

Effect of Thermal Annealing on Plasticizer Migration in Poly(Vinyl chloride)/Dioctyl Phthalate System

C. D. PAPASPYRIDES, S. G. TINGAS

Laboratory of Polymer Technology, Department of Chemical Engineering, National Technical University of Athens, Zographou, Athens 157 80, Greece

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ABSTRACT: Plasticizer migration studies dealing with poly(vinyl chloride) (PVC) sheets and liquid surrounding media revealed two parallel phenomena, migration of plasticizer and liquid penetration, that take place simultaneously. The present work was focused on correlating the structural differences of the PVC material with the aforementioned processes. The plasticizer and the liquid medium used were dioctyl phthalate and isopropanol, respectively. Emphasis was placed on any rearrangement of the polymer morphology occurring when elevated test temperatures were employed for a relatively long period of time (crystallization). The result was that the PVC structure seemed to become more compact, forcing the liquid medium that had already penetrated to come out. Furthermore, these experiments showed that plasticizer migration and liquid penetration were related to the polymer structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1780–1786, 2001

Key words: migration; counterdiffusion (penetration); food simulants; plasticized poly(vinyl chloride)

INTRODUCTION

Plasticizer migration is one of the most serious problems in packaging technology, especially in very sensitive products such as foodstuffs and pharmaceuticals. The loss of plasticizer results in contamination of the medium in contact, as well as in deterioration of the mechanical properties of the plastic. As a consequence, a great number of migration studies are being carried out worldwide for the best possible comprehension of this phenomenon.

It is well perceived that additive migration depends on a multiplicity of factors such as the temperature, the molecular size of the migrant, the compatibility of the migrant with the polymer

and the surrounding medium, and the interaction between the polymer and the external phase.^{1–13} However, the polymer structure itself has been examined less. This is due to the fact that the polymer phase is often assumed to be inert during the whole migration process, ignoring any diffusion or temperature induced phenomena and also previous history aspects of the samples tested.¹³ Moreover, the issue becomes more important in the case where counterdiffusion occurs.

Counterdiffusion is a common phenomenon in solid–liquid migration, and it refers to the penetration of the liquid medium into the solid polymer. This takes place during the migration process and sometimes can be readily noticed by macroscopic observation, because the liquid penetration may cause a considerable alteration in the optical properties of the plastic. As an example, surrounding liquid media of low viscosity, such as white spirits and kerosene, tend to pene-

Correspondence to: Prof. C. Papaspyrides.

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trate very easily into poly(vinyl chloride) (PVC) sheets while media of higher viscosity (e.g., white oil or lubricating oil) seem to not practically penetrate at all.^{5-7,11,14-17}

This study investigated the migration of dioctyl phthalate (DOP) from PVC sheets into isopropanol and the simultaneous penetration of isopropanol into the polymer. PVC/DOP is a very common system and isopropanol is considered to be a promising food simulant in migration tests, which was proposed by the EEC. In particular, the effect of the thickness of the PVC sheet is examined in an attempt to have the best understanding of the response of the polymer structure against migration and counterdiffusion. The principal concept of choosing the thickness as the main parameter is that different thicknesses mean different degrees of structural order achieved during the specimen preparation stage by compression molding. In this stage, the settlement of polymer chains takes place while their mobility is gradually restricted by cooling. The degree of order attained strongly depends on the time offered to the polymer chains for settling into the new created structure. The thicker the polymer sheet is, the more awkward the heat transport, resulting in a longer settling period (i.e., in less amorphous material). As the sheet thickness decreases we expect the degree of structural order to be reduced because of the more rapid cooling (i.e., quenching conditions prevail). According to the above concept, three different thicknesses were selected: 1, 2, and 3 mm.

The temperature at which the migration tests were carried out was selected to be 60°C. The condition of elevated temperature is essential for two reasons: the acceleration of the diffusion processes involved so the equilibrium can be achieved faster than at room temperature; and the preservation of the rubbery state is indispensable to exclude any transition from the rubbery to the glassy state, which may occur because of plasticizer loss. The temperature of 60°C seemed satisfying, because the glass-transition temperature (T_g) of the plastic was not expected to exceed the above value, even though a large amount of plasticizer migrated.¹⁸

EXPERIMENTAL

Synthesis of ¹⁴C-Labeled DOP

Labeled phthalic anhydride (5.2 g, 7-¹⁴C, 1 mCi) was transferred to a reaction flask equipped with

a stirrer, thermometer, N₂ inlet tube, separating funnel, and side condenser. The reactor was then charged with 2-ethyl hexanol (211 g), phthalic anhydride (80 g), and concentrated sulfuric acid (1.5 mL). The 2-ethyl hexanol was in a 50% excess over the theoretical value, and toluene was also added to the reaction mixture (25%, v/v, based on the amount of 2-ethyl hexanol). The mixture was heated under stirring in an oil bath for 2 h while the temperature was gradually raised to 170°C. During this period, a slow stream of N₂ was passed and toluene was periodically added to the compensate for distilling. After 2 h at 170°C the mixture was cooled and diluted with 1 L of ether. The ether solution was washed with 10% aqueous sodium carbonate solution, then washed with water, and finally evaporated. The diester obtained was further purified by vacuum distillation. The yield was 89% on phthalic anhydride in labeled DOP. Products with lower radioactivities were obtained by dilution with pure unlabeled DOP.

Specimen Preparation

Suspension PVC was blended at 80°C with the calculated amounts of labeled plasticizer and Ca-Zn stabilizer. Three different levels of plasticizer concentration were examined (28, 40, and 49% w/w) while the stabilizer was always added at the level of 3 g/100 g of PVC resin. The dry blend was plasticized for 7 min in a Brabender Plasticorder at 170°C and 30 rpm. The plasticized mass was then compression molded to form sheets of about 1-, 2-, and 3-mm thickness. From these sheets 20 × 50 mm specimens were cut.

Immersion

Each specimen was immersed in 200 mL of liquid contained in a glass-stoppered 300-mL Erlenmeyer flask. All tests were performed in duplicate, and the flasks were kept in ovens fixed at 60°C (±1°C).

Radioactivity Measurements

The radioactivity (R_t , counts/mL/min) of the liquid medium represents the concentration of the plasticizer migrated at immersion time t . Dividing by the radioactivity of the plasticizer employed ($R_0 = 1044.8$ counts/mg/min) and reducing per liter of the liquid medium provided the DOP concentration data (Q_t , mg or g/L).

The radioactivity of the liquid medium at a given time after immersion was measured by

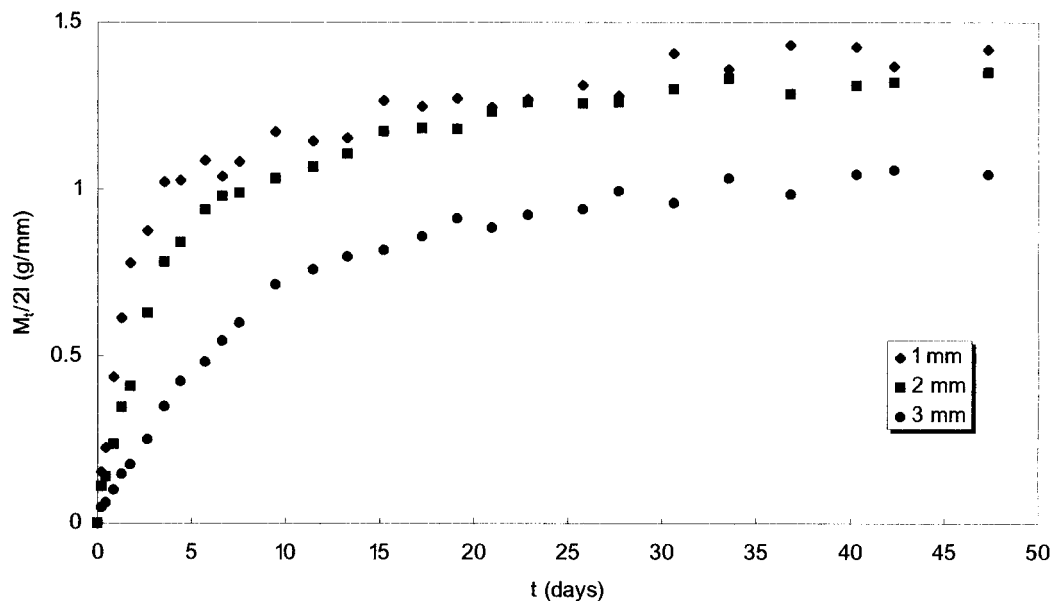


Figure 1 Plots of the plasticizer loss versus the contact time for different specimen thicknesses; 40-phr initial plasticizer concentration.

transferring 1.0 mL of the contents of the flasks to a glass measuring vial containing 10 mL of the scintillation solution [5 g of 2,5-diphenyloxazole (PPO) and 0.3 g of dimethyl-1,4-bis(5-phenyl-2-oxazolyl)benzene (dimethyl-POPOP) in 1 L of toluene] and shaking to ensure complete dissolution using a Packard 3003 Liquid Scintillation Spectrophotometer over a period of 10 min. Before sampling, the contents of the flasks were homogenized by swirling.

Weight Loss Measurements

To monitor weight changes, the specimens were removed from the liquid environment, wiped gently with a tissue, and immediately weighed.

Theoretical

In this study the following approximations of Fick's law were used:

$$M_t/M_\infty = 1 - (8/\pi^2)\exp(-D\pi^2t/4l^2) \quad (1)$$

$$M_t/M_\infty = 2(Dt/\pi l^2)^{1/2} \quad (2)$$

The theory concerning this approach is given elsewhere.¹⁹

RESULTS AND DISCUSSION

In Figure 1 typical migration curves are plotted for different specimen thicknesses. For the kinetic

study of the migration process, Fick's law approximation for short times was used, to which all our migration data fit sufficiently. Figure 2 plots the corresponding curves of M_t/M_∞ versus the $t^{1/2}/l$. The curves are initially linear and their gradient provides the diffusion coefficient. Table I presents these data versus the specimen thickness and initial plasticizer concentration. The figures and the table show that the initial trend for plasticizer migration is more intense as the specimen thickness decreases. The reason is that the thinner specimens have a less ordered structure because the polymer chains are not given enough time to settle after molding. Thus, the plasticizer molecules are able to diffuse more fluently through a much more amorphous structure.

As far as the counterdiffusion of the liquid medium is concerned,¹⁹ the diffusion curves are characterized by a maximum appearing at the early stages of the immersion runs (Fig. 3). In other words, the amount of isopropanol transferred into the polymer sheet (S_t) rises quickly to a maximum value and then decreases until equilibrium. This phenomenon was quite common in previous studies on plasticizer migration into liquid environments.^{5-7,16,17} Furthermore, it was proposed that counterdiffusion can be separated into two distinct processes comprising liquid transfer into and out of the PVC sheets. Thus, the maximum of the counterdiffusion curve is considered to be the equilibrium value for the sorption (or penetration) process, as well as the initial

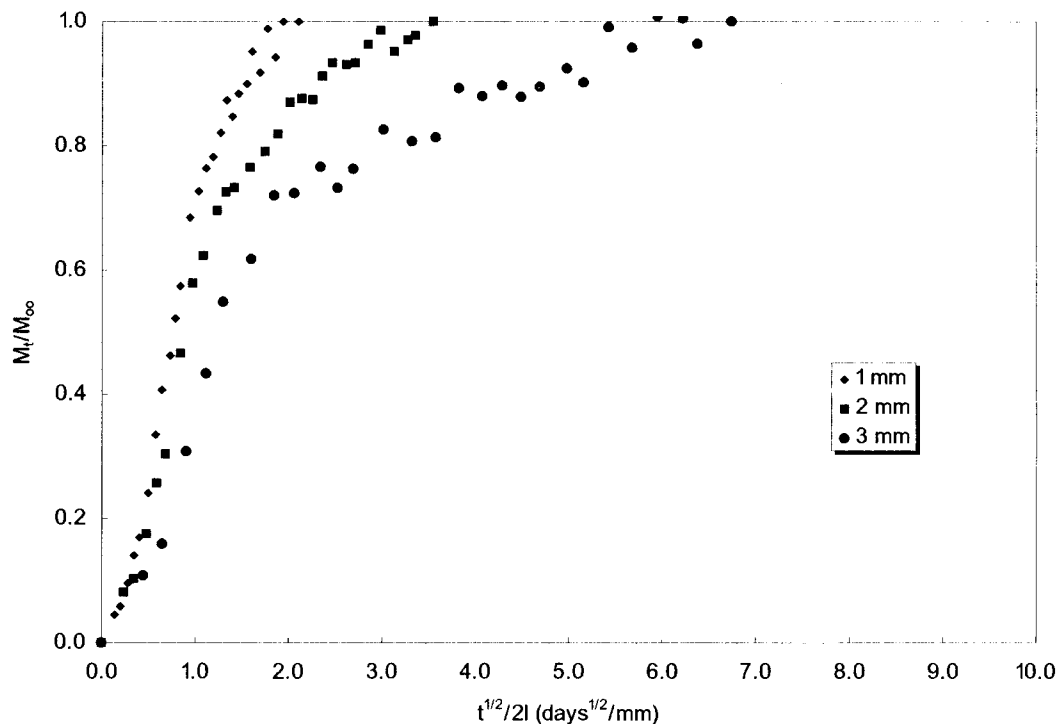


Figure 2 The relationship between M_t/M_∞ and $t^{1/2}/2l$ for different specimen thicknesses; 40-phr initial plasticizer concentration.

value of the desorption process.^{16,17} In the sorption data, the Fickian approximation for short times seems to be appropriate because the liquid penetration process occurs within a period of a few days. On the contrary, the desorption stage is certainly a long-term process that requires the long-term approximation of Fick's law for a satisfactory fitting.^{17,19} In Figure 4 typical sorption and desorption curves are plotted for isopropanol. Tables II and III present diffusion coefficients for the sorption and desorption stages versus the sheet thickness and initial plasticizer concentration.

Based on the aforementioned results, we can proceed to a discussion. Tables I and II show that

Table I Migration Process: Diffusion Coefficients of Plasticizer in Isopropanol (cm²/s)

Specimen Thickness (mm)	Initial Plasticizer Concentration (phr)		
	40	70	100
1	6.11×10^{-9}	1.67×10^{-8}	3.21×10^{-8}
2	4.32×10^{-9}	1.59×10^{-8}	2.78×10^{-8}
3	3.43×10^{-9}	1.28×10^{-8}	2.39×10^{-8}

the plasticizer and isopropanol diffuse more easily as the thickness of the PVC sheet decreases. As already mentioned, we assumed that as the sheet became thinner, the structural order attained decreased and therefore the plasticizer and liquid molecules were able to diffuse more easily. However, the long-term diffusion coefficients of the desorption stage (Table III) indicated that here the diffusion process was enhanced as the specimen thickness increased. This observation seemed to contradict the aforementioned assumption on the relationship between the thickness and structural order, and it should only be attributed to a significant alteration of the polymer structure during the immersion run. Also, the phenomenon of desorption itself could be considered as a paradox because the liquid medium diffused from a region of low concentration to another of 100% concentration.

The above behavior can be explained by an increase in the order of the polymer structure. We can call this phenomenon "crystallization" and, as far as polymer crystallinity is concerned, the term is used to describe the increase in lamellar crystal thickness when the material remains at elevated temperatures for a long period of time.²⁰⁻²⁵

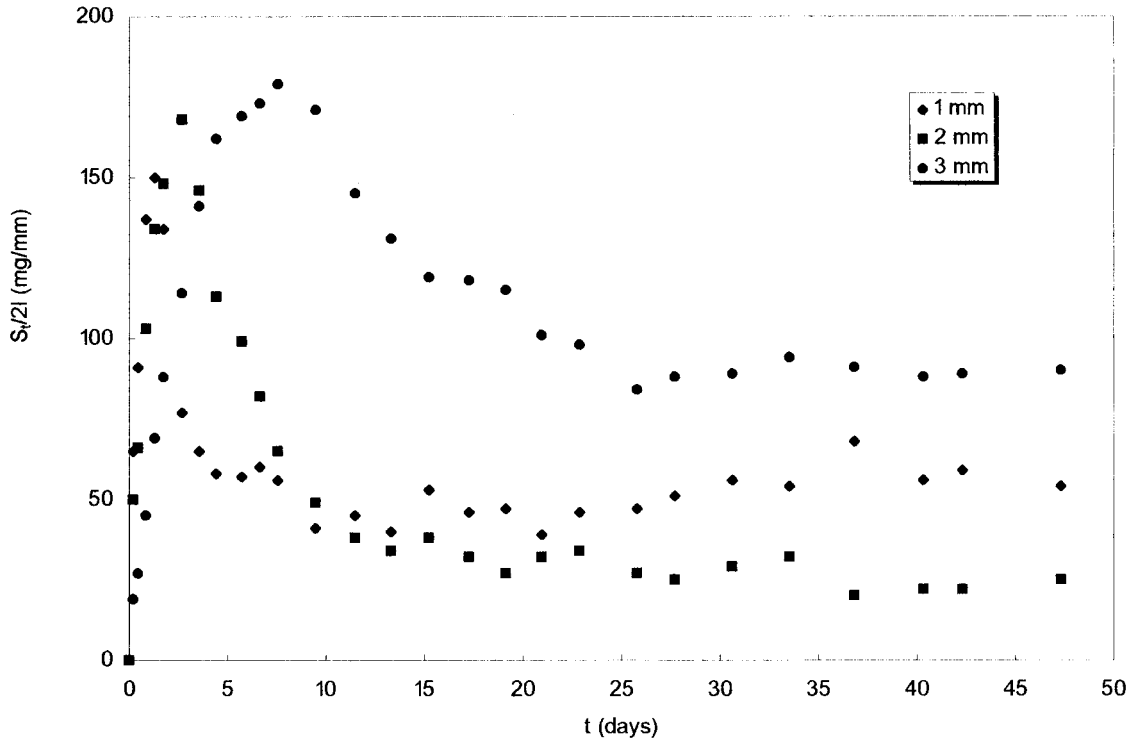


Figure 3 Plots of the isopropanol counterdiffusion for different specimen thicknesses; 40-phr initial plasticizer concentration.

The main consequence of this phenomenon is that the polymer structure becomes more compact as the chains are allowed to move one to another

in order to form a more organized structure. In other words, the structure is “squeezed” and the free volume decreases. As a result, part of the liquid medium that is entrapped in the polymer structure is forced to come out. Moreover, the increase in order that was achieved makes isopropanol diffusion much more difficult, and this is clearly confirmed by comparing the desorption diffusion coefficients with those of sorption, the former always being smaller (Tables II, III).

The comparison of the diffusion coefficients corresponding to the sorption and the desorption stage also suggests that a more organized structure is achieved by the initially more amorphous

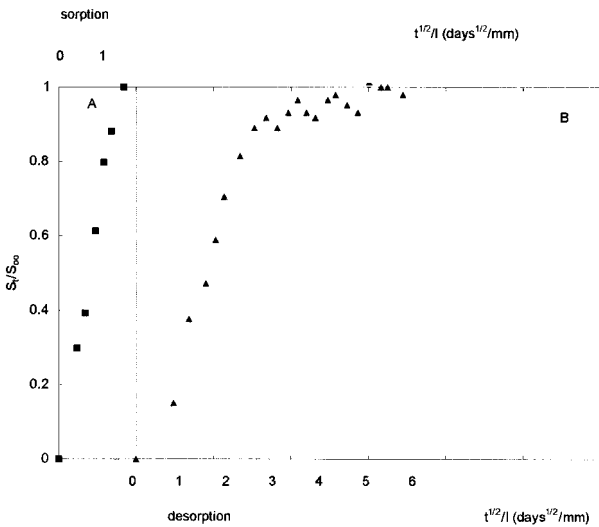


Figure 4 The Fickian correlation of counterdiffusion data for the (A) sorption and (B) desorption stages; 2-mm specimen thickness; 40-phr plasticizer concentration.

Table II Counterdiffusion Process: Diffusion Coefficients of Isopropanol Sorption (cm²/s)

Specimen Thickness (mm)	Initial Plasticizer Concentration (phr)		
	40	70	100
1	7.83×10^{-8}	9.94×10^{-6}	2.14×10^{-6}
2	3.64×10^{-8}	7.98×10^{-7}	1.07×10^{-6}
3	4.45×10^{-8}	4.19×10^{-7}	7.03×10^{-7}

Table III Counterdiffusion Process: Diffusion Coefficients of Isopropanol Desorption (cm²/s)

Specimen Thickness (mm)	Initial Plasticizer Concentration (phr)		
	40	70	100
1	5.44×10^{-9}	1.12×10^{-8}	1.63×10^{-8}
2	7.48×10^{-9}	1.62×10^{-8}	2.37×10^{-8}
3	1.88×10^{-8}	8.39×10^{-8}	2.11×10^{-7}

specimens (i.e., the thinner specimens). In other words, as one would expect, it seems that the more amorphous material is more susceptible to annealing.

An interesting observation that elucidates the above concept more comes from the comparison of the maximum quantities of the isopropanol sorbed into the polymer (Fig. 5). It seems that a larger amount of the surrounding medium penetrates as the PVC sheet becomes thicker whereas the analysis of the sorption diffusion coefficients (Table II) suggests exactly the opposite (i.e., the liquid medium has less tendency to penetrate in the thick specimens). However, it should be mentioned that the diffusion coefficients correspond only to the first hours of the entire diffusion process and consequently reveal only the initial tendency of the liquid to penetrate. The attention should be focused once more on the phenomenon of crystallization. Apparently, the whole process of crystallization takes place within an extended

period of time rather than instantaneously. The exact length of time is quite difficult to measure; however, the start should be placed in the first hours of the migration test before the maximum of the counterdiffusion curves is achieved (Fig. 3). If this is true we can argue that the thinner specimens start with a high trend to accept isopropanol; but they are, as discussed already, more susceptible to annealing. In other words, they become gradually less permeable to penetration and eventually the maximum amount of liquid sorbed becomes lower in comparison with the thicker specimens.

Finally, the diffusion processes involved seem to be strongly affected by the initial plasticizer concentration. Increased amounts of plasticizer in the sheets lead to high migration rates as the concentration gradient, which is the driving force, increases (Table I). Also, the initial level of plasticizer concentration has a significant effect on penetration of the surrounding medium. The specimens that contain large amounts of plasticizer give high diffusion rates in both the sorption and desorption stages (Tables II, III). From the above it is clear that there is a strong relationship between plasticizer migration and liquid medium diffusion into and out of the polymer.

CONCLUSIONS

1. The extended maintenance of PVC specimens at elevated temperatures resulted in

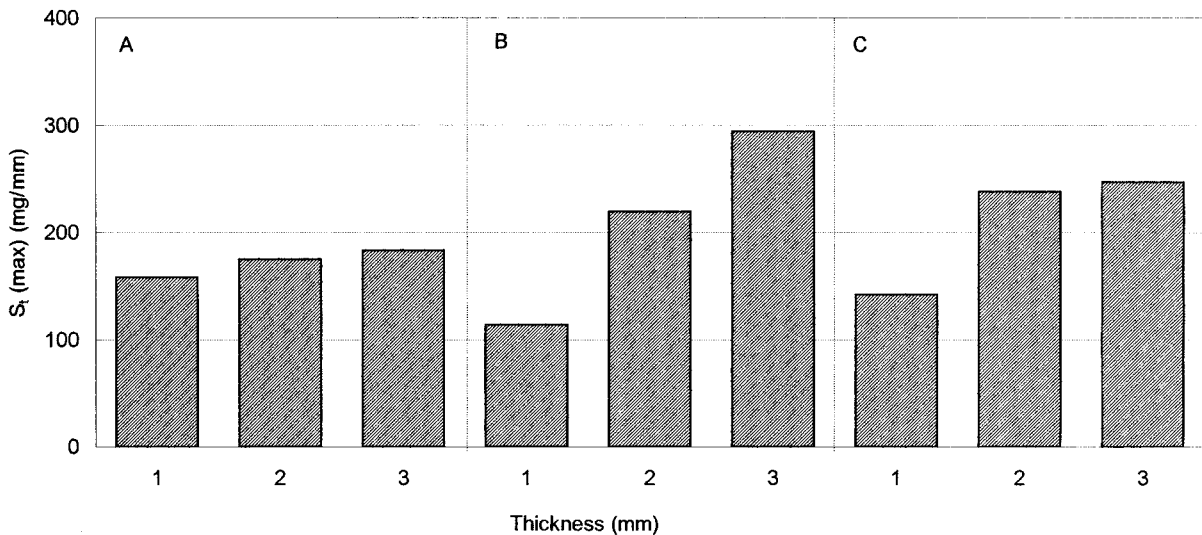


Figure 5 The maximum amount of the isopropanol penetrated for the initial plasticizer concentrations of (A) 40 phr, (B) 70 phr, and (C) 100 phr and for different specimen thicknesses.

a rearrangement of the polymer structure toward a more ordered structure. Tailoring the structural order in the specimens tested by thickness variation led to results fully compatible with such a concept.

2. The rearrangement of the polymer structure (crystallization) seemed responsible for the desorption of the penetrating isopropanol from the PVC specimen.
3. Crystallization seemed to occur in the early stages of the migration test and well before the maximum noticed in the counterdiffusion curves.

The affinity of isopropanol and DOP substantially favored the plasticizer migration, as well as the penetration (counterdiffusion) of isopropanol into the PVC specimen. The two phenomena that took place simultaneously, plasticizer migration and isopropanol penetration, were strongly associated with the PVC structure.

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