

Barrier Properties of a Thermotropic Liquid-Crystalline Polymer

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ABSTRACT: A developmental thermotropic liquid-crystalline polymer (TLCP) made by Eastman (trade name LN001) was used for barrier property studies. This material is a highly aromatic TLCP with a T_m of 332°C. A permeability study was carried out to determine the chemical resistance of the TLCP. The permeability of methanol and toluene through a membrane of the TLCP was studied using a two-part cell and a gas chromatograph to monitor the flux.

The membranes of the TLCP and LDPE (as control) were made by compression molding. Both solvents had higher permeability through LDPE than TLCP and that of toluene was higher than that of methanol. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2457–2463, 2003

Key words: liquid-crystalline polymers (LCP); barrier; gas permeation; membranes; glass transition

INTRODUCTION

Liquid-crystalline polymers (LCPs) are a relatively new family of polymeric materials that have potentially a wide range of applications. This class of materials arose out of the need to modify conventional polymers to achieve high performance character. In 1956 Flory suggested that polymers containing long rigid units could form anisotropic ordered solutions. Generally an LCP forms a partially ordered state on heating (thermotropic LCP) or in solution (lyotropic LCP). The part of the polymer molecule that causes liquid-crystalline properties is called a mesogenic group.¹ Liquid-crystalline polymers may be aromatic polyesters, polyester carbonates, polyester amides, polyester imides, or polyazomethines.²

The liquid-crystal structures can be used as building blocks to form a polymer. These anisotropic building blocks can be copolymerized with traditional flexible monomers, and the insertion of these flexible spacers in the main chain may be used to control the melting point and glass-transition temperature of the LCP.³

Thermotropic liquid-crystalline polymers (TLCPs) are a form of liquid-crystal polymers in which the molecule exhibits the liquid-crystalline phase only within a particular temperature range. This range is defined as existing between the melting point T_m or glass-transition temperature T_g if T_m is absent, and an upper transition temperature, $T_{lc \rightarrow i}$. At this tempera-

ture the liquid-crystalline phase reverts to an isotropic liquid having a high temperature stability.⁴ Lyotropic liquid-crystal transitions on the other hand, occur with the influence of solvents, and not by a change in temperature. Lyotropic mesophases occur as a result of solvent-induced aggregation of the constituent mesogens into micellar structures.⁵ Generally lyotropic liquid-crystals contain lyophilic (solvent-attracting) and lyophobic (solvent-repelling) ends. Lyotropic systems are particularly of interest in liquid-crystalline polymers, given that solvent addition is an important means of reducing the crystalline melting point to a level⁴ that is of practical use.

LCPs have found applications in the enhancement of crystallization of some semicrystalline thermoplastics, and when blended with other thermoplastics in small amounts, have acted as a processing aid by decreasing the viscosity of the blend.^{6,7} They have a very high modulus and excellent thermal properties, and they have generally been known to greatly increase the mechanical properties of certain thermoplastics.^{1,8} The high cost of the LCPs has made them ideal as a reinforcing component in a blend with another thermoplastic.⁷ Another attractive property of LCPs is the high chemical resistance against many common organic solvents such as alcohols, acids, and other hydrocarbons,^{4,6,9,10} but this has received less attention in the literature, and has been demonstrated in only a limited number of studies. One of the measures of the chemical resistance of a polymeric material is its permeability to vapors of various substances. The permeability of a polymeric film is of importance in the field of packaging where the film should possess very low permeability to oxygen, water vapor, carbon

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dioxide, and aromatic substances. Unlike conventional barrier materials such as EVOH and polyamide, LCPs do not have a high permeability in the presence of water and alcohols. In many applications where hydrocarbon-methanol mixtures are involved, the permeability of these conventional barrier materials is increased.^{11,12} The objective of this study was to investigate the barrier properties of a developmental TLCP by comparing its permeability to that of commodity LDPE by use of vapors of toluene and methanol.

THEORY OF PERMEABILITY

Permeation through polymer films is thought to occur through two distinct processes: solubility and diffusion.¹³ The former is a thermodynamic process, whereas the latter is a kinetic process.

The permeability coefficient is given by¹⁴

$$P = DS \quad (1)$$

where P has units of (mass·film thickness)/(area·time·pressure).

Hence the permeability coefficient can be determined if the diffusion coefficient and the solubility are known. It can also be determined from the flux J , if the pressure gradient across the film thickness is known.¹⁴ However, it is generally difficult to measure the pressure gradient across the membrane. Because P is directly proportional to J , the normalized flux is an indication of the barrier property. In addition, the flux J does represent the reality when a polymeric film is used for packaging. We will therefore use the normalized flux as a measure of the permeation of vapor through the polymer films.

To find a solvent to be used as a permeant, the first part of the study would involve the investigation of the solubility behavior of the TLCP material. The selection criteria for the solvents were based partly on past research work as well as on conventional criteria outlined in various texts. Generally solvent selection is dependent on the following factors: (1) polarity, (2) cohesive energy density, (3) solubility parameter, and (4) hydrogen bonding and dipole moment. The polarity of the solvent is important because it determines whether the substrate can be dissolved as a result of the action of the solvent. It is important that the polarity of the solvent and the solute be similar to achieve solubility. In the case of the TLCP material, there is no information on the presence of polar groups within its structure. Hence both polar and nonpolar solvents were included to investigate the solubility of the material.

The cohesive energy density (CED) is defined as the energy required to separate the molecules in 1 cm³ of liquid, that is,¹⁵

$$\text{Cohesive energy density} = \frac{\Delta H_v}{V} \quad (2)$$

where ΔH_v is the molar heat of vaporization in calories, and V is the molar volume in cm³. Usually the CED should be high for solvents that easily dissolve the substrate material. For very nonsoluble substrates this value is nonexistent or very low. For polymers the CED is a measure of its polarity and of the amount of energy forcing the chains together.¹⁶ In the case of the TLCP material used in this study, the CED values in various solvents have not been determined, and hence this criterion could not be applied in the solvent selection procedure.

The solubility parameter is related to the CED by the expression

$$\delta = \left(\frac{\Delta H_v}{V} \right)^{1/2} \quad (3)$$

where δ is the solubility parameter in cal^{1/2} or MPa^{1/2}.

Solvents that possess similar solubility parameters should be miscible and mix freely because of their similar internal cohesions. Hence the value of δ is used quite often to predict the miscibility of solvents or polymers.¹⁵ In the case of polymers, it is often necessary to determine the solubility parameter experimentally on the basis of the solvent or solvent mixture that is used to dissolve the polymer.¹⁵

To predict the solvent's compatibility with the TLCP, the solubility parameter of TLCP material in the various systems needs to be known or determined. There is no known documentation of the solubility parameter of the TLCP in the various solvent systems. The TLCP used in this study is essentially a polyester material, made up mostly of aromatic components. A small amount of aliphatic components may exist. The solubility parameters would differ for each of the components constituting the TLCP.¹⁷ However, if the components of this TLCP are known, then one could make better predictions toward their solubility in the various available solvents.

Sometimes when a solute and a solvent having similar solubility parameters are brought together, they still do not dissolve. This is attributed to the high intermolecular forces in one of the components. Hydrogen bonding is one such intermolecular force where the attraction between the two like molecules is higher than the attraction between the molecules of one component and the molecules of the other. In the case of polymer solubility, even if the solubility parameters of the solvent and polymer are widely differing, solubility can still be achieved depending on the intermolecular forces attributed to hydrogen bonding. With the TLCP material used in this study, this criterion was not applicable, given that the polymer structure shows no evidence of hydrogen bonding.

Among the LCP families, it is generally understood that lyotropic LCPs are the types that can be dissolved

in suitable solvents, followed by casting into thin films. However, to dissolve the thermotropic LCP supplied by Eastman, it was thought that the use of plasticizers would be ideal because they could act as a solvent as well as a compatibilizer. Moreover, a plasticizer acts as a lubricant in the host matrix. Hence it is expected that plasticization would produce interesting features in the behavior of liquid-crystalline polymers.¹⁸

It has also been established that some chlorinated hydrocarbons can dissolve TLCPs to a certain extent. Some of these solvents are DMF (dimethylformamide), NMP (*N*-methylpyrrolidone), THF (tetrahydrofuran), CHCl_3 (trichloromethane)-acetone mixture, CH_2Cl_2 (dichloromethane), methanesulfonic acid, and concentrated H_2SO_4 (sulfuric acid). Some TLCPs have been successfully dissolved in halogenated solvents like CH_2Cl_2 and CHCl_3 -acetone mixture,^{19,20} and subsequently cast into a brittle film.¹⁹ Other solvents that have been used are *o*-dichlorobenzene²¹ and pure CHCl_3 .²²

EXPERIMENTAL

Solubility studies

The TLCP used in this case was a developmental grade from Eastman of Tennessee, referred to as LN001. A DSC plot of the LCP showed that it has a glass-transition temperature T_g of 95°C and a melting point T_m of 332°C. With the high melting point of the TLCP, we can assume that it is wholly aromatic and has very few aliphatic spacers. The LDPE used was Petrothene NA95200 from Equistar Chemicals (Houston, TX). This material is a branched type of LDPE with a broad molecular weight distribution. It has a reported melt index of 2.0 g/10 min and a T_m of 120°C.²³ The TLCP obtained was in pellet form and after initial trials with the pellet form for solubility studies, it was decided to reduce the size of the pellet to increase available surface area. For this purpose, various types of mills were tried. These included jaw crushers, ultra-centrifugal mills, and disc mills. The milling service was provided courtesy of Glen Mills of Clifton, NJ.

For the solubility studies, a reflux setup was used where about 0.1 g of the TLCP in crushed form was added to about 20 mL of the particular solvent being studied. The flask was then heated and temperature and any visual changes were recorded. A magnetic stirrer and a stir bar were used to agitate the liquid in the flask while heating the charge. The classes of solvents used in this study were plasticizers (dibutyl phthalate and dioctyl phthalate), glycols (triethylene glycol and triethylene monomethyl ether), chlorinated hydrocarbons (chloroform), alcohols (methanol and benzyl alcohol), and other solvents (trifluoroacetic acid and dichloroacetic acid). From the reflux experi-

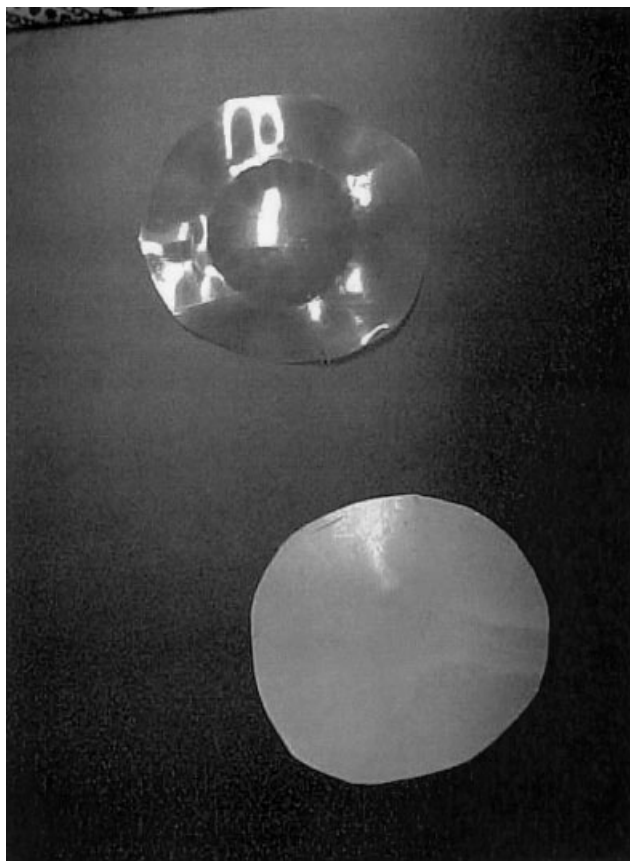


Figure 1 Compression-molded membranes of TLCP (left) and LDPE (right).

ments, most of the solvents showed no significant dissolution of the TLCP material; instead, the solvents tended to degrade. Certain conclusions could be drawn on the basis of the observations. The TLCP neither reacted nor dissolved in the plasticizers, that is, DOP and DBP. At elevated temperatures, the DOP and DBP were seen to degrade and change color. Similarly with TEG and its derivative TEGME, it was observed that the solvent refluxed without really affecting the TLCP. It was observed that some of the solvents did swell the LCP slightly; however, the initial interest was primarily to find a solvent that could dissolve the LCP. Hence no measurements were made of the amount of solvent absorbed.

Permeability studies

The solvents that were selected for the permeation study were methanol and toluene. The TLCP and LDPE materials were compression molded into thin films to obtain samples that could be used as membranes (Fig. 1). The compression-molding press was a model 30-1010-2TMX from Wabash of Wisconsin. This press was capable of a maximum load of 30 tons. The top and bottom platen temperatures can be individually controlled, and the press is equipped with a timer to control the total cycle time. The films were observed

visually for defects such as pinholes and microcracks^{13,24,25} because these could allow flow of permeant through the membrane. The presence of any pinholes would have resulted in unusual spikes in the concentration measurements. This was found to be the case when some samples containing pinholes were inserted in the apparatus and a high spike in the concentration was noted very early in the experiment. The thickness of the TLCP membranes was in the range of 228–355 μm (9–14 mil), whereas that of LDPE was about 355 μm (14 mil).

There are different types of cells that can be used for determining permeation of solvents through a polymer membrane. Among these are the following: (1) single chamber, (2) evacuated chamber, (3) pouch, and (4) two-part cells. The cell used in this study was a two-part cell that consisted of a charge chamber and a collection chamber. The cell design is in accordance with the specifications of ASTM Method F-739. The two parts of the cell are made of glass with sample ports on each part. These ports are provided with glass stoppers and on the collection chamber, there is a sampling port with a regular Teflon valve. The diameter of the cell is about 50 mm (2 in.) and the volume of each part is approximately 100 mL.

The monitoring method used in this study was a gas chromatograph. Other methods for monitoring have been documented. Gravimetric sorption studies can be carried out on uniform thickness solvent cast films. The advantage of this method is that both the diffusion and the solubility coefficients can be directly calculated²⁶ from the same experiment. Dish and chemical methods have also been discussed by Hennessy et al.²⁷

A 65 mm (2.5 in.) diameter circular section of the examined film was cut and prepared for testing. The thickness was measured at five locations on the film. These films were then secured in the permeation cell such that they formed a membrane between the two chambers of the cell. The membrane was secured between Teflon gaskets and the whole assembly was held together with two aluminum flanges and tightening bolts. This setup ensured a tight seal and prevented leakage. The permeant was loaded in the charge chamber, whereas the other side initially contained permeant-free air. The cell was closed and the concentration of permeant in the low concentration side was monitored periodically by a gas chromatograph.¹⁴ About 1 mL of the solvent was loaded into the charge chamber. To prevent the diffusion of the solvent into the atmosphere, the glass stoppers on the collection and charge chambers were closed and a seal was created by use of vacuum grease. The sample collection outlet on the collection chamber was also kept closed. Because the amount of liquid charged into the cell was relatively small compared to the volume of the chamber, the apparatus was oriented vertically by use of clamp stands. This ensured that the liquid

was spread out over the entire membrane area. The entire assembly was then kept in an oven where the temperature was maintained between 50 and 60°C. The reason for using the oven was to ensure that the solvent formed a vapor dense enough to allow detection by the GC given the small volume that was being withdrawn for sampling purposes (10 μL). Usually within a few hours, the solvent formed enough vapor. Samples of 10 μL were withdrawn periodically using a syringe and injected into the GC column. The peak obtained was recorded on the plotter.

Before starting to sample the vapor from the collection chamber, each solvent was run in pure liquid form through the GC column to obtain a standard peak for the solvent. The area under this standard peak can be correlated to the volume of the solvent used. For each experimental run, the setup was monitored over time and the temperature was recorded to maintain uniformity of the GC readings. The temperature of the oven was set so that the thermometer was in the range of 55.5–60°C. At this temperature, the vapor pressure of methanol is still below the atmospheric pressure. In the case of toluene, a slightly higher temperature could have been set; however, the LDPE membrane showed signs of softening that could lead to the leakage of the solvent through the membrane into the chamber, thus complicating data analysis. Hence, the system was kept at a constant temperature of 56°C to maintain a constant pressure under the assumption that permeant vapor obeys the ideal gas law. At periodic intervals, the vapor mixture from the collection chamber was withdrawn and injected into the GC column. The area under the peak was recorded. When a steady state was reached, as indicated by no further increases in peak area, the experiment was stopped and the system allowed to cool down for the next run.

It was also necessary to determine the normalized flux at each stage. For this, the procedure established by Murray¹⁴ was followed. In accordance with this method, standardization was carried out to obtain a factor, which is then multiplied by the ratio of the $\Delta\text{peak area}$ to Δtime . The factor was determined on the basis of about 10 μL of solvent being injected into the charge chamber, collecting the normal size vapor after about 30 min, and injecting this sample into a gas chromatograph. The calculation was carried out by use of the following equations¹⁴:

$$\text{Factor} = \frac{10 \mu\text{L} \times \rho_{\text{solvent}} \times \frac{24 \text{ h}}{\text{day}}}{A_{\text{peak}} \times A_{\text{sample}}} \quad (4)$$

$$J = \frac{\Delta A_{\text{peak}}}{\Delta t (\text{h})} \times \text{Factor} \quad (5)$$

where ρ_{solvent} is solvent density, A_{peak} is average standard peak area, A_{sample} is film sample area, and J is

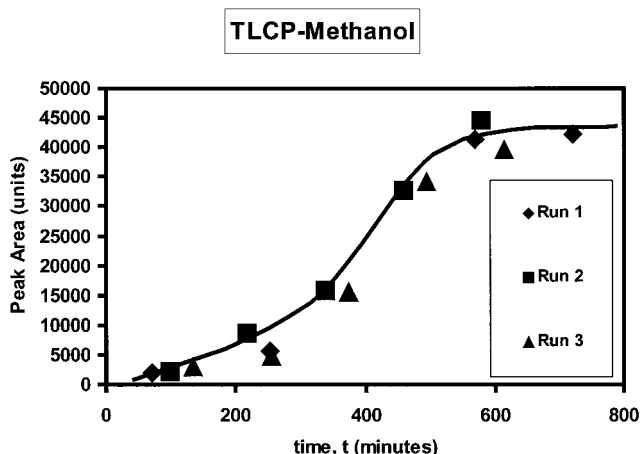


Figure 2 Peak area versus time for TLCP-methanol system.

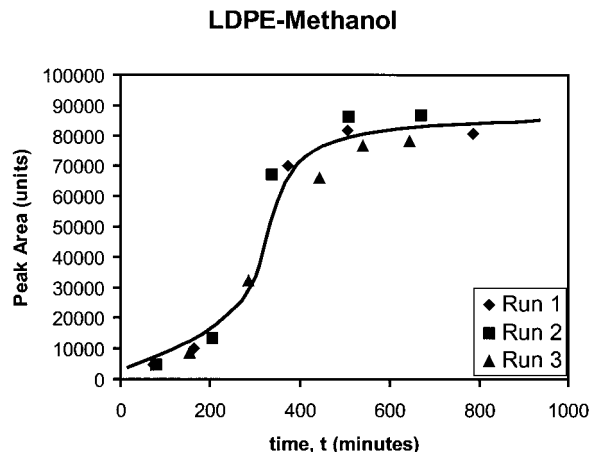


Figure 4 Peak area versus time for LDPE-methanol system.

normalized flux in $\text{mg m}^{-2} \text{day}^{-1}$. To further normalize this result over the barrier thickness, we can express this as $\text{mg mil}^{-1} \text{m}^{-2} \text{day}^{-1}$.

RESULTS AND DISCUSSION

The standard lines for the solvents, which show the relation between the peak area and a known volume of pure solvent in a liquid phase, were obtained. These standard lines were then used to estimate the volume of the solvent present in the vapor mixture drawn from the collection chamber by correlating the peak area with the standard plots. The plots in Figures 2 and 3 clearly show that the TLCP was permeable to both methanol and toluene. The permeability of toluene was an order of magnitude higher than that of methanol through the TLCP membrane. Both systems seemed to attain their maximum permeability in the 600- to 800-min range. However, it should be noted that the TLCP membranes were thinner (by 2.69 mils) for the toluene experiment; hence normalized results,

which take into account film thickness, need be used for comparison between the two systems.

Similarly, the experiments were repeated for LDPE-methanol and LDPE-toluene systems, which are shown as plots in Figures 4 and 5, respectively. A comparison of Figures 3 and 5 shows the permeability of toluene through LDPE is two orders of magnitude higher than that through the TLCP, whereas for methanol, the permeability through LDPE is only twice that of TLCP (Figs. 2 and 4). The shape of the curves is also of interest. In the case of methanol permeating either through TLCP or LDPE, the experimental results and the shape of the curve are qualitatively similar (Figs. 2 and 4). The S-shaped curve indicates that the initial flux is low, eventually becomes high, and then stabilizes at a certain equilibrium area. However, the shape of the curve is different in the case of toluene permeating through either TLCP or LDPE (Figs. 3 and 5). Here the curves show a very high initial flux rate, which eventually attains a constant value. A comparison of the relative permeability through each type of

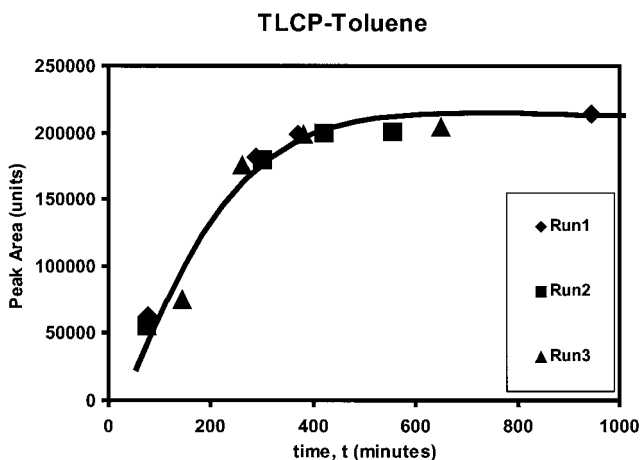


Figure 3 Peak area versus time for TLCP-toluene system.

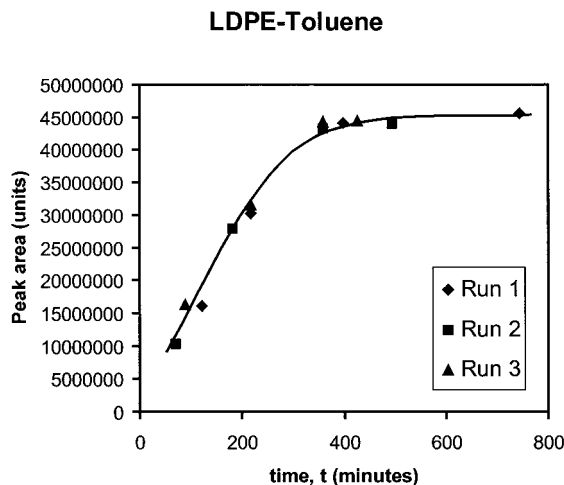


Figure 5 Peak area versus time for LDPE-toluene system.

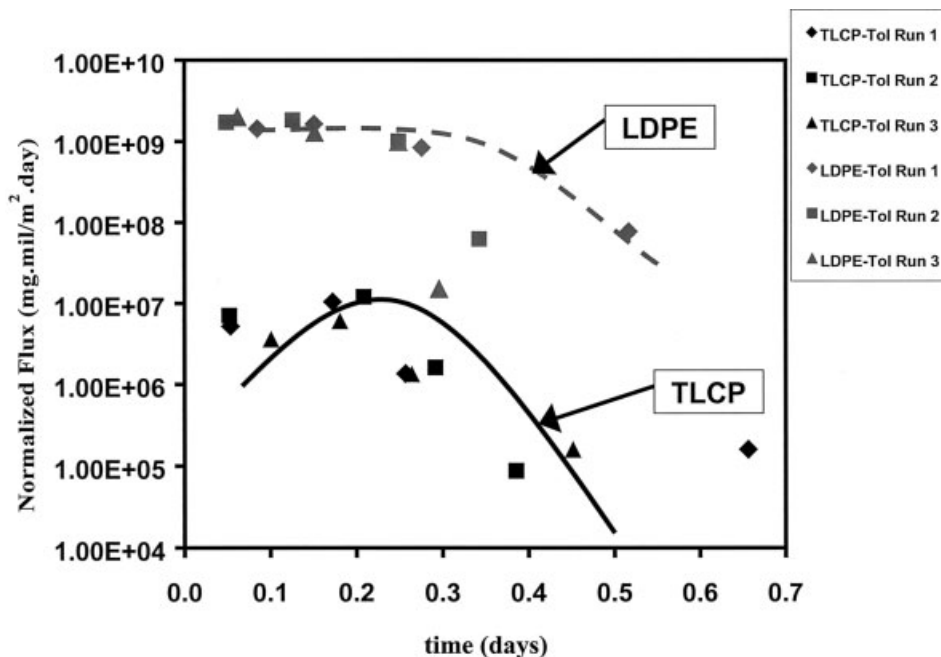


Figure 6 Normalized flux for TLCP–methanol and LDPE–methanol systems.

membrane shows that, in the case of TLCP, the permeability of toluene is higher than that of methanol (Figs. 2 and 3). The same observation is made in the case of LDPE (Figs. 4 and 5). This observation is not in agreement with the theoretical prediction that a smaller molecule (methanol, $M_w = 32.04$) would diffuse more easily through a membrane than would a larger molecule (toluene, $M_w = 92.14$). A similar behavior was reported by Hobbs et al.²⁸ It has been suggested that one of the reasons for this observation

is that the toluene might possess higher plasticization effects than methanol, one of which is swelling. The toluene, which is a bigger molecule, could swell the membrane to a greater amount than methanol over a long induction time. Another possible explanation is that toluene can dissolve LDPE more easily than methanol and at extended exposure to toluene at the elevated temperature of 50 to 60°C, the swelling and solubilizing effect could most likely be the dominating factor. This can be confirmed by the values of solubil-

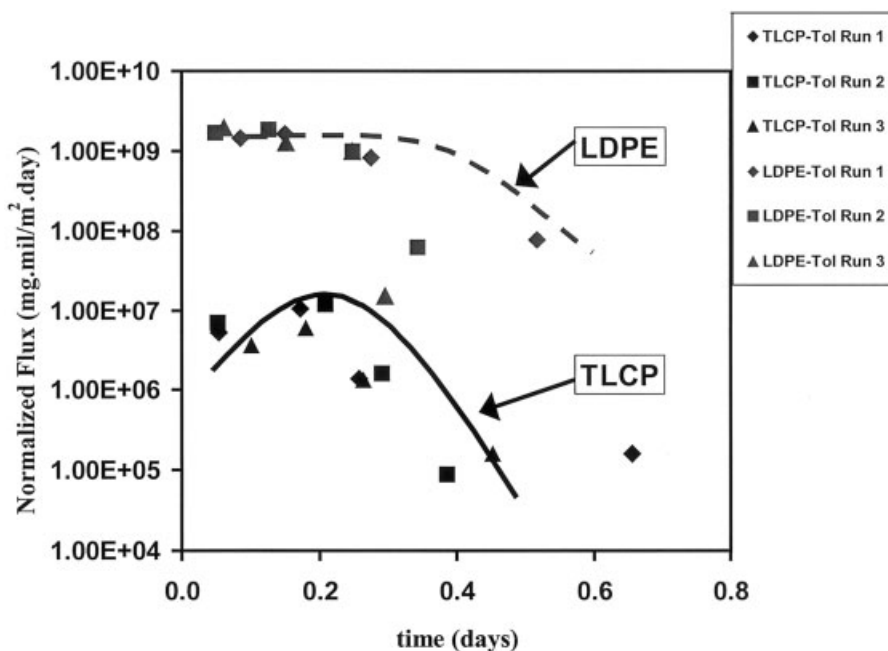


Figure 7 Normalized flux for TLCP–toluene and LDPE–toluene systems.

ity parameter data for polyethylene (PE) ($\delta = 8.0 \text{ cal}^{1/2}$), toluene ($\delta = 8.91 \text{ cal}^{1/2}$), and methanol ($\delta = 14.28 \text{ cal}^{1/2}$). The δ -values for toluene and PE are closer than those of methanol and PE.^{29,30}

To have a more objective comparison of the experimental results, it was necessary to calculate the normalized flux values, which were obtained by standardizing the gas chromatograph response. From Figures 6 and 7, we observe that the normalized flux is generally high at the beginning of the experiment and then decreases as the experiment progresses. In both the methanol and toluene systems, the decrease in flux is attributed to the reduction of the concentration gradient. As the permeant gas passes from one side of the membrane to the other, there is a decrease in the concentration gradient in the positive direction. This decrease reduces the driving force for diffusion in the positive direction, the positive direction in this case being from the charge side of the membrane to the collection side.

In the case of the toluene systems, this decrease in flux appears to occur sooner than in the case of the methanol systems. The flux for both solvents through LDPE is higher than that through TLCP. Also, the flux for toluene is higher than that for methanol through both membrane materials.

CONCLUSIONS

From this study, we have observed and confirmed that wholly aromatic TLCPs are highly resistant to solubility in many common organic solvents. However, when molded into thin membranes and subjected to permeation studies, there are indications of vapor permeating through the membranes. In our case, both toluene and methanol permeated through the membrane. However, the TLCP used in this study showed a considerably lower permeability than that of a commodity LDPE to vapors of toluene and methanol. The toluene had a permeability that is about one order of magnitude higher than that of methanol. This behavior was also observed in the case of the LDPE control film, although the increase in permeability of toluene over methanol is three orders of magnitude. Further investigation of the TLCP permeability should account for the temperature effect, given that permeability is strongly dependent on the temperature of the system.¹⁶ The results of such studies would help in making the determination on the suitability of this TLCP as a barrier material against various chemicals.

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