

# A Rheological and Morphological Study of Treated PVC

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**ABSTRACT:** This article reports a rheological and morphological study of poly(vinyl chloride) (PVC) that was subjected to a treatment capable of decreasing the simultaneous mass transfers occurring between liquid food (or simulant) and PVC packaging. The storage modulus ( $G'$ ), loss modulus ( $G''$ ), and the loss angle ( $\tan \delta$ ), have been used to determine the glass transition temperature using a Rheometric Scientific Dynamic Analyzer. Young's modulus was measured on a dynamometer, and a morphological charac-

terization was carried out with an optical microscope. The obtained results show that treated PVC behaves like a composite material, which is in agreement with a previously established model. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3497–3502, 2003

**Key words:** diffusion; poly(vinyl chloride) (PVC); additives; barrier; rheology

## INTRODUCTION

The preparation of useful articles from any polymeric material is virtually impossible without auxiliary additives. These include stabilizers, oxidation inhibitors, defoamers, pigments, UV absorbers, plasticizers, and other components. It is rare to use a simple polymer alone. Additives are necessary to improve the processability and/or the performance properties of the final plastic material. Unfortunately, these chemical components may migrate out of the material because they are not strongly bonded to the macromolecular skeleton. In addition, liquid is able to enter the polymer. This is a major inconvenience when the plastic is used as a food packaging material. The issue it attracts considerable legislation stipulating that the packaging material must not alter the quality of the food.<sup>1–4</sup>

This is the case for poly(vinyl chloride) (PVC), the second packaging material invented and the first polymer used in the French medical packaging market (as blood bags, pharmaceutical packaging).<sup>5</sup> In order to make PVC acceptable for these kinds of applications, it is necessary to try to prevent additive migration.

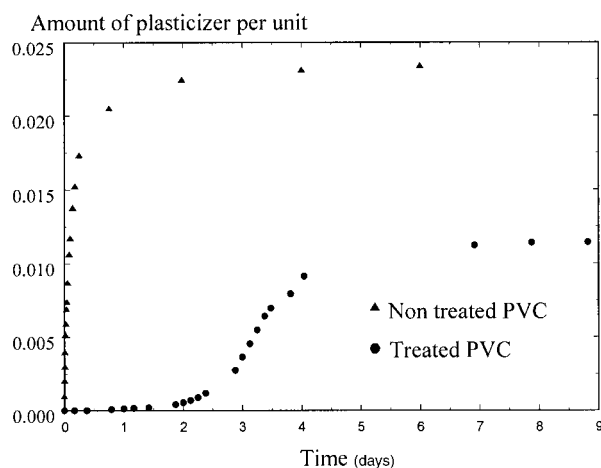
Previous studies<sup>6,7</sup> by our research group have reported a treatment capable of decreasing the pollution of food from PVC packaging. The treatment consists of the immersion of PVC in a liquid (*n*-heptane) for a

short time and then drying it at high temperature. In this way, the transfer of plasticizer is considerably reduced. The following kinetic analysis of the treatment shows not only a slowing down of the transfer but also a decrease in the amount of pollution. The effectiveness of this treatment depends on a number of parameters. Figure 1 shows that the plasticizer migration is delayed, slackened and reduced in the treated PVC. A similar phenomenon occurs with the transfer of liquid.

From the experimental data, a model has been developed to quantify and simulate the diffusion of both plasticizer and food simulants.<sup>8,9</sup> Of course, the treatment of PVC leads to some modification of the material. After the treatment, PVC is considered to behave as a 'sandwich material,' a strongly plasticized PVC layer between two almost unplasticized membranes. Di-2-ethylhexylphthalate (DEHP) is removed during soaking, and liquid is evaporated during drying. Because there is no remaining plasticizer in the membrane, PVC is in a glassy state; therefore, the slowest step of the mass transfer is the crossing of this membrane. We have already shown that DEHP diffusion increases when the DEHP concentration increases according to an exponential law.<sup>6,10</sup> The mathematical model allows us to quantify the rate of migration in terms of diffusivity.<sup>8</sup> For example, in the case of the treatment used in the present study and described in this article, the diffusivity coefficient of DEHP is  $6.8 \times 10^{-8}$  cm<sup>2</sup>/s for untreated PVC and  $8.5 \times 10^{-10}$  cm<sup>2</sup>/s for treated PVC.

The goal of this article is to verify some assumptions made in establishing the previous model and to prove

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**Figure 1** Comparison of DEHP migration in (▲) untreated and (●) treated 35% plasticized PVC. Soaking time: 4 min (*n*-heptane, 30°C); drying time: 40 s (200°C).

that treated PVC is acceptable for food packaging. Also, this work is a contribution to a better understanding of the mechanism of molecular transport into polymeric matrices.

## EXPERIMENTAL

### Chemicals

PVC is a commercial resin (Sigma Aldrich, France) in the form of a white powder ( $M_n = 25900$  g/mol and  $M_w = 54\,800$  g/mol).

DEHP (Prolabo, France), Diethylhexyladipate (Sigma Aldrich), *n*-heptane and absolute methanol (Sigma Aldrich) were used as received.

### Chromatography

The analyses of plasticizers (DEHP) were performed by gas chromatography (Thermoquest Trace GC) after the addition of DOA as an internal standard. The amount of liquid entering the PVC was determined by weighing the PVC disk at the same time that the plasticizer was measured.

### Rheological measurements

The storage modulus ( $G'$ ), the loss modulus ( $G''$ ) and  $\tan \delta$  were used to determine glass transition temperatures using a Rheometric Scientific Dynamic Analyzer (RDA 700). Young's modulus was measured on a dynamometer DY22 ADAMEL LHOMARGY.

### Morphological characterization

Micrographs were taken with an optical microscope (LEICA) with a X200 zoom and a CCD camera.

### Preparation of plasticized PVC samples

PVC resin and plasticizer were mixed in methanol to obtain a homogeneous mixture. Then methanol was completely evaporated at 60°C. The compounds (of PVC and plasticizer) were pressed into sheets (1 mm thick) in a steel mold at 150°C under a pressure of 10 MPa. Discs of diameter 13 mm (for dynamic spectrometer) were cut from these PVC sheets.

### Preparation of treated PVC

First, the PVC samples were soaked in *n*-heptane for a short period of time (4 min). Then the samples were dried at 200°C for 40 s, according to the operative conditions previously described.<sup>9</sup>

### Test for determining rate of plasticizer and liquid transfer

Migration tests were performed in a closed flask (50 cm<sup>3</sup>) kept at  $30 \pm 0.1^\circ\text{C}$  containing one PVC disk immersed in 20 cm<sup>3</sup> of *n*-heptane and stirred at a controlled rate. At different intervals, DEHP was analyzed in the liquid, and the disk was weighed in order to determine the amount of liquid entering the PVC. Experiments were repeated three times, and each experiment exhibited similar results because of the good homogeneity of the plasticized PVC sheets.

## RESULTS AND DISCUSSION

Migration tests enable us to graph and estimate the time lag. Figure 1 shows the transfer of plasticizer in treated and untreated PVC. These data have been used to develop a model capable of describing the phenomena observed.

The model shows two different zones of plasticizer content: a central zone with the original percentage of plasticizer and two smaller symmetric zones on either side of it, containing a smaller fraction of plasticizer. These two zones create a barrier at the diffusion surface (so migration is limited). Even though measurement of the glass transition temperature is not usually used to characterize the morphology of a polymer, the observation of two distinct transitions, corresponding to the respective components of the 'composite material,' indicates the existence of a multiphase structure. Similar results have been observed many times on immiscible polymer blends.<sup>11,12</sup> If one considers the proposed model for the treated samples, two different zones with two different amounts of plasticizer should exhibit two distinct glass transition temperatures. The same considerations can be taken into account when discussing the Young's modulus of the treated material. Knowing the structure of the material, it is possible to evaluate the modulus of each part during a

tensile experiment. This procedure is described later in this article.

Because of the specific shape of the samples used for the treatment, the glass transition temperatures of treated and untreated PVC have been measured using dynamic mechanical rheology instead of the usual methods (e.g. DSC). Dynamic mechanical studies of polymers are conducted using oscillating methods. In this case, the applied stress,  $\tau$ , is given by the following equation:<sup>11</sup>

$$\tau = \tau_0 e^{i(\omega t + \delta)} \quad (1)$$

where  $\tau_0$  is the maximum applied stress,  $\omega$  is the frequency and  $\delta$  is the loss angle.

The resulting strain,  $\gamma$ , is

$$\gamma = \gamma_0 e^{i\omega t} \quad (2)$$

where  $\gamma_0$  is the maximum strain.

The modulus is given by eq. (3):

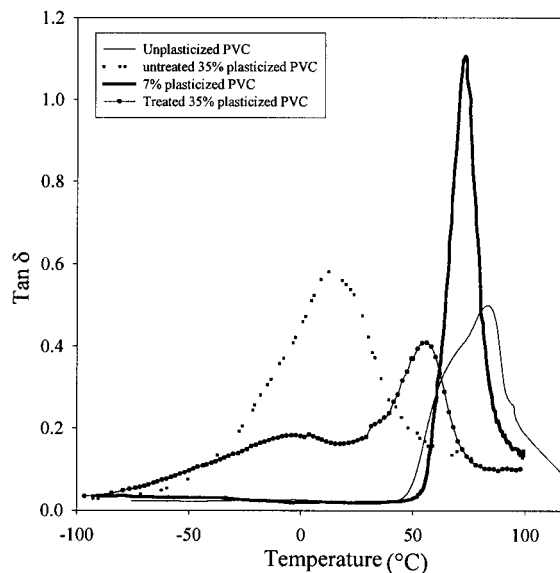
$$G^* = \frac{\tau}{\gamma} = G_0 e^{i\delta} = G_0 (\cos \delta + i \sin \delta) = G' + iG'' \quad (3)$$

$G'$  is the storage modulus,  $G''$  is the loss modulus and the loss factor,  $\tan \delta$ , is given by the following equation:

$$\tan \delta = \frac{G''}{G'} \quad (4)$$

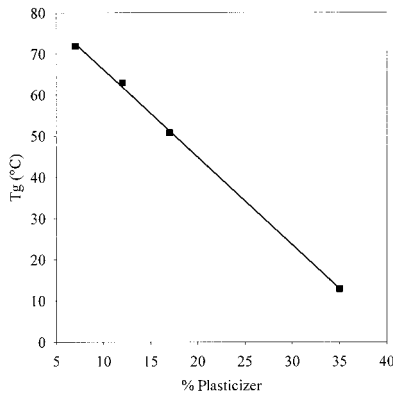
In this kind of experiment, glass transition temperature corresponds to an inflexion point on the  $G'$  curve, a maximum of  $\tan \delta$ .

The viscoelastic properties of untreated and treated PVC samples have been measured on a RDA700 between  $-100$  and  $100^\circ\text{C}$  at  $1^\circ\text{C}/\text{min}$  at a frequency of  $1 \text{ rad/s}$ . Figure 2 shows  $\tan \delta$  versus temperature for unplasticized pure PVC, 7% DEHP plasticized PVC, untreated 35% DEHP plasticized PVC and 35% DEHP plasticized PVC after treatment. Untreated materials were tested in order to prove that it is not possible, under the experimental conditions used in this study, to observe a  $\beta$ -relaxation at low temperatures, as shown by dielectrical spectroscopy.<sup>13,14</sup> Other experimental studies have already clearly shown that dynamic mechanical analysis is not capable of showing  $\beta$ -relaxation in the PVC samples.<sup>15,16</sup> As one can see, a single peak is found in the case of untreated materials, whereas two maxima of  $\tan \delta$ , corresponding to two different glass transition temperatures, are observed for the treated material. The lower one is at  $-2.5^\circ\text{C}$ , and the other is at  $56^\circ\text{C}$ . Knowing that  $\beta$ -relaxation cannot be observed here, one can conclude that the

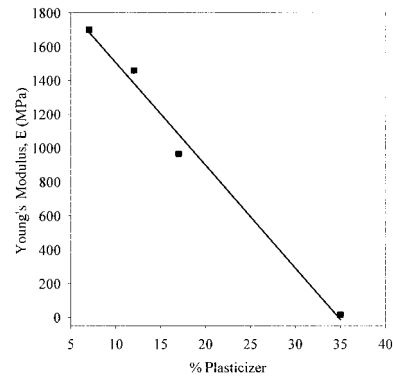


**Figure 2**  $\tan \delta$  versus temperature at  $1 \text{ rad/s}$  for (—) untreated pure PVC, (—) untreated 7% plasticized PVC, (...) untreated 35% plasticized PVC and (line with dot) treated 35% plasticized PVC.

first peak corresponds to the central zone (the 'core zone') of the material with 35% DEHP, and the second one corresponds to the 'barrier zone,' the zone that is less plasticized. Consequently, the treatment appears to be efficient and leads to the formation of a composite material, as proved by the two distinct glass transition temperatures. It has been noticed that the glass transition temperature of the first peak ( $-2.5^\circ\text{C}$ ) is lower than the glass transition temperature of the sample that is not treated ( $13^\circ\text{C}$ ). This is mainly due to the method of determining the glass transition by dynamic mechanical spectroscopy. In this technique, glass transition corresponds to the inflexion point of  $G'$ . For the present experimental data, the second transition interrupts the first before it is finished, leading to a shift of the inflexion point to the lower temperature. This leads to an underestimate the temperature of the first glass transition in the case of the composite material.<sup>17</sup> In order to determine the percentage of plasticizer in this 'barrier zone,' the evolution of the glass transition temperature against the percentage of DEHP for different untreated plasticized samples (7, 12, 17 and 35% DEHP) has been measured. As shown in Figure 3, the dependence of glass transition temperature on the amount of DEHP present is linear and allows us to approximate the percentage of plasticizer in the barrier. The results are in good agreement with Pena and coworkers,<sup>18</sup> even if the techniques used to determine glass transition temperature are not the same. Considering the glass transition temperature, the present treatment leads to the formation of membranes with about 15% DEHP. Note that this percentage is an average value. In fact, there is a plasticizer concentration gradient inside the barrier.<sup>6,10,19</sup>



**Figure 3** Evolution of glass transition temperature of PVC samples as a function of plasticizer (DEHP) content.

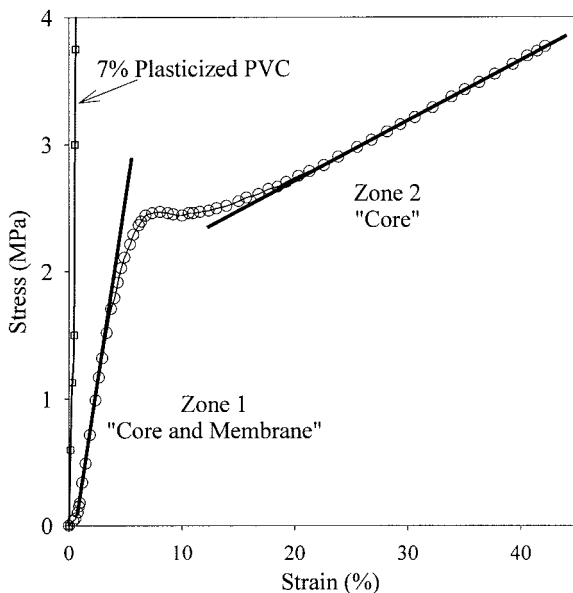


**Figure 5** Evolution of Young's modulus of PVC samples as a function of plasticizer (DEHP) content.

These results already validate the model of a 'sandwich' material made up of two distinct zones. To confirm these data, Young's moduli of the samples were determined. The tensile experiments, which were carried out on test specimens of 45 mm in length, 11 mm in width and 1 mm in thickness at room temperature and 100 mm/min, point out the two zones that compose the treated material, as shown in Figure 4. The first part of the curve corresponds to the modulus of the entire sample ('core' and membranes). The second part only corresponds to the core, because at this deformation the membranes have already broken up (because they are stiffer than the 'core zone'). In order to show that these two zones on the curve are characteristic of the treated material and not present in the untreated one, the curve of untreated 7% plasti-

cized PVC has been plotted on Figure 4. Note that under these conditions, this test doesn't show the presence of a  $\beta$ -relaxation.

Knowing the percentage of plasticizer inside the membrane, it becomes possible to determine its thickness. Therefore, the Young's moduli of untreated plasticized materials (7, 12, 17 and 35% DEHP) have been measured on an extensometer, and the results are shown in Figure 5. It becomes possible to calculate the modulus of the 15% DEHP membranes using the straight line plot of Figure 5. The value is about 1.2 GPa. Focusing on the first part of Figure 4 (corresponding to the 'core' and the membranes), it can be seen that, during the tensile test, the stress in the whole sample,  $\sigma_{c+m}$  and the stress in the membrane,  $\sigma_m$  are given by eqs. (5) and (6):



**Figure 4** Stress-strain curve for (O) treated 35% plasticized PVC and (□) untreated 7% plasticized PVC at room temperature.

$$\sigma_{c+m} = \frac{F}{S_{c+m}} = \varepsilon E_{c+m} \tag{5}$$

$$\sigma_m = \frac{F}{S_m} = \varepsilon E_m \tag{6}$$

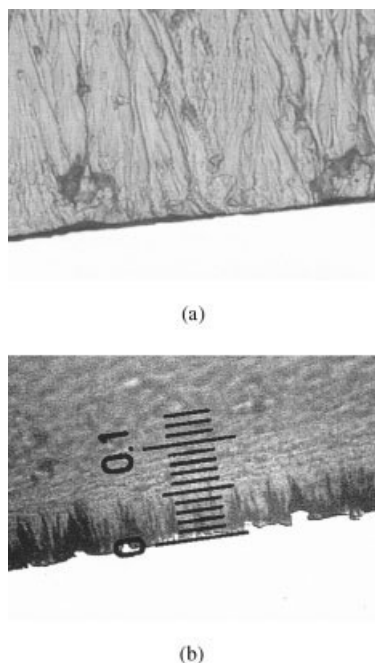
where  $F$  is the strength, and  $S_{c+m}$  and  $E_{c+m}$  are the section area and the Young's modulus of the whole test specimen, respectively;  $S_m$  and  $E_m$  are the section area and the Young's modulus of the membrane, respectively, and  $\varepsilon$  is the tensile strain.

Finally, because the strain and the strength are the same in the two zones of the treated sample, eq. (7) gives the ratio of the sections as a function of the moduli:

$$\frac{S_{c+m}}{S_m} = \frac{E_m}{E_{c+m}} \tag{7}$$

Due to the symmetry of the sample, we only consider the sample thickness instead of the section.

Remember that the membrane is not fully plasticized with 15% DEHP but is made of a concentration



**Figure 6** Micrographs of (a) the non treated and (b) the treated 35% plasticized PVC sample (cross section observation) during stretching.

gradient of DEHP. Besides, determination of the Young's modulus in the first part of the stress-strain curve is complex because of the composite morphology of the sample. These considerations lead to an underestimate of the membrane thickness. It is found to comprise about 5% of the complete treated PVC sample (i.e. 30  $\mu\text{m}$ ), and during the experiments concerning the migration study, the membrane thickness was estimated to be about 10% if the complete sample. The present technique, which gives another confirmation of the 'sandwich' model, must be more fully developed in order to give a precise estimation of the membrane thickness. A third technique has been used to obtain the thickness of the barrier.

Transparency of the PVC samples allows the use of optical microscopy as a powerful tool. In a first step, a simple observation of a treated sample does not show enough contrast to allow an estimation of the barrier. Specific equipment composed of two jaws and a single screw has been developed to observe the sample during stretching. Micrographs of untreated and treated samples (during stretching) are shown in Figure 6(a,b). As one can see, Figure 6(b) shows some crazes in the treated sample that are not visible in the untreated one [Fig. 6(a)]. These crazes, perpendicular to the stretching direction, are characteristic of the barrier. Indeed, the propagation of the crazes can only occur in the stiff zone with a high modulus. When the crazes encounter the core zone (plasticized), they stop

(so the untreated sample shows no crazes). Moreover, observation of the photographs allows the determination of the membrane thickness to be 40  $\mu\text{m}$ , which is in very good agreement with previous migration studies.

## CONCLUSIONS

The main point of this work is the strong confirmation of a previously proposed model to describe the morphology of PVC that has been soaked for 4 min in *n*-heptane (30°C) and dried for 40 s in an oven at 200°C. The model shows two different zones: a PVC strongly plasticized between two membranes containing less plasticizer. A combination of three different techniques has been used to characterize the treated material. Dynamic mechanical tests have pointed out two different glass transition temperatures characteristic of a composite material. Tensile experiments have exhibited two different behaviors, one corresponding to the core part of the sample and the other to the entire sample. An original analysis of the experimental data, using the Young's modulus of each part, has allowed a rough estimation of the membrane thickness. However, optical microscopy on PVC samples under stretching has given a precise measurement of this thickness and has strongly validated the proposed model. Later developments of this work will examine the mechanical properties of the treated PVC to confirm its utility in liquid packaging. It will be interesting to see if the experimental results are similar to those found with other plasticizers. Finally, this work shows that a specific treatment on polymers may bring new directions to research to decrease solvent and additive migration.

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