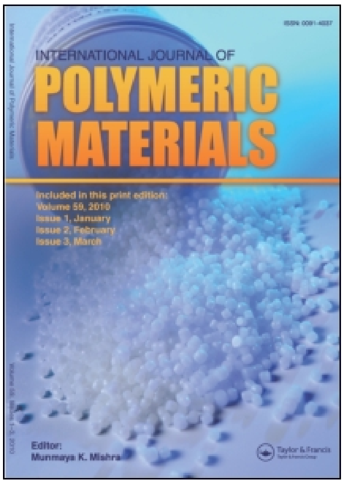

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Percolation Modeling of the Mechanical Behavior of the Composite Polybutadiene-Cellulose Diacetate

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Elastic modulli of the composite polybutadiene-cellulose diacetate (PBd-DAC) were obtained for different DAC concentrations within the range 0 to 30%. For low DAC concentrations, the mechanical modulus is well modeled by using the Kerner's model; however, for concentrations larger than 10%, the mechanical response of the material is higher than the predicted by this model. By introducing a percolation model that takes into account physical and/or chemical links between the domains of the discrete phase, it is possible to obtain a good agreement with the experimental data for DAC concentrations up to 30%.

KEY WORDS Percolation, composite, polybutadiene, cellulose diacetate.

INTRODUCTION

The word "composite" represents not only a whole family of materials with improved properties, but also an alternative way of thinking where synergetics is, in many cases, the key concept. From the structural standpoint, composite materials consist of two or more different materials that form regions that are large enough to be considered as continuous (usually with sizes between 10 and 1000 nm in the case of polymer-based composites), and which are strongly bounded to each other at their interfaces. There are many different kinds of composite materials; among them, one can mention: concrete, alloys, porous and cracked media, reinforced rubber, bone, etc.

In the recent past, much effort has been devoted to study how the mechanical properties of these two phase materials are affected by the structure and the volume

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fraction of the inclusions contained in them.[1-4] In particular, polymer-based composite materials draw a great deal of attention not only for their immediate technological applications,[5] but also for the enormous versatility in terms of compositions and micro-structures which these materials offer. Indeed, blending inmiscible polymers is now a common way to obtain novel and better properties which neither of the starting materials possesses.[6,7] More specifically, due to their interesting mechanical properties, rubbers are widely used in industry along with blends and composites in which rubbers contribute to a great extent.

Among all the possibilities for preparing rubber-based polymeric composites, the use of some biodegradable polymers (such as cellulose and its derivatives) for combining with elastomers,[8,9] opens a very interesting area of research in terms of their potential use as biomedical devices.[10]

Accordingly, the objective of this work is to model the mechanical behavior and its relation to the corresponding morphology of the discrete phase in a composite formed by Polybutadiene modified with Cellulose Diacetate. The morphology of the discrete phase and the adhesion between these phases, control to a large extent the mechanical properties of the composite material, and thus the morphology was a key parameter to study here and has been reported elsewhere.[9] Then, a percolation model is proposed in what follows, to account for the mechanical characteristics of the system.

BRIEF INTRODUCTION TO PERCOLATION

Let us assume that the system of interest consists of a collection of particles randomly distributed in space. When a rule is given to assign a link between a couple of particles, a percolation model is given; the links may, for example, depend on the positions of the particles.

A path between two arbitrary points A and B is given through a sequence of linked particles, beginning in A and ending in B. In this case, the points A and B are said to be connected. One important problem in percolation theory is to obtain the probability for a given pair of points to be connected. The probability that a site is occupied by a particle is related to the concentration of the solution, and the particles are considered linked if they, for example, overlap. The connectivity will depend on the relative position of the points and the concentration of particles. At some critical concentration of particles the connectivity becomes extremely large, comparable to the size of the system. Above this critical concentration, the system is in a percolated state.

The percolation models are important because they characterize a transition from a state of local connectivity to one in which the connections are extended indefinitely. This occurs at a concentration larger than the percolation threshold volume fraction v_c.

Usually, the percolation contribution to the mechanical response of a composite is introduced by using the percolation volume fraction Φ defined by:

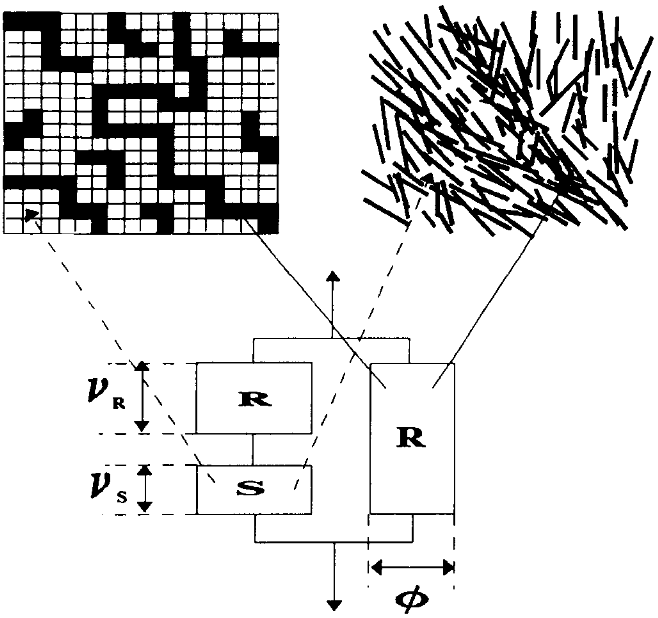

FIGURE 1 Schematical diagram of the percolation effect in a theoretical square lattice (left), the whiskers into the material for concentration above the percolation threshold (right) and the mechanical equivalent of a percolating system (bottom).

$$\Phi = \begin{cases} 0 & \text{for} \quad \nu_C < \nu_R \\ \nu_R\left(\dfrac{\nu_R - \nu_C}{1 - \nu_C}\right)^{\beta} & \text{for} \quad \nu_C \geq \nu_R \end{cases} \tag{1}$$

where ν_R is the volume fraction of the rigid phase (in this case the DAC) which is related to the soft phase volume fraction ν_S (in this case the rubber) by $\nu_S = 1 - \nu_R$.

Based on this, the dynamical modulus of the composite in a percolated state, can be obtained from a series-parallel model which takes into account the long distance connectivity; this is given by (see Figure 1):

$$\frac{G_C}{G_R} = \frac{(1 - \Phi^2 - \Phi\nu_S)G_S + \Phi\nu_S G_R}{(1 - \Phi - \nu_S)G_S + \nu_S G_r} \tag{2}$$

where G_C, G_R and G_S are the elastic moduli of the composite, the rigid phase and the soft phase respectively. The percolation contribution Φ depends on the excess of the volume fraction of the rigid phase respect to the percolation threshold concentration ν_C. For concentrations below ν_C, practically all the rigid portion is in the discrete phase, producing a modulus that is predicted by models like Kerner's model. Under these circumstances, the inclusions into the composite practically do not interact with each other.

For concentrations larger than ν_C, not all molecules of the rigid phase are in the discrete domains, but also forming links between them, in such a way that a percolation state is present in the composite. This connectivity among the domains increases substantially the mechanical modulus of the material.

The classical models (like Kerner's model) for spherical-like inclusions embedded in a matrix are not suitable in cases where non-linear behavior of the material is present or in the case where there exist interactions between the inclusions. As we said, when the volume fraction of the inclusion is larger than the percolation threshold volume fraction, links between the inclusions begin to appear, producing a high interaction among them. For this reason, a mechanical model that takes into account the percolation effects has to be used in order to explain the mechanical behavior of the composite.

In the model used here, the percolated volume fraction is only taken for the rigid phase. The value obtained for v_c was 9.8% that is in good agreement with the results reported for cellulose whiskers with an aspect ratio of around 8 (i.e., $L/d = 8$).[11]

SAMPLE PREPARATION

Chemical Functionallization of Poly-Butadiene and DAC

The composites were prepared by mixing commercial poly-butadiene (PBd) (Industrias Negromex S.A., México) and Cellulose Diacetate (DAC) (Aldrich Co.) which was previously functionallized as was described in previous publications.[8,9] The mixing was done mainly in solution for reasons that will be discussed later, and also with an extruder to determine the influence of these parameters on micro-structure.

PBd and DAC are practically immiscibles; then, these polymers are appropriated to produce a composite, because this feature helps to obtain a two-phase material where one of these is a mezomorphic domain; the size of this depends on the required properties.

However, one of the most important aspects of the composite, if a good performance wants to be obtained, is the adhesion among these phases. In order to have a good adhesion between phases, one of the materials was chemically functionallized. With this procedure it is possible to modify, and somehow to control the adhesion and the segregation between both kinds of polymers.

The DAC functionallization[9,12,13] was carried out by sterifying its primary hydroxile by using methactyloyl chloride (Aldrich Co.) and 1,3-dinitrobenzene (Aldrich Co.) as inhibitor. The adhesion is carry out through a chemical link between the double bond of the functionallized DAC and the double bond of the PBd by using AIBN as initiator.

On the other hand, the functionallization of PBd[14] was done by an addition reaction between the PBd and the anhydride maleic. The chemical link in the mixture was achieved by a sterification of the primary hydroxyl of DAC with the double bond of the substituting group (anhydride maleic) linked to PBd; in this case the catalyst employed was *p*-toluene sulfonic acid.

Scanning Electron Microscopy

The sample was prepared by including the composite in a commercial resin for microtomy Polybed 812 (epon) to provide the sample the required mechanical prop-

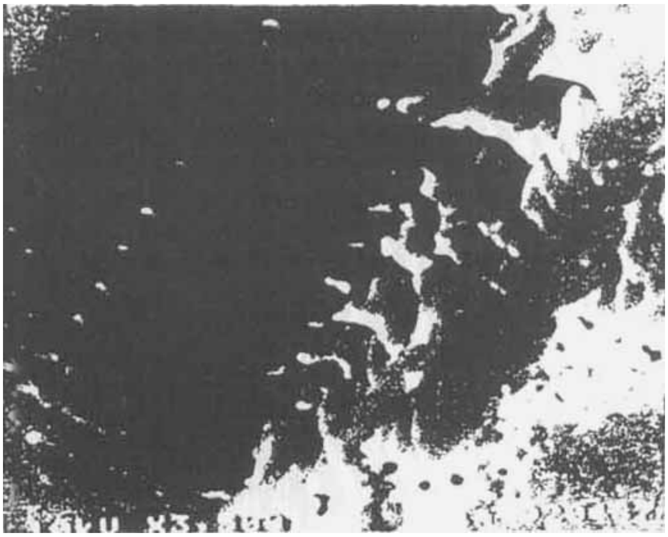

FIGURE 2 SEM micrograph of the composite with a composition of 10% DAC and 90 PBdf. It is possible to observe the discrete phase of the material.

erties in order to obtain very fine cuts (of the order of 5 to 7 μm). The sample was placed in a mold and covered with the resin epon. The system was heated to 60°C for 24 hours. After this, the system was ready for cutting in a microtome (Sorvan Porter Blum MT2). The slides were placed in a sample holder glued with silver paint and stained with osmium tetroxide vapors for 10 min. Once the slides were stained, they were coated with gold by sputtering. Samples prepared in this way were analyzed by Scanning Electron Microscopy (JEOL model 5200) in secondary electrons mode.

RESULTS AND DISCUSSION

When the mixing process is carried out in solution, all internal stresses are cancelled out, producing a material with a morphology in equilibrium. Most of the samples were mixed in solution in order to avoid all the parameters related to mechanical mixing; in this case, the chemical composition controls the morphology.

For this composite, the semi-rigid nature of DAC makes the mezomorphic domains have a locally anisotropic shape. In Figure 2 it is possible to observe the SEM micrograph of the composite prepared in solution, with a composition of 10% of DAC and 90% PBdf. Because the PBd was stained with osmium, the lighter part of the micrographs corresponds to the cellulose phase and the darker part to the rubber. As can be noticed, besides the presence of small and regular voids, due to both mixing conditions and shrinkage, the discrete phase is quite asymmetrical: locally the discrete phase is ordered in parallel strips (in Figure 2). In order to demonstrate that these features (bands) were due the domains of the cellulose and not the tracks produced by the cutting blade of the microtome, the sample was rotated 90° and the cuts were carried out again; the tracks, in this case, were perpendicular to the former,

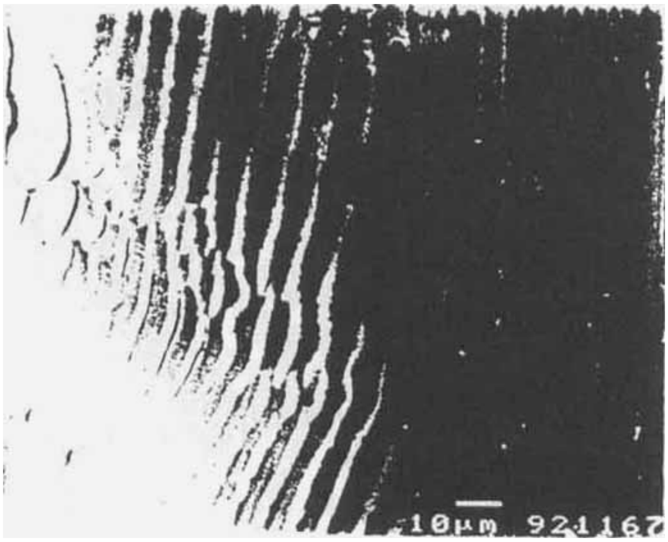

FIGURE 3 SEM micrograph of the composite 10% DACf and 90% PBd. In this case the sample was marked before cutting.

as is shown in Figure 3, which demonstrated that the observed morphologies truly correspond to the sample and are not artifacts of the preparation procedure. Even when there are local anisotropy in the material, macroscopically this material is completely isotropic, because the strips in the domains are oriented randomly.

Several composites were prepared at different chemical compositions with volume fractions up to 30%. For all these materials the same kind of structures were observed.

The Kerner's model is a self-consistent model, where the composite structure is modeled as a spherical dispersed phase with the same elastic properties as the constituent that appears at low concentration which is surrounded by a shell with the same elastic properties as the other phase, and finally they are in turn surrounded by another second shell with the elastic properties of the whole composite.

The mechanical properties of the composites were determined as a function of the chemical composition. In Figure 4 it is possible to see the Young modulus of the volume fraction of DAC.

From this plot, we see that there exist 2 different regimes: for volume fraction v_R of DAC lower than around 10%, the rate of change of the Young modulus as a function of the volume fraction has a value of 0.404 MPa, while for values of v_R higher than 10% the Young modulus increases faster respect to the former case, with a slope of 1.16 MPa. As was mentioned before, this effect is due to percolation: for volume fraction larger than v_C the interaction between discrete domains begins to be a long range interaction producing a connectivity between the whole material.

For the low volume fraction regime, the experimental data (discrete points in Figure 4) are well fitted by using the Kerner's model, however this model fails to fit the data corresponding to volume fractions higher than v_C.; these experimental data were fitted by using the equation (2) where Φ is given by equation (1); it is

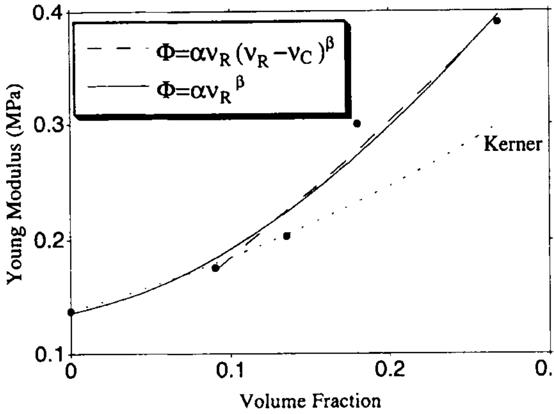

FIGURE 4 Plot of the Young modulus vs the volume fraction for the experimental data. It is possible to see the fitting obtained by using the Kerner's model, the percolating model and a model where $\Phi = \alpha v_R^{\beta}$.

important to remark that this fitting is only valid for $v_R > v_C$. The percolating model fits well experimental data in this regime and $\Phi = (0.0004)v_R\,(v_R - 0.0977)^{0.375}$, then the exponent is: $\beta = 0.375$, while the percolation threshold volume fraction is v_C = 9.8%. Then by using the Kerner and the Percolation models, it is possible to predict the mechanical behavior of the material for concentration up to 30% by volume.

It is interesting to mention that the complete set of data, from 0 to 30% of DAC, can also be well fitted by using the analytical expression (see Figure 4):

$$\Phi = \alpha v_R^{\beta'} \tag{3}$$

which is simpler that the expression in equation (1). In this case the fitting produces: $\Phi = (0.000535)v_R^{1.741}$, then the exponent has the value 1.741. This analytical expression for Φ is suitable for the prediction of the experimental data when, as in this case, there is not a sharp transition between a non-percolated and a percolated states.

The reason why this analytical expression fits the experimental data in the whole range of compositions, follows from the equation (1). From this equation, it is possible to see the two limiting cases: a) for $v_R << v_C$ we have $\Phi \propto v_R$ which corresponds to $\beta' = 1$; b) for $v_R >> v_C$ we have $\Phi = \alpha v_R^{\beta'+1}$ which corresponds to $\beta' = \beta + 1 = 1.741$. Then, in both cases Φ follows a power law with v_R. By using equation (1) the exponent is 0.375, while for equation (3) the combination of the two regimes give an effective exponent of 0.741.

Even when equation (3) is a phenomenological equation, it has the advantage that it has a simple analytical shape and it fits well the complete set of experimental data up to high concentration; additionally, this expression has only two parameters to adjust.

CONCLUSION

A composite material was prepared by mixing PBd and DAC, the latter one in a small proportion. Composites prepared at different volume fractions were used to observe the effect of the chemical compositions on the mechanical response of the material. The elastic modulus of the materials suffers a remarkable increment when the volume fraction exceeds the percolating threshold. Consequently, the experimental data was fitted by using the Kerner's model for volume fraction lower than the threshold concentration, and by using the percolating model for volume fraction higher than the threshold concentration. With these two models the complete set of data was well fitted. However, the use of $\Phi = \alpha v_R^\beta$ allows to fit the complete set of experimental data; this has the advantage that only two parameters are used to fit the data.

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