8-9]. This value of threshold corresponds to spherical 3D systems and can be used to predict the mechanical performance, specially the stiffness, by means of the following expression:

$$E = E_0 \bullet (v - v_c)^T$$

where E_0 is a constant of the system, v is the fraction in volume of the major component, v_c is the percolation threshold, and T is the universal critical exponent. The values of percolation that give good results are 0,16 and 1,9 for v_c and T respectively pertaining to discrete domains of spherical geometry.

Conclusions

Composites based on EVA matrix with metallic Zn powder as filler are quite interesting materials for its use as electrodes due to their excellent electrical properties as described in previous works[9].

At the same time, the mechanical benefits of the EVA-Zn system are interesting and can be predicted by means of the use of general theories such as percolation theory, most useful to establish thresholds which determine the behavior of the different components of the system.

Processing of these composites is quite easy, at low temperatures, due to the nature of both components. EVA must be subjected to a pulverization process to ensure good mixing with Zn powder.

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