Influence of Thermal Stabilizers on Diffusion of Poly(ε-caprolactone) in Poly(vinyl chloride)/Poly(ε-caprolactone) Blends

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SYNOPSIS

The influence of thermal stabilizers on the poly(ε-caprolactone) (PCL) diffusion in poly(vinyl chloride) (PVC)/PCL blends was studied with the addition of various concentrations of dibasic lead phthalate and dibutyltin dilaurate. The rate of PCL diffusion was followed by differential scanning calorimetry and IR spectroscopy in three series of experiments: the migration of PCL at the surface of the sample; the extraction of PCL in a fluid surrounding the sample; and the sorption of liquid PCL in the blend. In the last two series, mass losses and mass uptakes were measured as a function of time. As compared to the blend without additive, dibutyltin dilaurate induces an increase of the PCL rate of diffusion whereas dibasic lead phthalate gives a decrease. These trends are explained by: first, the formation of an associative complex between dibutyltin dilaurate and PVC, which can compete with the PVC/PCL interactions in the blend and thus favor the PCL migration; and, second, the modification of the T_g of the blend induced by the addition of a third component, which can modify the diffusion rate by changing the free volume fraction at the diffusion temperature. T_g decreases slightly in the presence of dibutyltin dilaurate but increases with dibasic lead phthalate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Flexible poly(vinyl chloride) (PVC) is obtained by plasticization. The plasticizers used need to be non-migrating in order to maintain the PVC mechanical properties over long periods of time and at the same time, to avoid the contamination of products in contact with the PVC material.[1-3] The widespread use of PVC also requires the incorporation of a wide variety of other additives: stabilizers, lubricants, impact modifiers, processing aids, fillers, pigments, etc.[4] The efficiency and permanency of each of them depend upon the presence of the others. These interference effects seem to be commonly admitted in industry, but only a few articles address the question of PVC.[3,5]

The plasticizers can be polymeric. Poly(ε-caprolactone) (PCL), which is miscible with PVC over the entire range of composition[7-13] and exhibits a low glass transition temperature, seems to fullfil the conditions of a good plasticizer. In a previous article,[6] the diffusion of low molecular weight PCLs in PCL/PVC blends was studied as a function of the PCL molecular weight and temperature. Generally, a decrease of the PCL molecular weight was found to increase the rate of diffusion to the surface. However, when the temperature was in the vicinity of the PCL melting temperature, the reverse trend was observed: the low molecular weight PCL still migrated to the surface of the blend, but it could diffuse back without being trapped as a crystalline PCL. Inversely, higher molecular weight PCL diffuses slowly to the surface but remains there due to its crystallization. In the literature, even for very high molecular weights, a PCL surface enrichment was observed by Clark et al.[14] in PCL/PVC blends prepared from solution and having PCL contents between 50 and 70 wt %. This surface segregation was attributed to the lower surface tension of semicrystalline PCL as compared to PVC.

These behaviors can be modified if additives are added to the binary blend. Indeed, Kampouris et al.[3] observed that the presence of Ba-Cd and alkyl aryl phosphite type thermal stabilizers increases the extraction rate of plasticizers by alcohols, but no attempt was made to explain this behavior. Inversely, Parker and Vesely[5] noted that the diffusion of PCL into unstabilized PVC is faster than in the presence of a tin-based thermal stabilizer. This difference was attributed to the mode of preparation rather than to the presence of a third compound because unstabilized PVC films, prepared from THF solutions, showed lower T_g (and density) than the stabilized PVC sheets produced by compression molding, revealing a higher free volume.

The lack of data in the literature concerning the influence of additives on the behavior of plasticized PVC led us to the present study. Thermal stabilizers were chosen for this purpose because they are the second most important class of additives to PVC after plasticizers. More specifically, the migration of PCL out of a PCL/PVC blend in the presence of two different thermal stabilizers (a dibasic lead phthalate and a dibutyltin laurate) was investigated. In the first part, the PCL concentration at the surface of the blend is followed by Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflectance (ATR) mode, and differential scanning calorimetry (DSC). In the second part, PCL is extracted from the same PCL/PVC blend by 1-butanol and mass losses calculated; this calculation will lead to diffusion coefficients. Finally, in the third part, the sorption of PCL by the stabilized and unstabilized PCL/PVC blend are monitored by mass uptakes and diffusion coefficients also calculated.

EXPERIMENTAL

Sample Preparation

PVC (M_n 45,000, M_w 60,000) and PCL (MW 1250) were purchased from Aldrich Chemicals. The dibasic lead phthalate ($2PbO \cdot Pb(O_2C)_2C_6H_4$) was kindly supplied by Synergistics Industries (Montréal); dibutyltin dilaurate was purchased from Omega Inc. All products were used without further purification unless specified.

All films were 200-μm thick and were prepared by pressing (5 min at 120°C) blends that were initially mixed at 120°C (plastisol) in a Minimax-Molder for 5 min. Quantities of thermal additives of 5.0 and 10.0 phr (with respect to PVC), corresponding respectively to 2.9 and 5.7% of the weight of the total mixture, were employed.

Measurements

DSC measurements were obtained using a Perkin-Elmer DSC4 apparatus equipped with a TADS 3600 data station and calibrated with an indium standard. All scans were made from -100 to 100°C at a heating rate of 20°C/min. Glass transition (T_g) and melting temperatures (T_m), and enthalpies of fusion (ΔH_m), were recorded from the second heating scan.

ATR spectra were obtained on a Mattson Sirius 100 FTIR spectrometer using a KRS-5 crystal oriented at 45° to the incident beam. An acquisition of 200 scans and a digital resolution of 2 cm^{-1} were used.

PCL extraction measurements were made on 2.3 $\pm$ 0.1 cm diameter disks at 41 and 60°C. The samples were immersed in 1 L of 1-butanol under vigorous stirring and maintained at the desired temperature for specific amounts of time. They were then removed from the liquid, dried under vacuum, and weighed to determine their mass loss. 1-Butanol was chosen for this purpose because it is a nonsolvent for both polymers: this means that it does not dissolve or swell the PCL/PVC disk, which can be fully recovered at the end of the experiment.

PCL sorption by 40/60 PCL/PVC films was studied at 60°C. Mass–uptake was measured as a function of time on 2.3 $\pm$ 0.1 cm diameter disks deposited on microscope slides, which had been previously treated with HF 49%. The samples were immersed in a beaker containing melted PCL for specific amounts of time. They were then removed from the liquid, rinsed with acetone, dried under vacuum, and weighed to determine their mass uptake.

All experiments were carried out at temperatures of 20, 41, or 60°C, well above the -19°C T_g of the 40/60 PCL/PVC blend used herein.

RESULTS

Surface Concentration

In this study, a PCL/PVC blend containing 40% PCL was employed; this composition is the upper limit to avoid the spontaneous crystallization of PCL in the material.[13] Nevertheless, it has been shown that, at this composition, PCL preferentially migrates to the surface of PCL/PVC mixtures[14] and crystallizes there at low temperatures.[6] To study the influence of thermal stabilizers on the PCL migration to the surface of blends, a PCL molecular weight of 1250 and an aging temperature of 20°C were used because Meltzer et al.[6] obtained the fastest PCL surface crystallization under those conditions.

ATR-FTIR spectra between 1500 and 1400 cm^{-1} are shown in Figure 1. The first spectrum for the nonaged blend exhibits a band centered at 1460 cm^{-1} for amorphous PCL and a peak at 1428 cm^{-1} for PVC, both corresponding to C—H deformations. The evolution of the spectra with time of aging at 20°C shows that the PCL 1460 cm^{-1} band shifts to 1471 cm^{-1}, which is characteristic of crystalline PCL; at the same time, the peak attributed to PVC progressively disappears. These two observations indicate that the crystallization of PCL occurs at the surface of the blends, as pointed out by Meltzer et al.,[6] and that the PCL layer becomes thick enough to mask PVC from the IR beam. This trend is the same for each sample. However, it appears that the rate of the evolution depends strongly on the nature of the sample.

In the case of a PCL/PVC blend containing no additive [Fig. 1(a)], a relatively slow PCL crystallization is observed. After 3 days at 20°C, the PVC band at 1428 cm^{-1} is found as a shoulder of the peak at 1419 cm^{-1}; and after 6 days, it has completely disappeared. When the PCL/PVC blend contains 5 phr dibasic lead phthalate [Fig. 1(b)], after 3 days at 20°C practically no crystallization has occurred. After 6 days, the PVC band remains as a shoulder of the 1419 cm^{-1} peak, and disappears entirely after 9 days. The same behavior was observed when 10
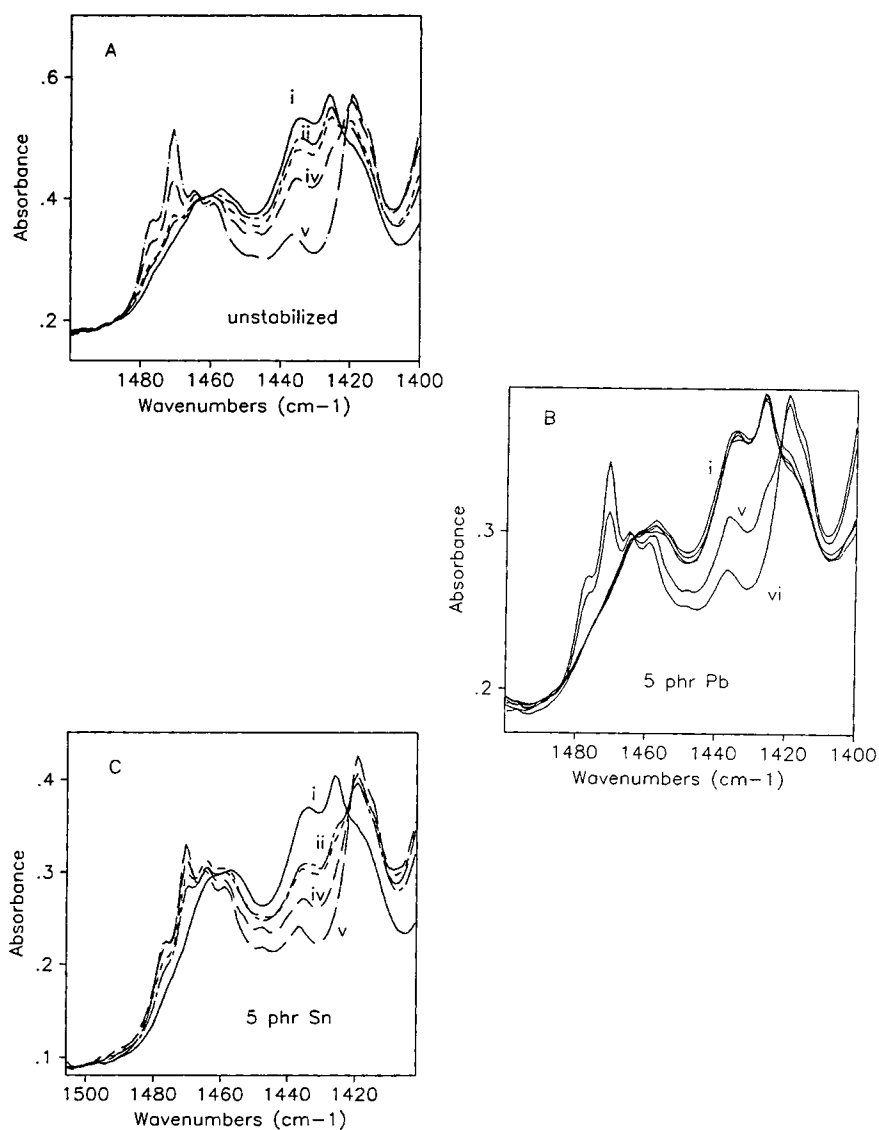

Figure 1   ATR-IR spectra of 40/60 PCL/PVC blends aged at 20°C for (i) 0, (ii) 1, (iii) 2, (iv) 3, (v) 6, (vi) 9 days; (A) unstabilized blend; (B) with 5 phr dibasic lead phthalate; and (C) with 5 phr dibutyltin dilaurate.

phr dibasic lead phthalate was used. When dibutyltin dilaurate is present in the PCL/PVC blend [Fig. 1(c)], the crystallization is more rapid because 3 days are enough to completely mask the PVC signal and, after a single day, it is found as a shoulder of the PCL peak at 1419 cm^{-1}.

From these observations, we can conclude that the PCL crystallizes more rapidly at the surface of the blend in the presence of dibutyltin dilaurate, but more slowly with dibasic lead phthalate, as compared to the blend without additive, which indicates that the PCL migration is more rapid in the first case and slower in the second. These trends reveal that the presence of an additive can modify the thermodynamic equilibrium of the PVC–plasticizer blends and, consequently, the migration of the plasticizer out of the blend.

ATR-IR spectroscopy is a very sensitive method to observe the surface of materials, but the maximum penetration depth of the incident beam in the 1500–1400 cm^{-1} spectral range is about 4 μm. Moreover, PCL, and especially semicrystalline PCL, has a higher IR absorption coefficient than PVC in this frequency range.[14,15] Therefore, the PCL crystallized layer tends to mask the presence of PVC in the ATR-observable layer before it becomes thick enough to be detected by DSC and no further observation can be made: this happens, for each sample, after 6 days of aging, when the PCL signal dominates the spectra and no differences between them can be detected. DSC can be used to follow the PCL concentration at the surface of the materials for longer periods of aging time. The weight fraction of PCL that has migrated at the surface of the blend, W_s, is given by[6]:

$$W_s = \frac{\Delta H_{m,s}}{\Delta H_m W_b}, \qquad (1)$$

where W_b is the weight fraction of PCL in the blend, $\Delta H_{m,s}$ is the enthalpy of PCL melting measured at the surface as a function of time, and ΔH_m is the enthalpy of melting of the PCL removed from the surface of the blend. To check that PCL crystallized only at the surface, measurements were also made on a blend sample where the migrated PCL layer had been scraped off, but no endothermic peak was observed for this sample.

Figure 2 gives the weight percent of PCL found [from eq. (1)] at the surface of the blend sample (at 20°C), with and without dibasic lead phthalate [Fig. 2(a)] and dibutyltin dilaurate [Fig. 2(b)]. In both cases, after an induction time of several days where PCL cannot be detected at the surface (although a

small amount is seen by ATR-IR spectroscopy), the amount crystallized increases regularly. In the first case, the presence of the lead thermal stabilizer slows down the migration of PCL at the surface: the larger the concentration of dibasic lead phthalate, the smaller the PCL concentration. In contrast, in the second case, the rate of PCL migration to the surface increases in the presence of the tin thermal stabilizer. These results indicate that the trend observed at the initial stage of the migration by ATR-IR spectroscopy is continued at longer periods of aging time, for example, at least for 60 days under the conditions used herein.

Extraction Measurements

The presence of PCL at the surface of PCL/PVC blends is then due to the combination of two phenomena.[6] First, the PCL diffuses to the surface of the blend in order to minimize the surface free energy[14]; second, the PCL crystallizes at the surface and is, therefore, trapped there. If the PCL is extracted at the surface by a solvent, its crystallization can be avoided and diffusion of PCL out of the blend monitored.

Typical mass–loss curves, obtained at 41°C in 1-butanol for stabilized and unstabilized PCL/PVC blends containing 40% PCL, are shown in Figure 3. The linear relationship between weight loss and the square root of time (t) indicates a Fickian behavior.[16] From the slopes (s) of these curves, the diffusion coefficient of the PCL out of the blend can be calculated,

$$D = \frac{\Pi s^2}{16q^2C^2}, \qquad (2)$$

where q is the cross-section area of the sample and C the PCL concentration in the blend. It is assumed here that the PCL concentration in the solvent remains negligible. In fact, it never exceeded 0.25 g/L, which is well below the PCL solubility limit at this temperature.

The diffusion coefficients calculated with eq. (2) are reported in Table I. When dibutyltin dilaurate is added to the PCL/PVC blend [Fig. 3], the diffusion coefficient of PCL out of the blend increases significantly as compared to the blend containing no additive. The inverse trend is observed in the presence of dibasic lead phthalate [Fig. 3], but to a lesser extent. If the PCL extraction by 1-butanol is done at 60°C, the diffusion coefficient obtained for lead stabilized and unstabilized blends are the same within experimental error (Table I).
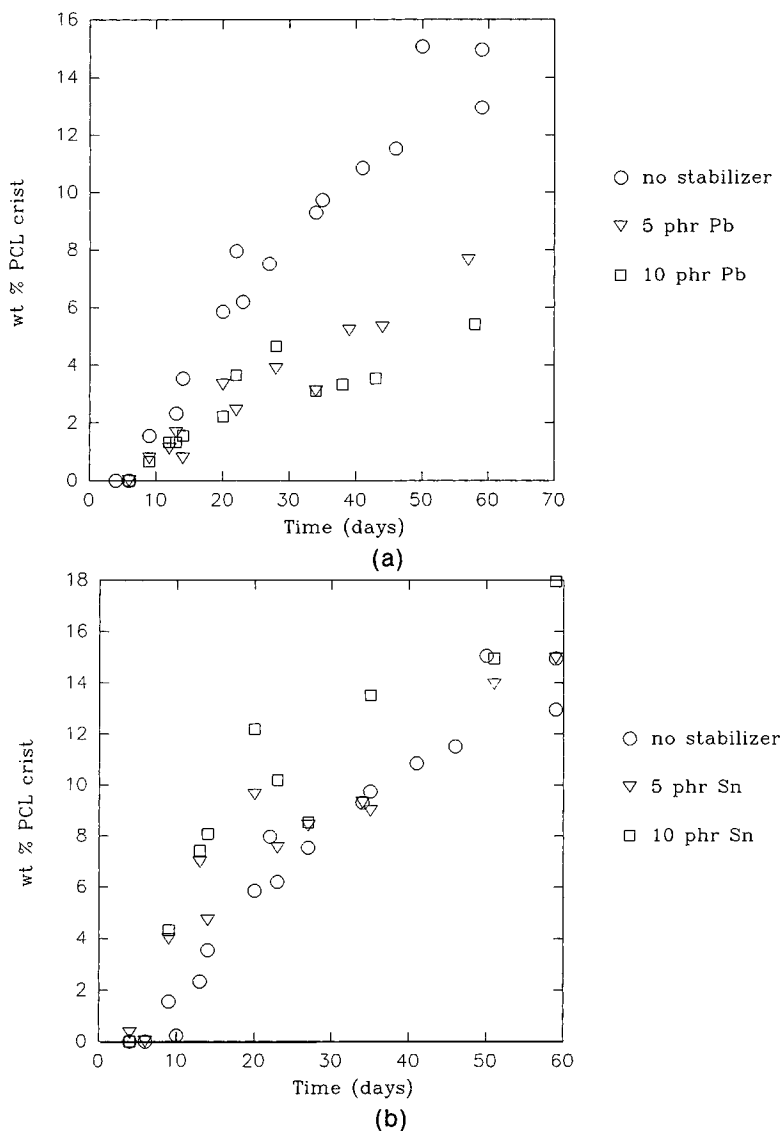
Figure 2   Percentage of PCL migrating on the surface of stabilized and unstabilized 40/60 PCL/PVC blends at 20°C: (a) with dibasic lead phthalate and (b) with dibutyltin laurate.

Sorption of PCL

Diffusion coefficients can also be measured from sorption experiments. The study of PCL sorption by PCL/PVC films, as a function of the additive present in the blend, is shown in Figure 4 in the form of mass–uptake curves, measured at 60°C. The linear relationship between mass–uptake and $t^{1/2}$ reveals a Fickian behavior. Diffusion coefficients were calculated using eq. (3).

$$D = \frac{\Pi s^2}{4q^2(C_0 - C)^2},\qquad (3)$$

where s is the slope of the mass–uptake curves, q is the sample section area, C_0 is the PCL concentration at the surface of the blend, and C is the PCL concentration in the blend (Table II). When dibutyltin dilaurate is added to the blend, the rate of PCL sorption increases as compared to the blend containing no thermal stabilizer. However, no significant change is observed when using dibasic lead phthalate. It should be noted that the diffusion coefficients obtained by extraction experiments are different from those obtained by sorption. This difference indicates that the diffusion coefficients depend on the concentration in the blend,[16] which means that the PCL activity is not equal to its concentration.
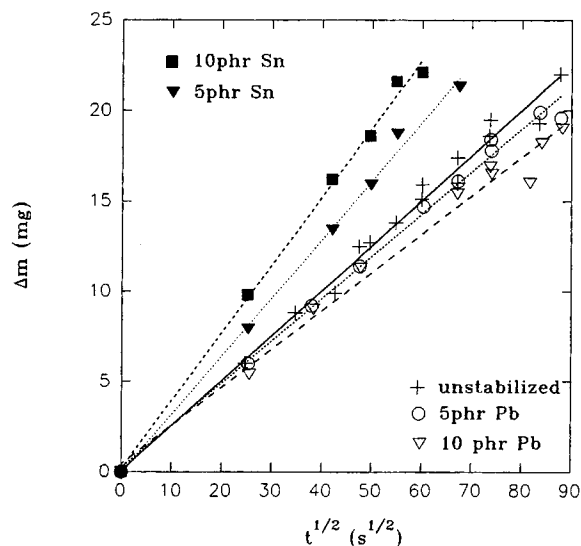
Figure 3 Mass–loss curves obtained for the extraction of PCL from stabilized and unstabilized 40/60 PCL/PVC blends in 1-butanol at 6°C: (O, ∇) with dibasic lead phthalate; (■, ▼) with dibutyltin laurate; and (+) without additive.

DISCUSSION

These observations lead to the conclusion that the presence of thermal stabilizers in PCL/PVC blends has a significant influence on PCL migration, but this influence is different with different stabilizers. For example, the PCL concentration at the surface increases in the 40/60 mixture at 20°C, for a given period of time for migration, in the following order: dibasic lead phthalate < blend with no additive < dibutyltin dilaurate.

However, the presence of PCL at the surface is due to a combination of the diffusion of the PCL out of the blend, which can depend on the presence of other additives in the sample, and its crystalli-

Table I Diffusion Coefficients of PCL out of 40/60 Blends PCL/PVC

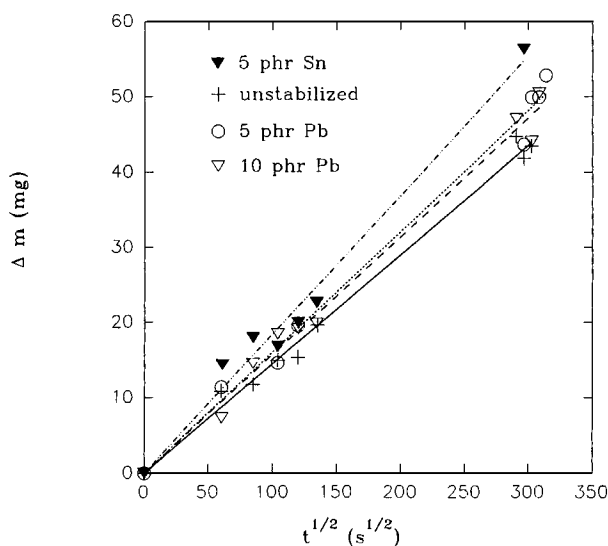|	$D \cdot 10^9$ (cm²/s)	
Sample	41°C	60°C
No thermal stabilizer	3.0 ± 0.4	14 ± 3
Dibasic lead phthalate		
5 phr	2.5 ± 0.4	12 ± 2
10 phr	2.0 ± 0.3	11 ± 2
Dibutyltin dilaurate		
5 phr	5.2 ± 0.9	
10 phr	7.1 ± 1.0	

Figure 4 Mass–uptake curves obtained for the sorption of liquid PCL in stabilized and unstabilized 40/60 PCL/PVC blends at 60°C: (O, ∇) with dibasic lead phthalate; (▼) with dibutyltin laurate; and (+) without additive.

zation at the surface of the material, which depends mainly upon the temperature. In our second and third series of experiments, the crystallization of PCL was avoided and the diffusion effects could be isolated.

The extraction measurements at 41°C show that when dibasic lead phthalate is added to the blend, PCL diffusion out of the mixture occurs slightly more slowly than in the absence of this thermal stabilizer; at 60°C, this slight difference is no longer observed. In PCL sorption experiments at 60°C, the diffusion coefficient of PCL is the same in the pure and stabilized mixtures. In contrast, the presence of dibutyltin dilaurate in the blend increases the PCL diffusion coefficient in both experiments and at the two temperatures. These trends are in agreement with the surface segregation results,[14] mainly controlled by the diffusion process.

However, the reasons for the differences observed between the two stabilizers need to be elucidated.

Table II Diffusion Coefficient of PCL in Stabilized or Unstabilized PCL/PVC Films at 60°C

Sample Nature	$D \cdot 10^9$ (cm²/s)
No additive	2.5 ± 0.5
Dibasic lead phthalate	
5 phr	3.0 ± 0.6
10 phr	2.8 ± 0.7
Dibutyltin dilaurate, 5 phr	3.8 ± 0.8

First, the interactions between the components must be considered because, in order to be efficient, thermal stabilizers, as any other kind of stabilizers, have to be miscible with PVC, miscibility occurring when favorable interactions between the polymer and additives are present. In the case of tin-based thermal stabilizers, it has been shown[17] that there exists an associative complex between the tin compound and the PVC, which is the precursor step of one of the different stabilizing actions of this sort of compound. A dative link is formed between the chlorine atoms of PVC and the two free Sn orbitals as shown here:

$$\sim\sim\sim CH_2\!-\!CH\!-\!CH_2\sim\sim\sim$$
$$|$$
$$Cl$$

$$|$$
$$Cl$$
$$|$$
$$\sim\sim\sim CH_2\!-\!CH\!-\!CH_2\sim\sim\sim$$
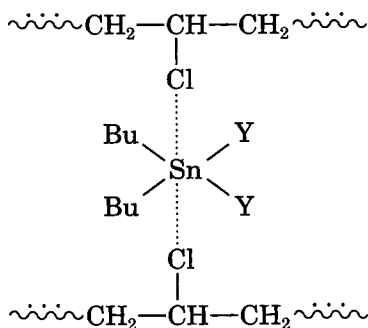
Because the PCL miscibility with PVC is mainly due to the interaction between the carbonyl group of PCL and the hydrogen atom of the $H\!-\!C\!-\!Cl$ sequence of PVC,[11] a competition exists between the thermal stabilizer and the PCL for interacting with PVC. Therefore, the tendency of PCL to migrate to the surface of the blend can be favored by this competition with dibutyltin dilaurate. No such interaction has been reported between PVC and dibasic lead phthalate.

Second, the addition of a third component can modify the T_g of the material and, therefore, its diffusion rate as it depends on the free volume fraction. DSC measurements gave a T_g of 254 K for the PCL/PVC blend, which decreases to 251 K with 5 or 10 phr of dibutyltin dilaurate, but increases to 261 K in the presence of dibasic lead phthalate. Because the plasticizing effect of tin stabilizers,[18] and especially of dibutyltin dilaurate,[19] has already been noted, this decrease of T_g certainly contributes to the increase of the PCL diffusion coefficient.

When dibasic lead phthalate is added to the blend, the decrease of the PCL migration rate to the surface and its lower extraction rate at 41°C can also be explained, at least partly, by an increase of T_g. However, at 60°C, no more influence can be observed on the PCL diffusion coefficient. Differences between the activation energies of the PCL diffusion in stabilized or unstabilized blends could explain this behavior.

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