

## A NEW METHOD TO CALCULATE THE ACTIVATION ENERGY FOR THE GLASS TRANSITION OF AN ELASTOMER IN HDPE/PP BLENDS

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**Abstract-** Blends of two highly crystalline polymers containing an elastomer were prepared to study the glass transition of the confined elastomer. Polymers chosen are high density polyethylene (HDPE), polypropylene (PP), and two elastomers of different nature: natural rubber (NR) and ethylene-propylene-diene (EPDM). Dynamic mechanical thermal technique was used to analyze the storage modulus of blends with elastomer content from 0 to 30% by weight, but equal relative amounts of HDPE and PP, and blends with 10 % of elastomer, but varied content of polyolefins. The differentiation method of the Arrhenius method in the kinetic analysis, assuming an  $n$ -order relaxation mechanism, allowed detecting the percolation threshold of NR about 15 % rubber content where  $n=2.5$ , while the  $n$  value for pure NR was 1.5 and for other rubber contents was between 1 and 1.5. Results indicate that both temperature ( $T_g$ ) and activation energy ( $E$ ) for glass transition are dependent on type of polymers in the blend and blend composition.  $T_g$  and  $E$  values of unblended elastomer are higher than in blends; this is associated with the elastomer confinement and blend morphology. These results provide guidelines to calculate  $T_g$  and  $E$  for glass transition of a confined polymer.

### Introduction

The activation energy for the glass transition is interpreted as the height of the energy barrier which has to be overcome by the motion of the chain segments to occur the transition. This concept is basically correct but oversimplified since the probability of transition is a complex function of internal energy and geometrical configuration<sup>1</sup>. Also, the molecular motion in the amorphous region of a semicrystalline polymer is suggested to differ from those in a completely amorphous polymer because of the restriction by the crystalline components or the different crystal/amorphous structures<sup>2</sup>.

Determination of kinetic parameters associated with glass transition of a complete or partially confined elastomer in a blend is the focus of the current investigation. We propose a new method to determine the glass transition temperature, the activation energy, and the relaxation mechanism of pure elastomer and when the elastomer is incorporated in a blend of HDPE and PP. The elastomers (NR and EPDM) have individually different behavior and when incorporated to this blend<sup>3</sup>.

### Experimental Section

**Materials.** The characteristic parameters of the commercial polymers here used are as follows. HDPE (LR7340-00) produced by Quantum Chemical with molecular weight  $M_w=1.75 \times 10^5$ , and polydispersity  $M_w/M_n=14.4$ ; the measured density is  $0.945 \text{ g/cm}^3$ . PP extrusion grade produced by Pemex with molecular weight  $M_w=1.01 \times 10^5$ , and  $M_w/M_n=3.49$ . Natural rubber Hevea SMR-5,  $M_w=1.05 \times 10^6$ , and  $M_w/M_n=5.9$ . EPDM Nordel 1040 from Dupont,  $M_w=4.72 \times 10^5$ , and  $M_w/M_n=4$ .

**Sample preparation.** The blends were prepared by mixing the polymers in a Brabender Banbury type apparatus at  $180^\circ\text{C}$  for 3 min at 15 rpm, and an additional time of 15 min at 30 rpm. The blends were laminated to a thickness of 0.7 mm by compression molding under a pressure of 3.5 MPa, at  $180^\circ\text{C}$  for 5 min. The plates were quenched in water at room temperature ( $25^\circ\text{C}$ ). Two sets of blends were prepared. In one set the elastomer content was varied from 0 up to 30 % by weight, but each blend contained equal relative amounts of PE and PP. The other set with 10 % of the elastomer, but the content of the polyolefins was varied. The first set was prepared to investigate

the effect of the complete or partial confinement on the glass transition. The main goal in the second set was the measurement of the glass transition parameters of the elastomer limited by the effect of the different morphologies imposed by the HDPE/PP blends.

*Dynamic Mechanical Measurements.* The viscoelastic properties of each elastomer and blends were measured using a Perkin Elmer DMA-7. Deformation was applied in the 3-point bending mode. The dynamic storage modulus,  $G'$ , was measured between -150 and 150 °C at a constant frequency of 1 Hz and a heating rate of 1 °C/min. The properties of each pure elastomer were measured using the parallel plates mode.

## Results y Discusion

*Kinetics of the elastomer glass transition.* It is known that the mechanical properties of a polymer undergo a drastic change while passing from the glassy state to the elastomeric state<sup>4-6</sup>. In terms of

$G'$  we define the normalized function over the glass transition region  $g(T) = \frac{G'(T) - G'_e}{G'_b - G'_e}$ , where

$G'_b$  and  $G'_e$  are the modulus evaluated at the beginning and the end of the relaxation, and  $G'(T)$  is the modulus at any temperature in the glass transition region. This is a decreasing function of temperature, and its values at the beginning and the end of the transition are 1 and 0, respectively. This function at any temperature represents the fraction of the number of the interactions that disappear during the transition. Since the glass transition is a thermally activated process, the kinetics of this phenomenon in terms of the function  $g$  may be represented as

$$\frac{dg}{dt} = -kg^n \quad (1)$$

where  $t$  is the time,  $n$  a constant which may be interpreted as a way to identify the relaxation mechanism, and  $k$  is the constant of the rate of the transition, which is dependent on temperature. We do not have arguments to *a priori* fix a value to the constant  $n$ , so that it must be evaluated from the experimental data. Since the Arrhenius model is valid for thermally activated processes, the

temperature dependence of  $k$  is expressed as  $k = A \exp\left(\frac{-E}{RT}\right)$  where  $R$  is the gas constant,  $T$  the temperature,  $E$  the activation energy, and  $A$  the preexponential factor. Both  $E$  and  $A$  are assumed to be temperature independent. The time derivative of  $g$  can be expressed in terms of the temperature derivative as  $\frac{dg}{dt} = \beta \frac{dg}{dT}$ , where  $\beta$  is the heating rate. Substituting the Arrhenius equation, equation (1) may be written as

$$\frac{dg}{dT} = -\frac{Ag^n}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (2)$$

The curve of the derivative exhibits a minimum. One fixed value of  $\frac{dg}{dT}$  has associated two different values of  $T$ ; but only one value of  $g$  is associated to one value of  $T$ . This means that equation (2) is satisfied by the two values of  $g$ , which correspond to only one value of its derivative. Thus, evaluating equation (2) at two temperatures,  $T_1$  and  $T_2$  with  $T_1 < T_2$ , for the same value of  $\frac{dg}{dT}$ , taking logarithms, can be written as:

$$-\ln\left(\frac{g_2}{g_1}\right) = \frac{E}{nR}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

This expression represents a straight line with slope  $\frac{E}{nR}$  when the left member is plotted against the factor in parenthesis of the right member, for different pairs of points of the curve  $g$  vs  $T$  where  $\frac{dg}{dT}$  two equal values has. Equation (2) can be rewritten as

$$-\frac{\beta}{g^n} \frac{dg}{dT} = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

We can make plots of  $\ln\left(-\frac{\beta}{g^n} \frac{dg}{dT}\right)$  versus  $\frac{1}{T}$ , in the temperature range of the glass transition, for different values of the parameter  $n$ , and choose that value of  $n$  for the best linear fitting. Then, using this value for  $n$ , the activation energy value for the glass transition of the polymer can be calculated from the value of the slope  $\frac{E}{nR}$ . Equations (3) and (4) allow the direct analysis of the experimental data obtained from the measurements of the evolution of the storage modulus and its temperature derivative recorded as a function of the temperature under a linear heating program. The values obtained for  $E$  and  $n$ , following this procedure, can be considered correct because no approximation is used for deriving these equations.

*Glass transition.* The spectra of the pure polyolefins exhibit the relaxation zones typical of PE and PP. The  $\alpha$ -relaxation zones of both polyolefins occur at very close temperatures, they overlap in the corresponding spectra of their blends. The unblended elastomer shows only one relaxation, which corresponds to the glass transition. The glass transition temperature occurs at 204.9 K and 211 K for NR and EPDM. This relaxation for each elastomer occurs in a temperature interval where the polyolefins do not exhibit relaxations. This fact offers the advantage to study the glass transition of the elastomer even when is incorporated to the blend.

The determination of the temperature limits for the elastomer glass transition was straightforward because the  $G'$  curve for the blend without rubber presented a straight line in a broad temperature range, which included the interval where the rubber transition occurred. The  $G'$  curves for blends containing rubber have this same behavior outside the glass transition region. This allowed extrapolating the curve with straight lines of the same slope on both sides of the transition. The limits of the temperature interval of the glass transition of the elastomer in the blends were shifted toward lower temperatures with the increase of rubber content, decreasing the glass temperature. The beginning and end of the transition are not far from equal distances from  $T_g$  for elastomers in all blends. A somewhat broadened glass transition is observed for blend 45/45/10 with EPDM. This effect may be caused by the inability of the macromolecules to fully mix<sup>7</sup>.

The incorporation of 5 % of elastomer to the blend causes a change in the elastomer  $T_g$  value respect to that of the unblended case. The  $T_g$  value for unblended NR decreases from 205 K to 201 K. In contrast, the  $T_g$  value for unblended EPDM increases from 211 to 214 K. Although it is known that the thermal environment of a sample inside a DMA furnace may vary considerably depending on the mode used<sup>8</sup>, it would be expected that the temperature differences to have the same sign. This shift in  $T_g$  values may be ascribed to the more affinity of NR to HDPE, and the more affinity of EPDM to PP. The different interactions between each elastomer and the polyolefins are the responsible for such a behavior.

The  $T_g$  values in the range 5-15 % of rubber content are constant for blends with NR but gradually decrease for those with EPDM. However, between 15 and 20 % both rubbers show changes. The  $T_g$  values for NR show an abrupt drop while for EPDM the change is small. Later, from 20 % on, both rubbers have practically constant  $T_g$  values. For the NR case, the percolation threshold occurs at 15-20 % of rubber content<sup>9</sup>. Therefore, in the range up to 15 % the NR particles are completely confined within the HDPE/PP matrix, but after 15 % the confinement is partial. The finite specimen size, resulting from confinement within small spaces, affects  $T_g$  significantly<sup>6,10</sup>. The glass transition temperature for confined elastomers in the second set of blends, where the rubber content is of 10 %, for NR has two values close to each other. However, for EPDM the  $T_g$  is more sensitive to the morphology of the blend HDPE/PP and to the type of polymeric matrix (PP or HDPE).

*Activation energy.* The  $E$  value for pure NR is found to be of 28 kcal/mol, while the corresponding experimental value for EPDM is of 26 kcal/mole. The experimental activation energy value for the glass transition of the unblended natural rubber (Hevea) falls between 13 and 30 kcal/mole while a reported theoretical value is of 22.0 kcal/mol<sup>11</sup>. The activation energy for NR glass transition determined here compares very favorably with the range cited. This parameter exhibits a marked decrease at the composition of about 20 % of NR, while for EPDM shows a decrement at 15 %.

The activation energy for blends containing fixed amount of NR has only two different values. It seems that the activation energy of natural rubber in a blend is mainly determined by which component is the continuous phase. In contrast, the  $E$  values for EPDM increase with PE content. The discrete domains of each rubber interact differently with each polyolefin as is observed in blends with 0 and 90 % of HDPE content. The physical meaning of the activation energy and its identification with the mobility of the elastomer chains imply that the value of  $E$  deduced from blended and unblended elastomer should be different. We find that this is indeed the case.

The activation energy of the both blended rubbers for the two sets of blends always remains lower than that of the corresponding pure rubber. Reported values for the Arrhenius glass transition parameters are quite varied, depending on the kind and purity of the materials, heating procedure, and method of calculation<sup>12</sup>. In our case these factors are maintained fixed. Therefore, the results here reported mean that the mobility of the chains, and therefore the activation energy, is affected mainly by the morphology of the polyolefin blends and the size of the rubber domains. It has been reported that the incorporation of these rubbers to these polyolefin blends causes a reduction of the viscosity<sup>3</sup>. As the glass transition is related to movements of the molecules, this fact means that smaller energy is required to get the mobility of the elastomer chains in these blends. Because percolation threshold occurs around 15-20 % of natural rubber content, it is expected that NR molecules increase their mobility at this rubber content. The connection of the rubber particles is a consequence of the increase in rubber content. This could cause the high decrease in the activation energy for the glass transition.

Ha and Kim<sup>13</sup> studied the morphology of blends of HDPE and PP. In the polyolefin-rich zones one component is continuous and the other one dispersed, but the blend with equal content of each material has interconnected phases. These authors also studied tensile properties of blends containing EPDM and found that small amount of EPDM acted as a compatibilizer to HDPE and PP. However, Lovering and Williams<sup>14</sup> found that the structure of the binary blend up to 50 % PP consists primarily of interpenetrating networks of the two polymers, while blends of 50 % PP or more are typified by islands of HDPE dispersed within the continuous matrix of PP. These different morphologies may be ascribed to the different relative molecular weights. In a previous study<sup>9</sup> was proposed that the morphology of our system was that observed by Ha and Kim because it is also in accordance with the rheology of these blends<sup>3</sup>.

*Relaxation mechanisms.* The exponent  $n$  of the function  $g$  was determined by fitting the plot described by equation (4). Its value for the unblended rubbers is of 1.5. For small NR content the

value of  $n$  is smaller than 1.5, but for the blend with 15 % of NR the value is 2.5, almost double the value for pure NR. This would mean that at this composition there are two mechanisms: the glass transition and the percolation threshold. However, the values of  $n$  for the second set of blends (containing 10 % of either rubber) fall between 0.9 and 1.4. This result is expected because only the glass transition mechanism is present.

The parameter  $n$  for the EPDM rubber has a value of 1.7 at the composition of 10 % but has an abrupt drop at 15 %. Although at this time we are not able to identify the exact origin of this composition variation of  $n$ , it may be caused by contribution of a second mechanism additionally to the activation energy. The changes of  $E$ ,  $n$ , and  $G'(T_g)$  with elastomer content are significant. This fact and the behavior for EPDM observed (about a content of 15 %) in the values of  $T_g$ ,  $E$ , and  $G'(T_g)$  permit to assume that this rubber also percolates.

## Conclusions

Dynamic mechanical analyzer was used to study the thermal behavior of the dynamic storage modulus and its temperature derivative for different polyolefins blends containing NR or EPDM rubbers. By defining a function containing the information of the storage modulus, which meaning is as a concentration of the interactions disappearing with the transition, allowed to propose a method to calculate the activation energy. Interpreting the curve of the temperature derivative of the normalized dynamic storage modulus in terms of the Arrhenius model permits to determine the activation energy associated to the glass transition.

It was shown that the glass transition temperature and the activation energy of an elastomer in a HDPE/PP blend vary considerably depending on the rubber content, the type of material of the other components in the blend, and the morphology of the matrix which in turn depends on the blend composition. The confined elastomer accelerates the glass transition region, as shown by the lowering of the glass transition temperature. This finding is consistent with the physical basis for activation energy and its identification with the motion of the elastomer chain.

Assuming an  $n$ -order mechanism (equation (1)) in the glass transition region, a better description of this phenomenon was achieved, and was possible to register the percolation threshold for natural rubber.

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