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Prediction of properties value in thermoplastic mixtures applying box equivalent model incompatibility in recycled polymer blends

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The usefulness of a theoretical model of behavior of a mixture of materials is given by the ability to predict their properties from the elements that comprise it. In the equivalent box model (Equivalent Box Model, EBM), is evaluated in mixtures to mechanical behavior from analysis of contributions in parallel and in series of the different elements. We have used this model successfully in quantifying the strength properties of the materials from the individual properties, and its content has been modified to predict properties that are dependent not only on mechanical stress but also on the thermal behavior of materials. These properties can be studied by the heat deflection temperature or the Vicat temperature of plastic matrices, where temperature determined that yields a material subjected to a standard strain. In this paper, we propose extending the EBM model to analyze thermal properties. It is suggested that the contribution to the Vicat softening temperature for a given volume fraction of one of the linear combinations is a function dependent only on the thermal properties and on the other hand, a contribution to consider the compatibility between materials and in dependence of the parameter "A", which is determined within the EBM model from the variation of mechanical properties. Therefore, determining the Vicat softening temperature in a mixture of materials for a given volume fraction, depends on the temperature difference of the components of the lower factor temperatures and miscibility of the materials.

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1. Introduction

The incompatibility is the main impediment to the recovery of plastics. The plastics blends can be incompatible because of processing conditions matters and also due to plastics' chemical nature. In this sense, thermosets plastics, characterized by not being meltable, could be harmful to the recovery of other materials. On the other hand, several thermoplastics present different range of melting and/or transformation, resulting in the impossibility to be recovered all together [1]. Furthermore, according to their chemical nature, polymers could be more or less miscible with each other. In general, semi-crystalline and amorphous materials show incompatibility in the final blend [2]. These incompatibilities generate a lamination in the material (shown as skins in Fig. 1). Furthermore, the incompatibility depends on the percentage of impurities present and on their ability to enhance the polymer chain mobility [3]. The incompatibility is highly dependent on the percentage of contamination present too.

If the impurity is present in less than 3% and causes problems either in the final product or also during processing, these are considered incompatible materials. If this limit increases to 7-10%, materials are considered partially compatible. When it is possible blend up to 20-25% are considered compatible materials. Mixtures where the majority component does not reach the 70% are not recommended, even if the materials are completely miscible. The properties of these mixtures are dependent on the percentage of each plastic in the final blend, and taking into account that is difficult to control the exact composition during the recycling, is better not performing them.

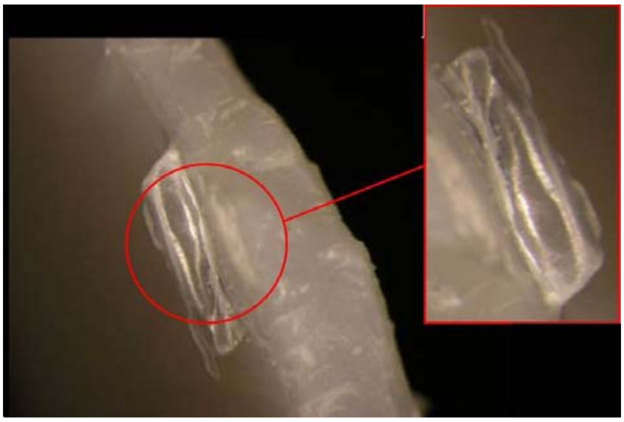

Fig 1. The lamination effect in PET blends with 15% PE.

Moreover, the compatibility between materials is not symmetrical. A polyamide can be recycled with some impurities of polyethylene (up to 5%). However, polyethylene with impurities of polyamide cannot be recycled because of the polyamide obstructs the transformation process due their high melting point.

1.1 Miscibility: Structural factor (entropic factor)

The miscibility of the blend components highly determines their final properties. The state of miscibility in a blend is governed by the Gibbs free energy of mixing, ΔG_m [4]. The thermodynamics of polymer solutions and mixtures was analyzed independently by Flory and Huggins, who proposed a regular solution model, based on the polymers' behavior in a network, where the free energy of mixing changes per unit volume (Δg_{mix}) at a given temperature is given by the following model:

$$\Delta g_{mix}/kT = \frac{\phi_A}{N_A v_A} Ln(\phi_A) + \frac{\phi_B}{N_B v_B} Ln(\phi_B) + \frac{\phi_A \phi_B}{v} \chi^{FH} \quad (1)$$

Where ϕ_i is the volume fraction and N_i the number of segments of volume v_i for molecules i, v is the average segmental volume $(v_A\ v_B)^{1/2}$ and χ^{FH} is the so-called Flory-Huggins interaction parameter. This equation is called "molecular basis", and it could be derived in the following expression which is based on the molecular weight (Mi) and in the density of the different components. The expression could be decompose in a factor (F(1)) which depends on polymer molecular weight [5].

$$\Delta g_{mix}/RT = \frac{\rho_A \phi_A}{M_A} Ln(\phi_A) + \frac{\rho_B \phi_B}{M_B} Ln(\phi_B) + \chi^{FH} \phi_A \phi_B$$

$$\Delta g_{mix}/RT = F(1) + F(2) \quad (2)$$

$$F(1) = \frac{\rho_A \phi_A}{M_A} Ln(\phi_A) + \frac{\rho_B \phi_B}{M_B} Ln(\phi_B)$$

$$F(2) = \chi^{FH} \phi_A \phi_B \quad (3)$$

The first factor is always negative, and it represents a factor that contributes to the mix. This factor depends on the composition and size of the polymer. Two extreme cases can be considered. First we consider that both polymers have a similar molecular weight and density close to the unity.

$$M_A \approx M_B$$

$$\rho_A \approx \rho_B \approx 1$$

This factor directly related to the relative size of the chains:

$$F(1) = (\Delta G_{mix})_{M1=M2}/RT = \frac{\phi_A}{M_A} Ln(\phi_A) + \frac{1-\phi_A}{M_A} Ln(1-\phi_A)$$

$$F(1) = \frac{1}{M_A}\left[\phi_A Ln\left(\frac{\phi_A}{1-\phi_A}\right) + Ln(1-\phi_A)\right]$$

In the opposite case, polymers with density close to unity but with different molecular weight although the similar density. Therefore, one of the factors is much lower.

$$M_A <<< M_B$$

$$\rho_A \approx \rho_B \approx 1$$

$$F(1) = (\Delta G_{mix})_{MA<<MB}/RT = \frac{\phi_A}{M_A} Ln(\phi_A)$$

When these values are represented always will be negative. It presents one case of a maximum value in the center for mixing similar molecular weights, which is displaced in the case of one of the molecular weight, is predominant.

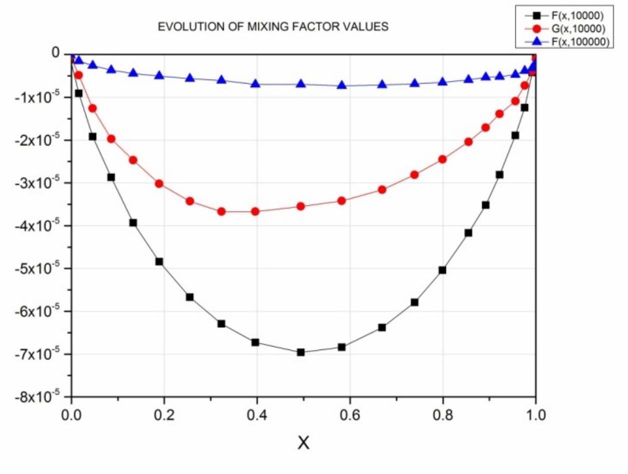

Fig 2. Evolution of mixing factor values dependent on the molecular weight with volumetric fraction under following conditions: A) Similar Mw, Mw = 10000, B) Similar Mw, Mw = 100000. C) Different Mw, minor Mw = 10000.

1.2 Miscibility: chemical compatibility factor (enthalpic factor)

The mixture is favored for the above values. However, in the practice the second factor that marks the characteristics of the mixtures at room temperature. Its shape is generated by the product of the volume fractions multiplied by the interaction parameter (χ^{FH}). Therefore, in the case of constant interaction factor, it represents a symmetric shape with a maximum value of 0.5. The value of this parameter could be determined experimentally and theoretically. Usually, the following approximation is assumed:

$$\chi^{FH} = \frac{\sqrt{v_A v_B}}{kT}(\delta_A - \delta_B)^2 = B(T)(\delta_A - \delta_B)^2$$

Where δ is the solubility parameter which can be determinate experimentally and calculated theoretically using molecular group contributions of the polymer on the basis of Small law. Since it is the most influential factor, the next goal is to understand the relationship with the mechanical properties.

1.3 Correlation with mechanical properties

The possibility to linking the interaction parameter or the difference in solubility between the components in the mixture with the mechanical properties of materials has been studied. This study was carried out by using the Equivalent Box Model, EBM, which considers that certain fractions of each material contribute to mechanical properties as in series work, while other fractions contribute in parallel [6,7]. The mechanical properties of composites could be estimated by using the EBM with some variations [6,8]. Furthermore, EBM allows to model long term behavior. However, there is a problem associated to the application of these models which consists in the difficulty of determining which fraction works in series and/or in parallel. Moreover, sometimes the obtained adjustment from the experimental data is not the optimum [6]. Since there is a higher number of parameters, more complex boxes models have been proposed, which reproduce the experimental data more faithfully. Kolarik and colleagues have successfully implemented a box model that considers two parameters [9,10,11]. The greatest difficulty in the application of this model is in the prediction of the tensile strength of the blends, due to the importance of the adhesion processes related to the miscibility. The model is useful not only for the prediction of the mechanical properties of polymeric material system; it also results practical for the study of any other property on the system composition [12]. This model proposes that in the mixture, a portion of each of the components behave mechanically as if in series, while the remaining portion behaves in parallel (Figure 3). Depending on the fractions of each component that act in series and in parallel, it is possible to predict the mechanical performance of the system. The uses of these relatively simple models could be useful to estimate the mechanical properties' values of heterogeneous isotropic materials blends, such as elastic modulus, tensile strength and yield strength [9].

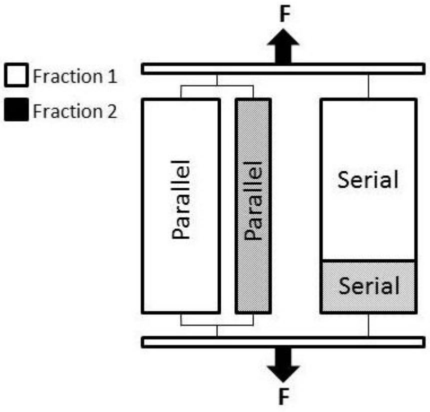

Fig 3. Basic scheme of Kolarik's Equivalent Basic Model with two parameters.

The parallel coupling fractions means that the elongation in each of the components is performed under iso-deformation and also the contribution of each of these parallel working fractions to the final value of the mechanical property is determined by the rule mixtures.

For parallel working fractions there is a continuity complete phase. Meanwhile, the series working fractions determine the minimum mechanical properties of the system, since the components are discontinuous in this coupling. As the strain is transmitted through the different sewn of the components, the interfacial adhesion phenomena are of greatest importance. This model is characterized by the use of two parameters, defined through four volume fractions, where only two are independent, and allows obtaining a better agreement between the values acquired with experimental values.

The notation used in the EBM of two parameters is the following:

$\mathbf{v_{np}}$ Volume fraction that works in parallel with component n
$\mathbf{v_{ns}}$ Volume fraction that works in series with component n
$\mathbf{v_s}$ Total volume fraction that works in series.
$\mathbf{v_p}$ Total volume fraction that works in parallel.

The relationships between variables are defined by:

$$v_n = v_{np} + v_{ns}$$

$$v_1 + v_2 = v_p + v_s = 1$$

The prediction of the tensile strength (σ), the model allows to estimate the boundaries between which are the tensile strength properties of the mixture. When the strength of the binding interaction tends to zero, the connection in series does not contribute to the resistance of the system, and this is defined by the parallel coupling, defining the lower limit of material resistance.

$$\sigma_{R(min)} = \sigma_1 \cdot v_{1p} + \sigma_2 \cdot v_{2p}$$

When the interaction between the phases of the mixture is high, it is possible to transmit efforts between the components in the union, so that the minimum value is added to the series coupling contribution. Assuming that the series breaks to achieve the lowest strength of the two components of the blend, we have the following expression for the upper limit:

$$\sigma_{R(min)} = \sigma_1 \cdot v_{1p} + \sigma_2 \cdot v_{2p} + \min(\sigma_1, \sigma_2) \cdot v_s$$

For intermediate situations a parameter *A* is proposed as indicative of the bonding interactions intensity in the union. Parameter *A* low values represent a low interaction intensity. Meanwhile, nearly to the unit values indicate a good quality adherence in the union.

$$\sigma_{R(\min)} = \sigma_1 \cdot v_{1p} + \sigma_2 \cdot v_{2p} + A \cdot \min(\sigma_1, \sigma_2) \cdot v_s$$

The main problem of this model is to obtain the system's parameters, v_{ij}, where *i* is the component and *j* is the way of work (in series or parallel). The percolation theory, have been widely used in a lot of applications, and it is useful to acquire these parameters [13]. Several blends of two materials were analyzed by using the EBM model and it was possible to obtain the *A* parameter value, which is between 1 and 0. The experimental values confirmed that at low *A* values the cohesion between system's materials is bad; being systems with values nearly to 1 which showed good cohesion and therefore, a good behavior in the mixture. The *A* parameter could be calculated by the following equation:

$$A = \frac{\left(\sigma_{R(\min)} - \sigma_1 V_{1p} - \sigma_2 V_{2p}\right)}{\left(\min(\sigma_1 \sigma_2) V_s\right)}$$

For a blend of 50% by volume, $V_{1p} = V_{2p} = 0'2$ y $V_s = 0'6$, therefore:

$$A = \frac{\left(\sigma_{R(50\%)} - 0'2 \cdot (\sigma_1 + \sigma_2)\right)}{\left(\min(\sigma_1 \sigma_2) 0'6\right)}$$

2. Results and discussion

In present work, several thermoplastics materials blends have been studied (Table 1). The mechanical properties were assayed across the whole composition range. Therefore it was possible to apply the EBM to obtain the parameter *A* (Table 1).

Table 1. Parameter A and differences in solubility parameter for thermoplastic blends

Materials	Parameter A	Δδ
PE/PP[14]	0.77	0.16
PP/PVC[15]	0.29	1.69
PP/PC[16]	0.21	5.29
PVC/ABS[17,18]	0.83	0.09
ABS/PC[6]	0.72	0.49
PE/PVC[16]	0.43	0.81

For these mixtures the difference between their solubility parameter could be calculated with the Small's law, which takes into account the contributions of each group. An empiric relation between both parameters is obtained when for the same material, or for two high compatible materials, Δδ = 0 and *A*=1. On the other hand, for high values of Δδ, the parameter *A* tends to zero. Empirically the shape descends asymptotically whit x axis, through 0.1 value. The simplest expression is:

$$A(\delta) = \frac{1}{1 + \Delta\delta}$$

This expression leads to good fittings to the experimental results, allowing us to use calculated values or known values of Δδ to calculate the parameter *A*. Ones we have the parameter *A*, it permits the determination of mechanical properties and therefore the prediction of their behavior during mechanical efforts.

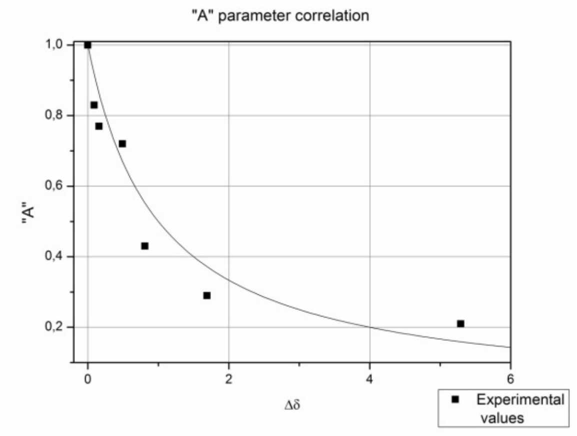

Fig 4. Correlation between parameter "A" and the solubility parameter differences in of blend components. Solid line: theoretical curve.

3. Conclusions

The Flory-Huggins theory is one of the first theories that attempts to explain and also predicts the polymer blends behavior. It is based on the statistical thermodynamic and indicates that the behavior of a mixture is a factor which mainly depends on the length of the chains, and another factor that depends on the chemical nature of the polymer. Although the Flory-Huggins theory describes the behavior in solution, and also shows some problems, it has been used as a basis for describing the behavior of plastics blends made by extrusion process. It qualitatively responses to the blend expected behavior. It also allows us to propose semi empirical models, which relate the chemical compatibility obtained theoretically (from the solubility parameter) with the mechanical behavior of the equivalent box model (EBM).

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