Using Cycloolefin Copolymers as Pharmaceutical or Cosmetic Storage Material. I. A Study of Adjuvant Migration and of Polymer Ageing

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ABSTRACT: The aim of this paper is to study the interaction between alcoholic solutions of different polarities and a new class of packaging polymer, the cycloolefins, which can be used in pharmaceutical and cosmetic fields. Different consequences of this interaction were studied as adjuvant migration, and polymer swelling. Very extreme storage conditions were used to accelerate the ageing of the polymer. This study shows the great influence of solvent polarity on the material's thermomechanical properties as well as on its barrier properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 585–593, 2007

Key words: cycloolefins; ageing; antioxidants; diffusion; swelling

INTRODUCTION

Studying interaction between the polymeric container and the contained solution is an important safety deal, especially concerning pharmaceutical, cosmetic, or food industry; polymeric material may indeed contain not chemically bound species such as volatiles, oligomers and monomers, metallic catalyst residues, and additives. To improve their initial properties or to increase their lifetime, mostly all commercially available polymers contain indeed one or several additives, for example antioxidants or plasticizers. All these small molecules can freely move inside the polymer matrix and thus migrate from the material into the solution, raising problematic toxicity issues. At sufficient concentration, these molecules may damage human health, bring unacceptable modifications in the formulation properties or change its organoleptic properties. Moreover, because of migration of additives from the polymer, its properties may be modified and its lifetime shortened. Long contact between a polymer and a solvent can however have some other disadvantages: it can induce a diffusion of the solvent into the polymeric chains, depending on the affinity of both of the components. If this affinity is high enough, polymer can be swollen by the solvent and its resulting plasticization may cause a drop in the thermomechanical properties as in its barrier properties.

Cycloolefins are quite new industrial olefinic polymers. Because of their high purity, glass-like texture, transparency, very low permeability to water and gas, these amorphous polymers are more and more used in the cosmetic and pharmaceutical packaging. But only few studies are reported on their properties and especially on their ageing behavior as a storage material. We were thus interested here in its ageing behavior as container for alcoholic solutions. In this study, we used some extreme storage conditions to accelerate the ageing of the polymer and its additives. We changed some parameters such as solvent polarity, storage time, and temperature. The aim was to follow the migration and degradation of additives, especially of phenolic antioxidants; we were also interested in pointing out the swelling of the matrix and its consequences.

EXPERIMENTAL

We used a cycloolefin copolymer (COC) called TOPAS 8007® provided by Ticona (Germany). It was used as granules, or as plates 3.25-mm thick. This polymer is an ethylene and norbornene based copolymer (Fig. 1). For additives extraction, only granules were used. For thermogravimetric measurements (TGA), both plates and granules were used. Plates were molded and provided by Ticona. For differential scanning calorimetry (DSC), annealing study was made on granules and the study of polymer plasticization by solvents was realized on plate pieces. The weighting measurements were only realized on plates.

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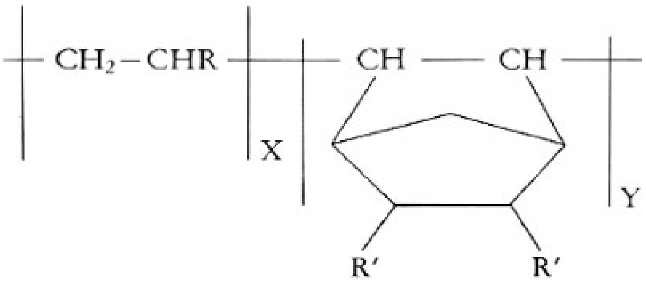

Figure 1 TOPAS® cycloolefins formula.

Sample storage

For additives analyses, around 2.5 g of polymeric granules were immersed in 15 mL of solvent in a hermetically closed vial. For swelling rates measurements, we used both granules (only for TGA) and plates (the dimensions of the plates were around 7 × 41 × 3.25 mm^3) immersed in 15 mL of solvent. For these studies, the concentration of the polymer in alcohol used was 0.04 to 0.05 g/mL (with a surface area ∼ 0.6 cm^2/mL).

Before storage of samples dedicated to annealing analysis by DSC, samples were heated for 10 min in the DSC crucible at 150°C to give to all of them the same initial thermomechanical history and to assure a good contact between crucible and sample. The samples were then annealed in the crucible. For swollen samples, we used the most flat pieces of the plates.

We used two storage temperatures of 60 and 83°C. It should be noted that one was below the glass-transition temperature and the second was above. Five alcoholic solvents were used as storage solutions: methanol (Merck; HPLC grade), ethanol (Carlo Erba; HPLC grade), propanol (Prolabo rectapur), octanol (Merck; > 99%), and decanol (Merck; > 99%); all the five solvents are linear alcohols.

Additives extraction

To quantify and to identify the additives present in the polymer, we used a dissolution/precipitation process. In the case of polymer granules stored in solvents, they were rinsed twice in methanol (HPLC grade; Prolabo) before dissolution process. The storage solvent was kept apart and evaporated by rotavapor (except for the octanol and decanol that could not be easily evaporated). Amount of 2.5 g of polymer were then dissolved at reflux in 50 mL of toluene (HPLC grade; Carlo Erba) at ∼ 70°C. After complete dissolution, the polymer was precipitated by slowly adding 50 mL of methanol under stirring. Polymer was then removed from the additives solution by filtration on a paper filter, and the precipitate was carefully rinsed with methanol. Solutions containing potentially additives, monomers, oligomers, and degradation products were then evaporated by rotavapor between 60 and 80°C (under vacuum) depending on the solvent used. In the case of a nonstored polymer, five extractions were realized to check the reproducibility of the extraction process.

Additives analysis

Before injection, the dry residue containing additives, monomers, oligomers, and degradation products was dissolved in a mixture of 0.5 mL of THF (HPLC grade; Prolabo) and 0.5 mL of acetonitrile (HPLC grade; Prolabo). Then, the solution was filtered on a 0.45 μm Teflon filter.

We used an HPLC method, which was previously developed in our laboratory, to analyze additives in pharmaceutical polymers. This method used three mobile phases composed by a mixture of 1–5 solvents [methanol, acetonitrile, THF, water, and ethylacetate (all HPLC grade)], and a gradient elution that consisted on linear gradients from one mobile phase to another. The apparatus used was constituted of a gradient pump Spectrum System P4000 (TSP) (flow rate of 1 mL/min), of an automatic injector AS 3000 Spectro System (TSP), and of an UV detector Spectro System 1000 (TSP); the detection wavelength was of 280 nm. The column was a LiChrocart 250-4 RP select B (5 μm) Lichrosphere (Interchim). The injection volume was of 20 μL. Acquisition was done using the Chromquest software (TSP, version 3.0). Identification of the additives was performed by comparing retention times of pharmaceutical additive standards (Irganox® from Ciba and BHT from Sigma) with that of extracted solutions. Quantification was carried out by establishing a calibration plot with prepared solutions of known concentration in additive.

Thermogravimetric analysis

TGA was used to study polymer swelling by a given solvent. The apparatus was a PerkinElmer TGA7. The temperature range was between 35 and 470°C under nitrogen blanketing, and the analysis was stopped just before the polymer's temperature degradation. The scanning heating rate was 20°C/min.

Weighting

This experiment was performed on thick plates of sufficient weight on a M220D Denver Instrument balance. Sample dimensions were around 3.25 × 7 × 41 mm^3, and sample weight was ranging between 0.65 and 0.80 g.

TABLE I
Solvent Polarity by Using SPP Scale

Solvent	Polarity
Methanol	0.857
Ethanol	0.853
Propanol	0.847
Octanol	0.785
Decanol	0.765

Differential scanning calorimetry

DSC analysis was done on a TA Instrument Q1000 in a modulated mode. The modulation parameters were the following: the amplitude was of ± 1°C, the period of 60 s, and the heating rate of 3°C/min under nitrogen blanketing. The temperature range was between 40 and 160°C. For annealing study, only the first temperature raise was exploited, by using the reversing signal for glass-transition study and the nonreversing signal for the enthalpic relaxation study. Hermetical aluminum pans (20 μL) were used.

RESULTS AND DISCUSSION

Polarity scale

To express the polarity of the different solvents, we used the scale defined by Catalan (SPP scale).[1] This scale is based on spectroscopic measurements. Polarity is calculated by analyzing absorption spectra of two molecules the DMAN (2-dimethylamino-7-nitrofluorene) and the FNF (2-fluoro-7-nitrofluorene) in different solvents. Solvent polarity is given by solvatochromism difference between DMAN and FNF [$\Delta\nu$ (solvent) $= \nu_{\mathrm{FNF}} - \nu_{\mathrm{DMANF}}$]. This allows establishing a scale going from 0 to 1 (DMSO). By convenience, we had placed at 1, samples that were not in contact with solutions (because of the nonpolar nature of the polymer chain used). Polarity values of our solvents are given in Table I.

Swelling of the COC

Swelling equilibrium, that is to say the solvent volume fraction in the polymer at the equilibrium, depends on the thermodynamic parameters and mostly on the polymer/solvent affinity that can be expressed through the polymer/solvent interaction parameter χ in Flory's theory or by using the solubility parameters δ (Hansen).[2]

The swelling is moreover influenced by a kinetic that may be quite long and complex, in particular in the case of glassy polymers. The sorption rate may strongly depend on size and shape of the solvent molecule: ramified structure and long alkyl chains significantly sorb at a slower rate than small, flat, and linear molecules. But interactions between polymer and solvent undoubtedly play a major place too, by plasticizing the polymer chains.

In our case, we used different solvents from the same family: they were all linear alcohols, to avoid shape effect. The differences between them was their alkyl chain length and, as a consequence, their polarity.

To measure swelling, two different methods were used: the first one resulted in weighting thick plates of significant weight (0.6 g minimum), the second one resulted in measuring the solvent weight loss during heating by TGA. Both of these methods provided different information. The TGA measurements gave the ''real'' mass solvent fraction in the matrix, by measuring the loss weight of the sample while it was heated. The direct weighting allowed by comparison with TGA to show a partial dissolution process of the polymer in the solution with time, because it was sensitive both to weight gain by swelling and to weight loss by dissolution.

TGA results showed that the best swelling was observed for solvents having the lower polarity, that is to say for alcohols having the longest alkyl chains (Fig. 2). The polymer, which is nonpolar, had indeed preferential affinity with the less polar solvents. After 7 months of storage, and for temperature equal or lower than 60°C, the swelling rates were in fact very small, even for the less polar solvents (below 6%) and the difference between the most polar solvents were very weak. The scattering of the results for octanol and decanol at 60°C was quite important and was certainly due to the existence of some microcracks enhanced by the swelling. The swelling was favored by higher temperature: at 83°C, the

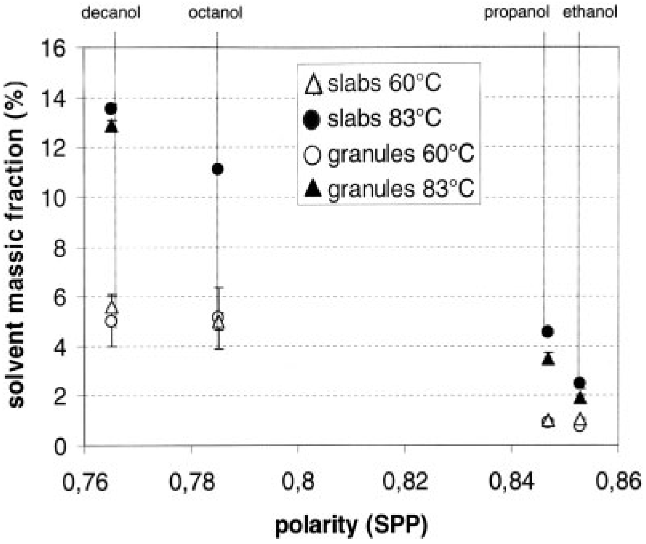

Figure 2 Evolution of the solvent massic fraction in polymer as a function of solvent polarity for storages at 60°C and 83°C. Results are given for plates and granules and for more than 200 days of storage.

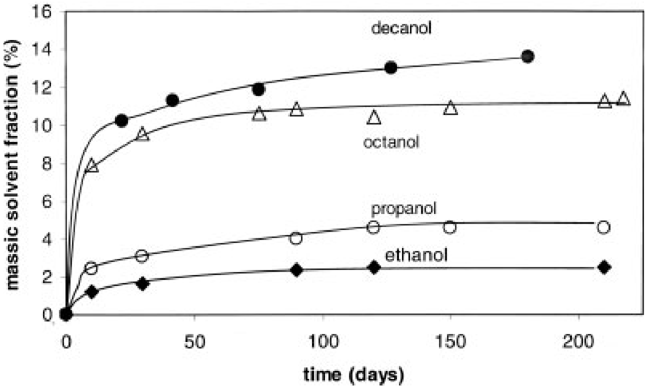

Figure 3 Granules swelling kinetics established from TGA measurements at a storage temperature of 83°C for different solvents.

swelling rate was over 10% for the less polar solvents decanol and octanol. The results obtained with plates and granules were quite the same for times not too far from an equilibrium state, but the kinetics were different because of the importance of the shape factor of the polymer sample. It should be noted that the swelling equilibrium was quite long to reach. After several swelling months, a kind of stabilization of the swelling ratio was observed (Fig. 3). Moreover, it was observed a partial dissolution of the polymer due to the migration of some oligomers, which are sufficiently soluble in the hot alcohols. For long storage times, the solutions stored at 83°C appeared cloudy at ambient temperature. The same observation was made for long storage times at 60°C at least for octanol and decanol. To quantify the amount of dissolved polymer or migrating oligomers after at least 300 days of storage of the plates, the swelling ratio obtained by TGA and the results of the weight measurements were used. The fraction f, which was dissolved or has migrated in the storage solution, was obtained by using the following formula: $f = 1 - [A\ (1 - F_S)]$, where A is the weight ratio between the stored plate and the initial plate and F_S, the solvent mass fraction obtained by TGA. The soluble fraction was generally quite low ($< 2\%$). The highest ratio was obtained with octanol ($\sim 10\%$ after 8 months at 83°C). This migration certainly essentially concerned the smaller polymer chains, as the oligomers, that could migrate from the matrix into the solution: to identify the nature of those oligomers, gel permeation chromatography has to be performed, which will be discussed in a next paper, where the oligomer migration will be deeply studied.

It should be noted that for the lowest swelling ratios (around a few percent), the solvent uptake might mainly result from the void filling, instead of the swelling of the polymer chains. This might be particularly true for the storage at 60°C with the most polar solvents.

Thermomechanical properties of the COC

To dissociate both swelling and temperature effect, the influence of storage temperature on the polymer ageing was first studied. The studied polymers were annealed for 15–30 days without any solvent. For the nonannealed polymer granules, we observed after a first heating up to 160°C, a reversing heat flow showing a glass-transition temperature around 79°C, and a nonreversing heat flow showing an enthalpic relaxation phenomena at 70°C. This relaxation was characteristic to the metastable glassy state (Fig. 4). It occurred at 70°C and had an enthalpy of 1.6 J/g (Fig. 4). Ageing is due to the evolution from a metastable glassy state towards a true equilibrium state. As polymer was stored at different temperatures, the physical ageing of the material was thus studied by following this relaxation phenomenon, which was associated to a material densification. The main effect of this annealing was observed on the relaxation enthalpy. The relaxation enthalpy presented a maximum for annealing temperatures ranged between 40 and 60°C (Fig. 5). Then, for annealing temperatures close to T_g, the relaxation phenomenon tended to disappear, because the glassy transition range was reached. This enthalpy increase corresponded to a rise of the relaxation temperature in the same area; for the glass-transition temperature, changes were not so obvious: it seemed to be quite constant, even though there might be a slight increase for annealing temperatures between 40 and 60°C (T_g was $\sim$ 82°C). But no sharp T_g increase, as described in the literature,[3–5] was observed even for annealing at temperatures as high as 115°C and for times as long as 1 month (Fig. 6). Chu et al.[3–5] had however shown an increase in the glass-transition temperature upon annealing for poly(norbornene-*co*-ethylene) COC. This resulted in a local packing of the rigid segments of the COC chains. For polymers exhibiting T_g around 81°C, they observed after 200 h

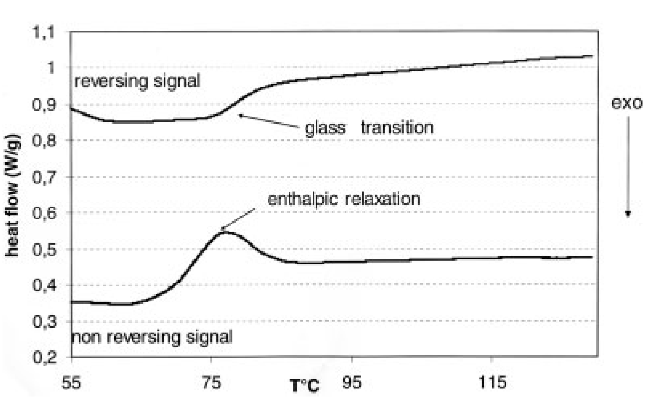

Figure 4 Modulated DSC thermogram for TOPAS 8007 granules.

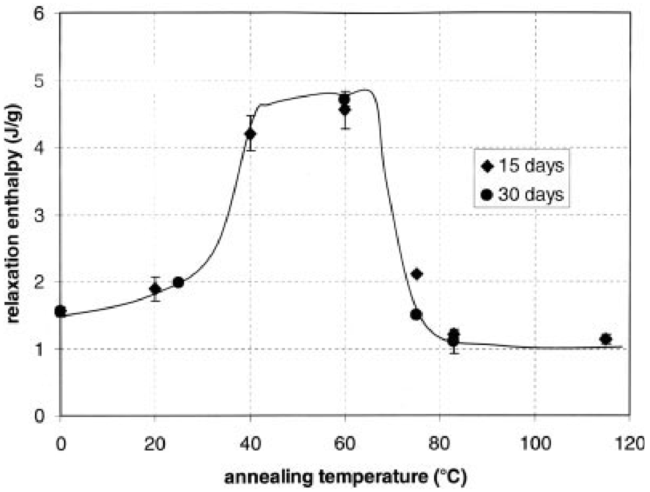

Figure 5 Evolution of the enthalpic relaxation with annealing temperature for two annealing times (15 and 30 days).

of annealing between 90 and 110°C a significant T_g increase to 155°C.

Concerning now the swelling effect, a chain plasticization was expected that should be evidenced by a T_g decrease and that could induce loss of the polymer thermomechanical properties. Some empirical relationships as Fox[6] or Bueche's laws that allow estimating the T_g of the gel knowing the T_g of polymer and solvent, do exist, but they could not be used here because for all these rules solvent's T_gs must be known. DSC measurements were done on swollen samples (Fig. 7). Our samples were only swollen by decanol, octanol, or propanol, because ethanol and methanol were too much volatile for this kind of analysis. For samples stored at 60°C, for which solvent ratios were ~ 6%, we did not observe any T_g lowering. The relaxation process associated with glassy transition was already around 75°C, a temperature which was observed too for samples annealed 15 days at 60°C without solvent. For these samples, the reversing signal was not always easy to interpret, but a C_p jump was generally observed between 81 and 84°C. These temperatures corresponded too to the T_g samples annealed 15 days at 60°C without solvent [Fig. 7(a) shows the case of a sample swollen by octanol at 60°C]. In the case of 83°C propanol storage [Fig. 7(b)], for which we had a mass fraction around 3.5% solvent in polymer plates, we observed two T_{gs}: the first one at around 63°C was associated with a relaxation process in the same range (51°C). This transition was then followed by a more intense one at 110°C. This second T_g was associated with a relaxation process at 102°C. The first T_g lowering suggested that some chains were plasticized by propanol, but the existence of a second higher T_g suggested there was in parallel a kind of local packing of rigid segments of the COC chains. In the case of the storage at 83°C in octanol or decanol (11–13% of solvent in polymer), nothing significant was visible anymore between 45 and 190°C for both reversing and nonreversing signals, what suggested the gel's temperature T_g decreased under 45°C [Fig. 7(c)]. These different results are given in Table II.

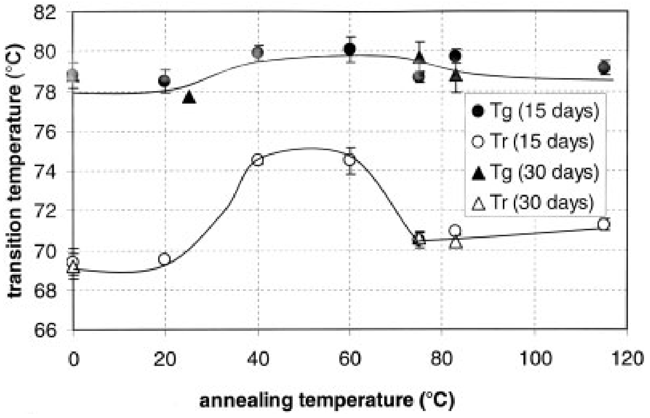

Figure 6 Evolution of the glass-transition temperature and enthalpic relaxation temperature of granules with annealing temperature for two annealing times (15 and 30 days).

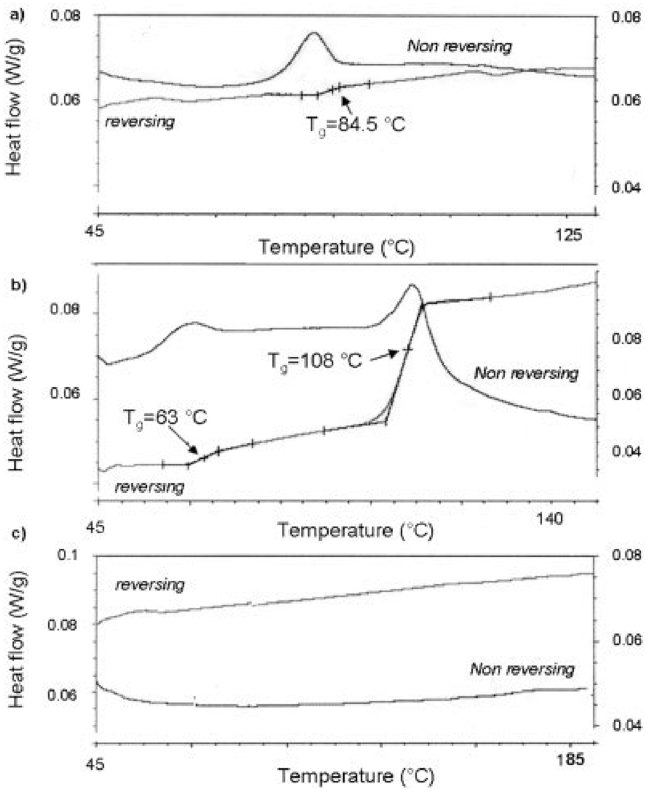

Figure 7 Modulated DSC thermograms for polymer stored in the solvent (reversing and nonreversing signals) (a) plate stored 340 days in octanol at 60°C; (b) plate stored 340 days in propanol at 83°C; (c) plate stored 340 days in octanol at 83°C.

TABLE II
Characteristic Temperatures of Some Annealed, Not Annealed, and Solvent Immersed Samples

Sample	Annealing T (°C)	Solvent	% Solvent in polymer	T_g (°C)	T_r (°C)
Granules	–	–	–	79	70
Granules	60	–	–	80	75
Granules	83	–	–	79	70
Plate	60	Octanol	5	81–85	75
Plate	83	Propanol	3.5	63 108	51 102
Plate	83	Octanol	11	–	–
Plate	83	Decanol	15	–	–

COC additives migration and degradation

As polymer storage into a solution occurs, different kinds of phenomena are expected:

- A diffusion of the additives from the matrix eventually followed by a degradation of the migrating additives in the solution.
- A degradation of the additives in the matrix followed by a diffusion of the degradation products in solution.

Migration rate of additives from a polymer matrix through a solution depends on a large extent on the size and the shape of the additive molecules and on the polymer structure (amorphous or crystalline…) and state (glassy or rubbery…). Actually the migration rate can be expressed by using the effective diffusion coefficient of additives in the matrix in some Fick's law, at least if no interaction between polymer and solution exists (no polymer swelling). Greater migration rates are expected as temperature is increased, because of the Arrhenius behavior for the diffusion coefficient and because of the possibility of evolution from a polymeric glassy state, for which diffusion through the matrix is quite difficult, to a rubbery state that promotes molecular motions inside the polymer. Solvent affinity for the polymer that results in some swelling of the matrix may play a great role too, by plasticizing the polymer chains and thus helping the adjuvant diffusion. Concerning additives ratios in the solution at the equilibrium state, they depend on the partition coefficient $K_{P/L}$ between polymer (P) and liquid (L) $K_{P/L} = C_P/C_L$ (C being the additive concentration). $K_{P/L}$ depends on the additives solubility in solution and on the respective polymer/additive and solvent/additive interactions. This partition coefficient fluctuates with temperature. It should be noted that additive amount can continuously decrease with time in polymer because of additive degradation in solution that continuously displaces the equilibrium additive concentration in solution. This is particularly true for phenolic antioxidants in aqueous media: because of degradation of them into smaller molecules, the expected additive migration ratio is significantly increased and this occurs even though these antioxidants are insoluble in water.[7] Lots of papers have tried to evaluate additives migration from polymer into solution by using diffusion and partition coefficients[8–11]: the migration of BHT and other antioxidants from HDPE into oils and fat simulating liquids can be predictable, but some key parameters have to be known such as the diffusion coefficient (D_p) of the additive in the polymer, the mass transfer coefficient or mixing coefficient (k_m), the partition coefficient (K) of the additive between the polymer and the solution, and the reaction rate constant (k_r) for the degradation of the additive in the solution. Moreover, the model often fails when interactions between solution and polymer occurred.

In our case, it could be foreseen that the less polar solvent would promote diffusion, by swelling the polymer matrix and thus lowering its barrier properties. Moreover, nonpolar solvents would have better affinity with phenolic antioxidants and enhance their diffusion. Indeed, Irganox 1010 is known to have a greater solubility in methanol when compared with that in water (2 g/100 g of solution for methanol and only 0.03 g in water).[7] However, additives degradation would certainly be greater in the most polar solvents and this could have an important impact on additive depletion in polymer. In this study, we tried thus to quantify the influence of polarity on all these potentially events.

First of all, polymer additives were analyzed considering phenolic antioxidants. The additive extraction process was quite reproducible (5 extractions). It was found that the polymer contained only one antioxidant, Irganox 1010® (indexed as peak 3 on Fig. 8) at a concentration around 1470 ± 50 ppm. Nevertheless, some small peaks appeared on the chromatogram (indexed as peaks 1, 2, and 4): they were characteristic to the synthesis or degradation residues of Irganox 1010 (Fig. 8).

Second, the effect of the polymer storage at 83°C without any solvent was studied as a reference to

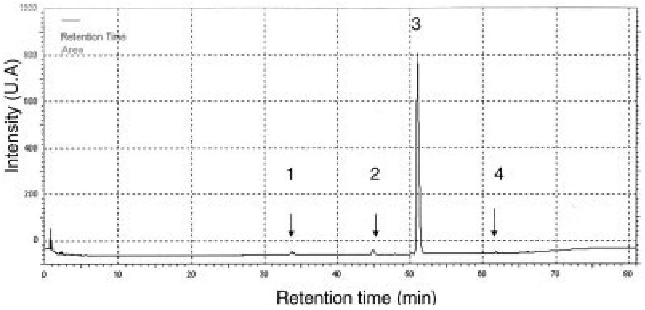

Figure 8 HPLC chromatograms of the TOPAS 8007 extractible. The detection is done by an UV detector at the 280 nm wavelength. The main peak correspond to the Irganox 1010 and the arrows show smaller ones that correspond to residues (indexed 1, 2, 4).

check the effect of the simple thermal oxidation process in air. During this storage, some antioxidants might be consumed to prevent the polymer from oxidation. A continuous decrease of the level of extractable antioxidants with time was thus observed. After 4 months storage, around 15% of the Irganox 1010 had been consumed. The decrease seemed to be quite linear for the first storage months with a total loss of 370 ppm after 6 months. On the chromatogram, some new peaks, characteristic of degradation products, and located between the synthesis residue (indexed 2) and Irganox 1010 peak (Fig. 9), were observed: two after 4 months of storage and four after 6 months of storage.

Finally, the effect of polymer storage in solvent of different polarities was studied. For short storage times (10 days) and temperatures as high as 60°C, the diffusion of Irganox 1010 in storage solutions did exist, but was very small: for the less polar solvents (Fig. 10), a slight decrease of the antioxidant amount in the polymer was observed, but it was less than 9% even for the decanol, the less polar of them. For the most polar solvents (methanol, ethanol, propanol), it was even no more possible to directly evidence the Irganox depletion in the polymer (Fig. 10 does not show any significant decrease). Only by the analysis of the storage solutions themselves, a small amount of antioxidant was quantified. 0.4–0.8% of the initial additive amount present in the polymer before storage was thus found in the storage solution. This percentage of migrating Irganox 1010 increased as solvent polarity was decreased, but as the additive degradation in the solvent was certainly promoted by the most polar solvents, both effects might be balanced and the observed differences were thus not very significant (Table III).

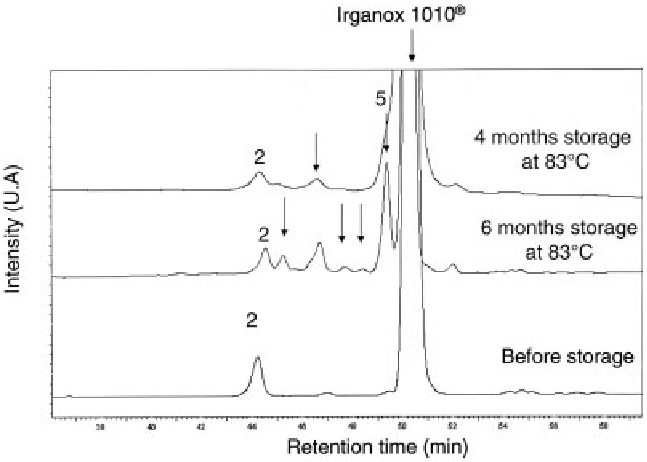

Figure 9 HPLC chromatograms of the TOPAS 8007 extractible for nonannealed sample and annealed samples. The detection is performed by an UV detector at the 280 nm wavelength.

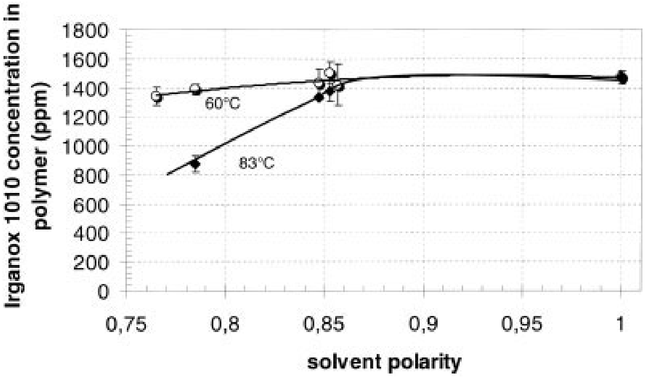

Figure 10 Evolution of the extractable amount of Irganox 1010 in TOPAS 8007 with the solvent polarity. Storage was realized at two temperatures 60°C and 83°C during 10 days.

As storage temperature was increased to 83°C, the effect of storage on additive depletion was much more significant even for the short storage times (10 days). In the case of storage in octanol, the additive depletion was ~ 40%.This was first due to the increase of the additive diffusion coefficient with temperature, which might be particularly important in our case because the new storage temperature was above the glass-temperature transition. Moreover, we have shown that polymer swelling was greater at 83°C, and this plasticization might significantly accelerate the diffusion process.

TABLE III
Percentage of the Initial Additive Amount Found in the Storage Solution

Solvent	% of migrated additive
Methanol	0.4
Ethanol	0.5
Propanol	0.7

10 days storage was realized at 60°C.

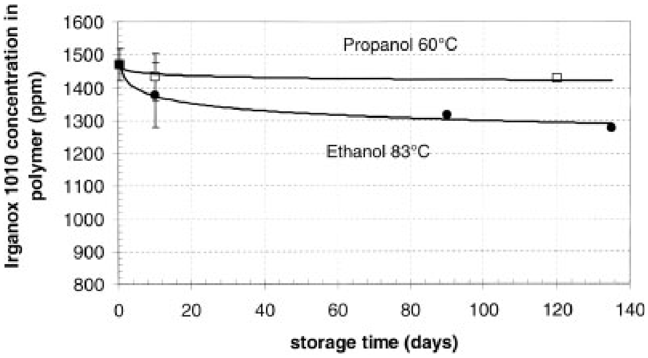

Figure 11 Evolution of the extractable amount of Irganox 1010 in TOPAS 8007 with time for samples stored in propanol (60°C) and in ethanol (83°C).

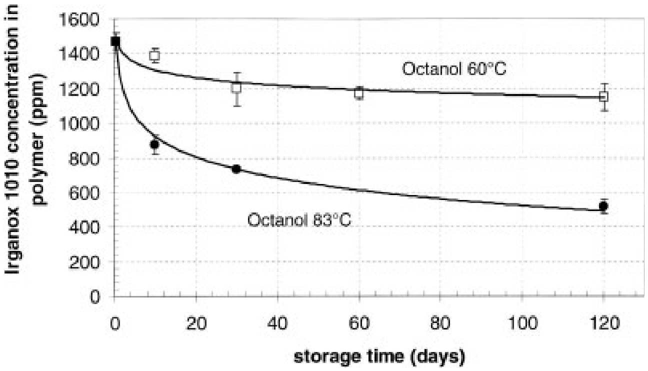

Figure 12 Evolution of the extractable amount of Irganox 1010 in TOPAS 8007 with time for samples stored in octanol. The storage was realized at two temperatures 83°C and 60°C.

At short storage times, the weak polarity of the solvent promoted thus additive depletion in the polymer. This was true too for long storage times. No enhanced degradation process of the additive in the polar storage solution or into the polymer swollen by the polar solvent that would continuously decrease the additive amount in the polymer had been observed (Fig. 11). For storage in propanol at 60°C, no variation of the amount of the additive in the polymer was put into evidence even after 4 months of storage. Another test was realized at higher temperature (83°C) in ethanol, a more polar solvent which was more susceptible of degrading the antioxidant. But after a slight decrease, certainly due to a migration phenomenon, we did not observe any sharp evolution due to a great degradation of additive. For the less polar solvents like octanol, a sharp decrease in Irganox 1010 concentration in the polymer was first observed, and then the Irganox 1010 concentration in the matrix reached a kind of equilibrium state that strongly depended on storage temperature. For storage times longer than 1 month, the amount of Irganox 1010 was indeed quite constant in the polymer and was higher for lower storage temperatures (Fig. 12): this was in agreement with a higher solubility of the antioxidant in octanol at higher temperatures. Equilibrium state of additive amount in polymer could occur because there was a very low additive degradation. The slow variations observed at long storage times might partly result from degradation of antioxidants in the polymer itself. The additive amount decrease was in fact quite equivalent to what was found for the ageing of the not immersed samples.

Additive depletion curve shape seemed thus to indicate that depletion resulted mainly from a migration process from polymer into solution (equilibrium states were reached). To check it, octanol storage solution was analyzed. Octanol containing a polymer sample was stored during 1 month at 83°C. It should be noted that the analysis was difficult to perform precisely because of the low additives concentrations in solutions (because of octanol high boiling point, it was indeed not possible to concentrate the solution by evaporating octanol without degrading Irganox 1010). We found that 25% of the amount of Irganox 1010 that was initially in the polymer before storage was in the storage solution, that is to say at least around 50% of the Irganox 1010 depletion in the polymer was due to a migration process. For the other percents, it might result from the additive degradation. Some degradation products of the Irganox 1010 were indeed found in the polymer after storage: extraction chromatograms showed the increase of the peak indexed 5 (Fig. 13) that was already observed for annealed, but not immersed polymer samples. This degradation product was present into solution too as shown by the storage solution chromatograms.

It was not easy to compare the COC behavior to that of other classical packaging polymers because it was very difficult to find analogue conditions of study: storage solutions (solvent, temperature, poly-

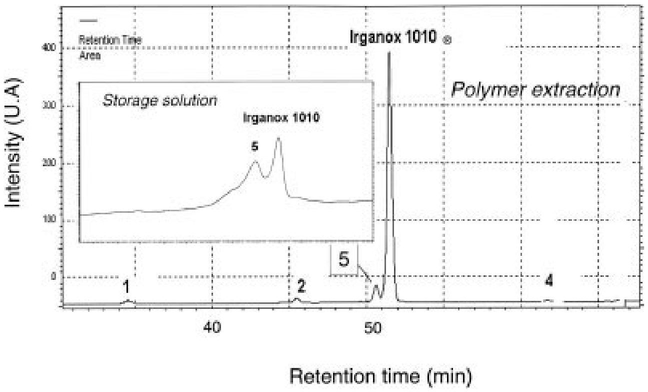

Figure 13 HPLC chromatograms of the TOPAS 8007 extractible for samples stored in octanol. The detection is made by an UV detector at the 280 nm wavelength. The chromatogram of the storage solution is given onto the first chromatogram.

mer surface, and concentration), polymer shapes and additive concentrations in the polymer were often not the same. For LDPE stored in water at 60°C, Gandek[7] showed an important influence of additive degradation in solution on the migrating rate and ratio, contrary to that shown by us. At 60°C, a two stage process was indeed observed: there was first a diffusion process the first 12 storage day, and pseudoequilibrium was reached (migration ratio of 6%). Then, additive depletion in water involved a further and continuous migration: after 2 months the migrating ratio reached the 20%. Migration with the COC stored in ethanol was much more limited than what was observed with other polyolefines. For ethylene–vinyl acetate films stored in ethanol at 49°C, Schwope et al.[12] observed indeed a quick and total migration of Irganox 1010 in only 1 day. For LDPE[13] (Irganox 1010 at 200 ppm) the migration after 2 weeks was almost total too.

CONCLUSIONS

By using some very aggressive storage conditions to simulate an accelerated ageing, we have shown migration phenomena between the polymeric material and the alcoholic liquid phase. Not negligible amount of solvent migrated through the membrane that should have affected the thermomechanical properties of the material. But this was the case for quite high temperature, long storage time, and not too much polar solvents. The swelling will favor the migration of phenolic antioxidant through the polymer into the solution, by lowering the barrier properties of the matrix, but this migration will be strongly influenced by the affinity of the migrant towards the liquid phase too. Low polarity solvents will favor a quick and great migration, and thus this kind of olefin material has to be avoided as primary packaging material as far as lipophilic formulations are concerned.

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