Approaches to Deal with the Issue of Plastic Packages and the Environment

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Abstract: Methods of treating the solid plastic waste are reviewed. The diffusion coefficients of toluene and benzyl alcohol in PET were determined from sorption experiments. For toluene, desorption (into water) experiments were also carried out and the diffusion coefficients were determined for various initial toluene concentrations in the polymer. The diffusion coefficients from the latter experiments were significantly lower than those determined from the sorption studies. In migration of toluene from the contaminated PET into water, a reduction of two orders of magnitude in the level of migration was achieved by sandwiching the contaminated PET between two layers of the virgin polymer. In another study, properties of Nylon 6/PE blends reprocessed at various shear rates were evaluated. The results showed that after minimum mixing of the blend obtained from a Nylon 6/PE laminate, the low oxygen permeability of the original film was preserved.

INTRODUCTION

Plastics are extensively used in packaging. They are used as primary packages, i.e., packages that come into intimate contact with products like food, pharmaceuticals, cosmetics, detergents and chemicals. They are also used as secondary packages, i.e., packages that are aimed at protecting fragile products against shock and vibration during handling and transportation. The most widely used polymers in primary packaging are different kinds of polyethylene (PE) like low-, medium-, high-density and linear low-density polyethylene (LDPE, MDPE, HDPE and LLDPE, respectively), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET), nylons and various copolymers. Polymeric foams of PE, PS, and PP and polyurethanes (PUR) are used in secondary packaging. About 30 % of the polymers are used for packaging applications. This utilization is still expanding for some polymers at a high rate of 12 % per year. In recent years, however, the environmental problem associated with the disposal of plastics in general and of plastic packages in particular has gained growing attention and concern. The main reason for this development stems from the increased awareness of the public of environmental issues and from the tightening of regulations and requirements imposed by

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the authorities. Due to their low density, large surface-to-volume ratio and bulkiness, plastic packages protrude and are visible from large distances. They are therefore blamed to be a major contributor to the pollution of the environment. It is also claimed that plastic packages are a major component in the municipal solid waste (MSW) stream which goes to landfills, in spite of the fact that all plastics contribute only about 4-7 % to the weight of the MSW (Ref. 1). The plastic and packaging industries have successfully dealt with the problem of plastic scrap, generated in the polymer converting plants, by incorporating a certain percentage of this scrap into the products. The major problem exists with the post-consumer used packages, the vast majority of which go to landfills. The common ways of treating the polymeric solid waste are *incineration, recycling, landfilling* and *pyrolysis.*

Incineration, burning the polymers (with or without other components) in order to generate steam, electricity or other forms of energy, is quite widely used in some countries and to a lesser extent in others. Polymers, being made primarily of organic compounds, possess high caloric values which can be utilized via burning. This method of dealing with the problem of solid polymer waste seems to be simple and straightforward. It is, however, not free of problems. Many polymers like PVC, poly(vinylidene chloride) (PVDC), PUR and other halogen- and nitrogen-containing polymers can form toxic substances upon burning and cause health hazards or pollute the environment in a different way. Moreover, many polymers possess excellent properties after their first use and can be utilized for many different applications after this use. It is therefore the opinion of the present author that incineration of polymeric packages after being used once is a waste of resources. A more efficient way of utilization would be to incinerate the polymer only after several applications, when it lost much of its mechanical properties.

Recycling means to reuse the polymer forming the package for additional applications. This subject will be dealt with later in the paper.

Landfilling is still the most widely used method of getting rid of the MSW by transporting it to special sites where it is dumped. Because of the decreasing number and size of these sites all over the world, ways of reducing the amount of polymers (and especially of bulky plastic packages) in landfills are being sought.

Pyrolysis is the decomposition of polymers upon heating to relatively high temperatures (about 600-700 °C) in the absence of oxygen. Under these conditions, the polymers decompose to their monomers, oligomers and other organic substances which can be separated into various compounds. The monomers and oligomers are repolymerized while the other components are used for generating energy. This method is still underdeveloped and inefficient and its application is limited.

To diminish the problem of polymers in the MSW stream, several solutions have been proposed, the most widely accepted one comprises four 'R's: *reduce, reuse, recycle* and ***recover***. The meaning of *reduce* is to diminish the amount of polymer in every package. New designs enabled the reduction in the polymer weight in packages. Also, refills were developed in which the consumer buys, in his first purchase, the product in a container. In subsequent purchases, he/she can buy the product in a plastic bag and transfer its content to the container. In *reuse,* multi-trip packages are meant. This method is commonly used with glass bottles. Plastic containers are much more difficult to clean. They may absorb organic compounds which are difficult to get rid of. They are therefore very seldom used as multiple-trip packages for food products. However, some European countries have initiated programs in which plastic beverage bottles are thoroughly cleaned and then reused. The term *recycle* is the same as explained before. *Recover* stands for the possibility of recovering energy namely, the same as *incineration* mentioned before. An additional approach taken by various scientists in order to ease the problem of solid polymer waste was to develop polymers that degrade under specified conditions. These include *photodegradable* and *biodegradable* polymers. These polymers are supposed to decompose during a relatively short time under the action of light (primarily the ultraviolet region of the sunlight) and of microorganisms, respectively. The author does not believe that these polymers could solve the problem of solid waste from plastic packages. They might assist in some areas like agriculture but not in packaging. To mention just several reasons for this attitude:

- In spite of their name, photodegradable and biodegradable polymers do not degrade easily, especially in landfills. The photodegradable polymers need sunlight and oxygen while the biodegradable polymers need microorganisms, oxygen and water in order to degrade. In landfills, only the outer surface layer is exposed to these conditions whereas the vast majority of the polymers are not, and therefore do not degrade.
- Polymers possess good properties after their first (and even additional) use and could be reused for many other applications. Photo- and biodegradation is therefore a waste of valuable resources.
- If photo- and biodegradable polymers are mixed (even at low concentrations) with other, nondegradable polymers, the latter cannot be recycled.
- The storage time and conditions of different products are not always known. Packages made of degradable polymers may degrade prematurely and cause severe damages.

The present paper deals with the subject related to *recycling* only.

Most of the polymers are incompatible and lose many of their mechanical properties when mixed together. Therefore, post-consumer plastic packages can be reused either after a separation process or as mixed plastics. Various methods for separation (of different polymers or of polymers and other materials) have been described in the technical literature. These methods include separation processes based on differences in density, electric or magnetic properties, or spectral absorption characteristics (like absorption in the infrared region). Without separation, the mixed polymers can be used for relatively low-cost products only, unless the properties of the mixture could be improved, primarily by using compatibilizers.

To ease the separation process, a coding system was developed in which the most widely used polymers in packaging are coded using numbers (Fig. 1).

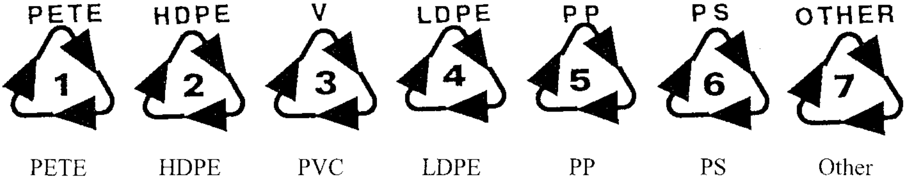

Figure 1: Codes of most important polymers used in packaging

Single-Component Systems

The two most widely used polymers in plastic containers are HDPE and PET. HDPE is used primarily for milk, motor oil and detergent containers. PET is used in bottles for carbonated and noncarbonated beverages and for edible oil as well as in jars for many food products. In most countries, post-consumer polymers are not allowed by regulatory agencies to be used in packaging aimed at direct contact with food (this subject is under reconsideration in several countries) because of the risk that possible contaminants might migrate into the food and pose a health hazard. An additional problem with reclaimed polymers is the lack of a steady supply and a cost-effective outlet. HDPE is a relatively cheap polymer. In a study on the properties of virgin HDPE/recycled HDPE blends, we found almost no change in the melt viscosity of the polymer (Ref. 2). There appeared to be only minor changes in the number- and weight-average molecular weights and in mechanical properties. Thus, the recycled polymer can be used in packaging applications other than food such as detergents, motor and lubricating oils.

PET is a very important food packaging material with far-ranging applications (Ref. 3). It is a relatively expensive polymer with very good properties, even after its first use. Although some programs to recycle PET have been developed and implemented in various countries, the percentage of the recycled PET is still low and most of the used packages go to landfills. Moreover, the vast majority of the recycled polymer is used for relatively low-cost products like fillers in sleeping bags and fibers for low-cost carpets. A proper, cost-effective, application for the recycled polymer, if found, would result in a great economic benefit. In addition, the contribution of PET to the plastic waste in landfills could be diminished.

One of the possibilities is to consider using recycled PET in a multilayer structure for food-packaging applications, provided that the level of the contaminant migrating into the food would be below the limits defined by the appropriate authorities. In order to determine the extent of migration, the diffusion coefficients of various organic liquids in PET are required. Organic liquids represent the "worst case" contamination that may be difficult to remove in recycling processes.

Migration from polymers is a diffusion process. Therefore, Fick's First and Second Laws apply (Ref. 4). Migration studies are normally carried out until equilibrium is reached (Fig. 2).

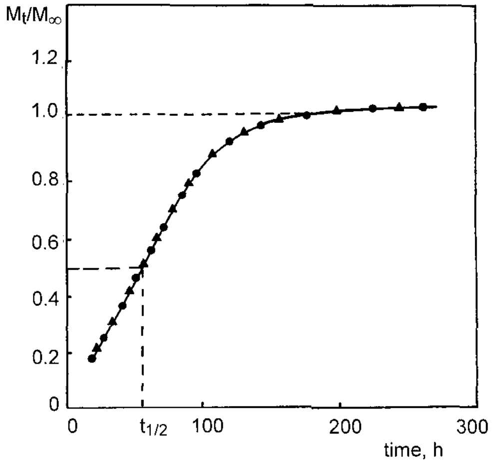

Figure 2:
Typical migration curve and a method of determining the migration half-life time, $t_{1/2}$ (M_t and M_∞ are the amounts migrated at time t and at infinite time, respectively)

Two solutions were described for analyzing migration from an infinite slab into an unlimited amount of simulant (Refs 5-7):

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi l^2}\right)^{0.5} \qquad \text{for short-term migration} \qquad (1)$$

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{l^2}\right) \quad \text{for long-term migration} \qquad (2)$$

For short-term ($M_t/M_\infty < 0.6$) and long-term ($M_t/M_\infty > 0.6$) migrations, plots of M_t/M_∞ vs $t^{1/2}/l$ and $\ln(1 - M_t/M_\infty)$ vs t/l^2 (l is half the slab thickness) should give straight lines (see Eqs 1 and 2) from which the diffusion coefficient, D (actually, the "effective diffusion coefficient"), can be determined based on experimentally obtained data. Another possibility is to use the "process half-life time", $t_{1/2}$, (M_t/M_∞=0.5, see Eq. 3) (Ref. 8).

$$D = 0.0492\, l^2/t^{1/2} \qquad (3)$$

A part of the present paper summarizes our work on diffusion and sorption of organic liquids in PET. Subsequent migration into water of a representative pollutant, toluene (widely used in adhesives and dyes), from the contaminated PET, unsandwiched and sandwiched between two layers of virgin PET, was investigated. The aim was to determine the extent to which sandwiching of a contaminated polymer between layers of the virgin material could lower the level of migration. In addition, the effect of initial toluene concentration in PET on its diffusion coefficient was evaluated.

Polymer Blends

In another study, we investigated properties of PE/Nylon 6 blends (Ref. 9). Polyethylene is a very good water barrier and has good heat-sealing properties. Polyethylene is, however, a poor oxygen and aroma barrier, which are properties important in food (as well as other products) packaging. Nylons are very good oxygen and aroma barriers but are sensitive to moisture, are poor water-vapor barriers and possess poor sealing properties. A two- or multilayer structure of these two polymers makes it possible to produce bags with desired properties. Polyethylene and Nylon are, however, incompatible and therefore these packages cause recycling problems. The aim of the work with the Nylon/LDPE blends was to determine the properties of the blends and to seek ways of improving their properties, either by using appropriate processing techniques or compatibilizers. As far as processing techniques are concerned, we investigated conditions of minimum and extensive mixing. Minimum mixing was achieved by compression molding or by roll milling for short periods. Extensive mixing was achieved in a Brabender mixer or in an extruder. The results of this study were reported elsewhere (Ref. 9).

EXPERIMENTAL

Materials

Thermoformed trays from amorphous PET (APET) were obtained from MCP Performance Plastics Co. (kibbutz Hamaapil, Israel). Biaxially oriented PET (BPET), was obtained from blow-molded bottles manufactured by Amraz (Rishon Letzion, Israel). Organic test liquids were toluene, benzyl alcohol, heptane and propane-1,2-diol representing aromatic nonpolar, aromatic polar, aliphatic nonpolar and aliphatic polar liquids, respectively. Hence, these solvents represent a range of different organic liquids. Double- distilled, deionized water was used as a food simulant.

Methods

Most of the experimental procedures were described earlier (Ref. 10). The effect of initial toluene concentration on its diffusion coefficient in PET during desorption was determined from the data of migration into water. The PET was soaked in toluene for different periods (determined from equilibrium absorption curves) to obtain the levels of 1/2 and 1/10 of the equilibrium sorption concentration. The change in the diffusion coefficient as a function of initial pollutant concentration was determined from subsequent desorption studies of toluene migration into water.

RESULTS AND DISCUSSION

For the aliphatic liquids, no sorption in PET (determined gravimetrically), or swelling (dimension measurements) could be detected, even after 30 days. Thus, the diffusion of these liquids in PET could not be determined. With the aromatic liquids, the average weight gain of APET, sorbed to equilibrium, was 11.4 ± 0.1 % with toluene and 21.7 ± 0.8 % with benzyl alcohol. The corresponding weight gains in PET were 9.5 ± 0.1 % for toluene and 13.5 ± 0.2 % for benzyl alcohol.

The sample length and width were about two orders of magnitude larger than its thickness and the amount of solvent was relatively large. Therefore, it was assumed that the system could be considered as an infinite slab immersed in an infinite medium. In this case, Eqs 1-3 apply. Figure 3 is a representative plot of M_t/M_∞ versus $t^{1/2}/L$ for toluene in BPET. Similar curves were obtained for benzyl alcohol and APET. It can be seen that a straight line was obtained up to $M_t/M_\infty = 0.5$.

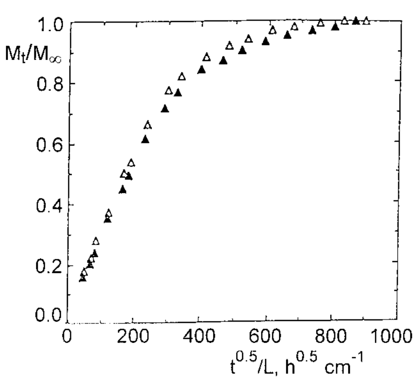

Figure 3: M_t/M_∞ vs $t^{1/2}/L$ for biaxially-oriented PET in toluene at 34 °C. (Different points indicate different samples.)

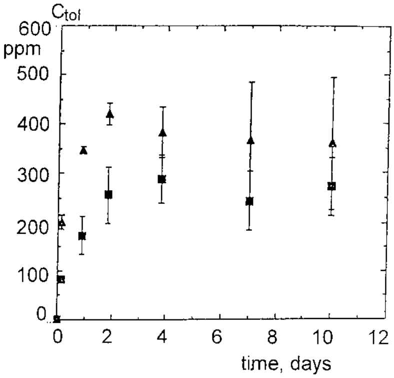

Figure 4: Concentration of toluene desorbed from amorphous PET placed in water. (Different points indicate the averages of three samples for two different controls.)

Table 1 summarizes the diffusion coefficients calculated from the short-term ($M_t/M_\infty < 0.6$) and long-term ($M_t/M_\infty > 0.6$) sorption data for the two liquids in APET and BPET.

Table 1: Diffusion coefficients ($D \times 10^{-9}$ cm^2/s, 34 °C) derived from short-term and long-term sorption curves

System	From M_t/M_∞ vs. $t^{1/2}/L$ (for $M_t/M_\infty < 0.6$)	From $-\ln(1-M_t/M_\infty)$ vs. t/L^2 (for $M_t/M_\infty > 0.6$)
APET / toluene	2.9 ± 0.7	1.5 ± 0.3
APET / benzyl alcohol	15.0 ± 2.7	1.9 ± 0.7
BPET / toluene	0.43 ± 0.03	0.16 ± 0.03
BPET / benzyl alcohol	0.30 ± 0.04	0.19 ± 0.01

It is evident from the table that the diffusion coefficients for APET were significantly higher than those for BPET. The diffusion coefficients calculated from the process half-life time (Eq. 3) were much closer to those calculated from the short-term than from the long-term sorption data. The percentage of crystallinity in BPET (as determined by DSC) was 33 % compared with 3 % in APET. The much higher degree of crystallinity together with orientation can explain the lower diffusion coefficients obtained in BPET. It should be mentioned that the diffusion coefficients of toluene in PET determined in our study are significantly higher than the values reported for diffusion coefficients of organic gases in PET. The present values, however, refer to liquid toluene. It was reported (Refs 11,12) that the partition coefficient (the ratio between the equilibrium migrant concentration in the polymer and that in the contacting phase) increases and the diffusion coefficient decreases with decreasing migrant concentration. The values reported in the present paper can therefore be considered as the upper limits for diffusion coefficients of toluene in PET. In Fig. 4, the concentration of toluene that migrated from the equilibrium-sorbed PET samples, which were then directly immersed in water, is shown as a function of time. An equilibrium concentration of 380 ± 80 ppm of toluene in water was reached after 10 days.

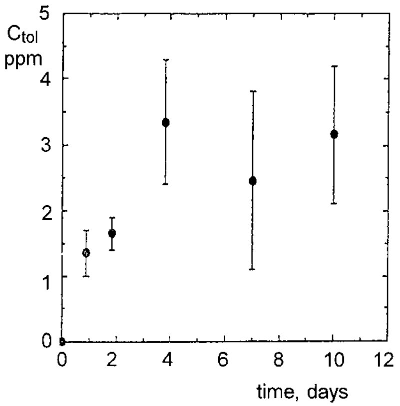

Figure 5: Average concentration of toluene desorbed in water from two sandwich PET samples

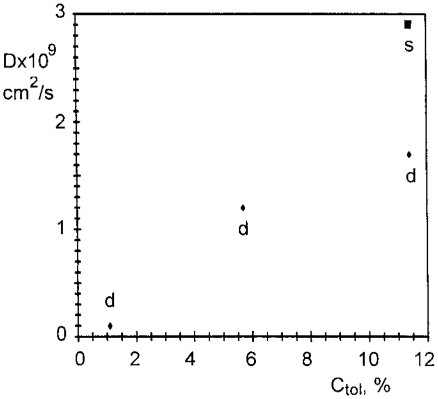

Figure 6: Effect of initial toluene concentration in PET on its diffusion coefficient in migration studies
(s sorption, d desorption)

In Fig. 5, the concentration of toluene that migrated into water from the sandwich (containing the same amount of toluene in the middle layer) is shown as a function of time. In the latter case, an equilibrium concentration of about 3 ppm toluene was found in water after 10 days of migration. Thus, a reduction of two orders of magnitude was achieved by burying the contaminated PET between two layers of the virgin material. As was pointed out earlier, these results refer to the worst case that is very unlikely to happen in actual situations. In real life, the level of contamination in recycled materials would be much lower. It can therefore be anticipated that for low concentrations of pollutants in packages made of recycled polymers, the propensity of the pollutants to migrate into the product contained would be low. In order to evaluate the effect of pollutant concentration on its migration, the study was repeated with one half and one-tenth of the equilibrium sorption values.

The diffusion coefficients of toluene in PET determined from the migration studies into water were lower than those determined from the sorption experiments. The diffusion coefficient determined from the migration studies decreased significantly with the decrease in initial toluene concentration in PET (Fig. 6). Even one-tenth of equilibrium sorption is considered to be a much higher pollutant concentration than that anticipated in actual situations. These results support the assumption that at low levels of pollutant found in recycled polymers, sandwiching of the latter between layers of virgin polymers might be a possible solution. However, additional studies, with even lower migrant concentrations in the polymer are required in order to better understand the system for prediction purposes.

In the LDPE/Nylon blend studies, we have shown (Ref. 9) that the permeability to oxygen of a film prepared from a reprocessed laminate depended on the reprocessing conditions. The film that was prepared from a least processed blend had almost the same barrier properties as an original multilayer, high-gas-barrier film. The reason for this good barrier property stems from the fact that the layered structure in the original (as received) multilayer film also remained in the film prepared from the least reprocessed material as was shown by scanning electron microscopy (Ref.10). On the other hand, during extensive mixing, the Nylon was uniformly spread as a separate phase in LDPE (Ref. 10), thus losing its continuity and barrier properties. Blends of recycled polyethylene/Nylon that were least processed can therefore be used as an inner layer in a multilayer structure with good gas-barrier properties. Such uses could be feasible provided that the reprocessed material is not contaminated to high levels and can be shown to be safe for indirect contact with food.

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