

Permeability of Semicrystalline Polymers to Toluene/Methanol Mixture*

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Received 24 September 2002; accepted 12 February 2003

ABSTRACT: In this article, we analyze the effect of the alcohol content in gasoline on the permeability of four semicrystalline polymers used in automobile fuel systems. More specifically, we are interested in the methanol/toluene mixture as a "binary" model of a complex gasoline to understand the selectivity brought about, in front of these solvents, by the nature of the polymer. We developed a permeation cell coupled to a chromatograph to analyze the composition of escaping toluene and methanol. These experiments allow us to demonstrate the strong "positive synergy" that exists between the flows of the methanol and the toluene when they are mixed, compared to the flows of these solvents on their own. This phenomenon is notably highlighted on polymers of very different kinds (PA12, PVDF,

HDPE, EVOH) and, in light of recent theoretical developments, we can consider that this property is general, because this "positive synergy" is a consequence of the evolution of the solubility of the mixture of solvents in the polymer film, and more particularly, of the highly positive value of the Flory-Huggins interaction coefficient between methanol and toluene. These experimental data allow one to better understand and predict the permeability behavior of the polymers in front of complex gasolines. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 676–682, 2004

Key words: barrier, films, gas permeation, chromatography, diffusion

INTRODUCTION

For over 20 years polymer materials have been successfully used for the fuel system in automobiles. One typically finds materials such as polyethylene for the tank and polyamide 12 (PA12) for the fuel lines. The fuel system must respect criteria of impermeability to the gasoline vapors. The quantity emitted must not exceed certain limits, and the maximum level is defined in the framework of regulations on evaporative emissions. Since the mid-1990s, air pollution reduction laws, notably in the United States, have imposed steadily-decreasing vapor emission levels. This has led car manufacturers to optimize the impermeability performances of the structures, which means that tank structure has evolved a great deal. Permeability can be sharply reduced by a surface treatment of the wall with polyethylene.^{1,2} Another method consists of introducing a barrier material into the polyethylene layer. This is done by mixture³ or by coextrusion to form a multilayer structure.⁴ The barrier materials are classically polyamide or an ethylene vinyl alcohol copolymer (EVOH).² In the fuel lines, PA12 is combined

in multiple layers with EVOH but also with fluorinated polymers.⁵

The permeability of the polymers is also strongly dependent on the nature of the gasoline. The composition of gasolines for the automobile is constantly evolving, and also varies from one country to another. The next feature is the introduction of oxygenated compounds in the form of alcohols such as methanol or ethanol. The proportion is variable, and can range from a low percentage in the United States and Europe all the way to fractions greater than 20 or 30% in some countries. The impact on permeability is significant, because the presence of alcohol reduces the impermeability of a large number of supposedly "barrier" polymers.⁶ This results in an increase of emissions from the car's fuel system, and can put the choice of certain materials and structural designs back into question.

In this article, we analyze the effects of the alcohol content in the gasoline on the permeability of four semicrystalline polymers used in the fuel system. For this purpose we developed a permeation cell to study the flow of solvent that crosses a polymer film. With these low-thickness samples, the stationary phase can be attained within relatively short periods, and the flows are rather high. This is an advantage compared to the tubes and tanks for which the substantial thicknesses entail increased measuring times and reduced precision. To simplify the analysis while retaining the most important parameters, we opted for a model

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This is an emended version of the article originally published in *J Appl Polym Sci* 2003, 90, 2727–2733.

gasoline. This is a miscible mixture of two organic liquids—toluene and methanol. Toluene represents the family of aromatics, and methanol was chosen because it is the most influential alcohol.⁶ The cell is coupled to a chromatograph to analyze the composition of escaping toluene and methanol. The method is described in the first part, and then the results for each of the polymers are presented. The influence of the composition of the toluene/methanol mixture is discussed. Finally, we conclude by proposing a theoretical interpretation of the results.

EXPERIMENTAL MEASURES

Samples

Four polymers were tested in this study: a polyamide-12 (PA12), a polyvinylidene fluoride (PVDF), a high-density polyethylene (HDPE), and an ethylene vinyl alcohol copolymer (EVOH). PA12 is a polymer that has been used for several years for the fuel line in the fuel system of cars. PVDF is a semicrystalline polymer with an excellent chemical resistance that constitutes a very good barrier to certain solvents. HDPE is a polymer that is both inexpensive and offers very good resistance to polar solvents. Finally, EVOH is a polymer known to be a barrier to gases and organic vapors. None of the polymers used contain any plasticizers. The first three (PA12, PVDF, and HDPE) are standard grades for extrusion procured by ATOFINA (the HDPE has a density of 0.96 and a fluidity index of 7 under 190°C and 2.16 kg), while the EVOH grade used is SOARNOL-DC from the company NIPPON GOHSEI (ethylene molar ratio of 32%).

All the samples used for the measurements are films with a thickness of around 100 μm , except for the HDPE film (which has a thickness of 400 μm). These films are obtained by "cast" extrusion in standard processing conditions.

Equipment

A gas chromatograph was used to analyze the composition of the organic vapors. This chromatograph is equipped with a system that permits an automated desorption analysis. Figure 1 shows a diagram of the equipment with the three main elements: a desorption oven (1), the permeation cell (2), the retention trap (3) that can be cooled or heated, and the chromatograph composed of the column (4) and the detector (5).

The desorption oven makes it possible to work at different temperatures ranging from room temperature to 150°C. The retention trap is a conventional system. The optimum retention power is obtained by maintaining a trap temperature of -130°C . In order not to saturate the FID detector, only a part of the vapors are sent into the column.

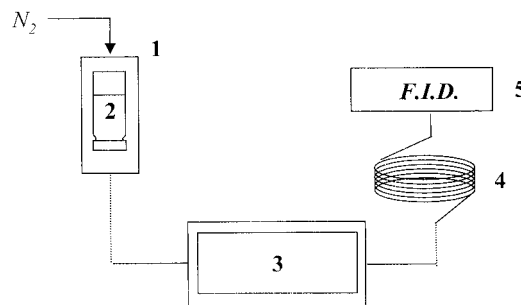


Figure 1 Schematic of the equipment for the permeation measurement: desorption oven (1), permeation cell (2), cold trap (3), column (4), flame ionization detector (5).

Two operating modes are possible. They correspond respectively to the phase of accumulation of the vapors on the trap (mode I) and to the liberation of the molecules accumulated in the trap towards the column and the FID detector (Mode II). In Mode I, the nitrogen carries the desorption vapors escaping the oven (1) towards the trap (3). The depleted nitrogen is then evacuated towards a vent. The retention trap is cooled with liquid nitrogen, and a flow meter allows us to verify at all times that the trap is not saturated. In Mode II, a valve isolates the trap from the oven. The trap is quickly heated to 250°C, and a flow of helium sweeps the trap in the opposite direction of the nitrogen flow. The molecules are desorbed from the trap and injected at the head of the column, then analyzed by the FID detector. The analysis is conventional. The area of the chromatography peaks is proportional to the masses of solvents. A liquid calibration was performed beforehand by using a known mixture of methanol and toluene injected into the oven with a syringe.

Methodology of the experimental measures

The cell (2) is a simple bottle of consumable glass. The diameter of the bottle is on the order of 1 cm, and its height, 3 cm. The polymer film is deposited on the neck of the bottle, and a joint made from a septum is placed between the film and the aluminium cap. The bottle is half filled with the mixture of solvents under consideration, then crimped and weighed on a microbalance. It is immediately introduced into and turned over in the oven (I) set at the fixed temperature for the measurements (Fig. 1). The temperature of the tests is 60°C.

The measurement then consists of a succession of vapor accumulation on the trap and desorption of the trap towards the chromatographic analysis. A temperature programming of the column allows us to optimize our analysis time. A total measurement cycle lasts 15 min: in Mode I for a period of 9 min, then Mode II during 6 min. By adding together the masses

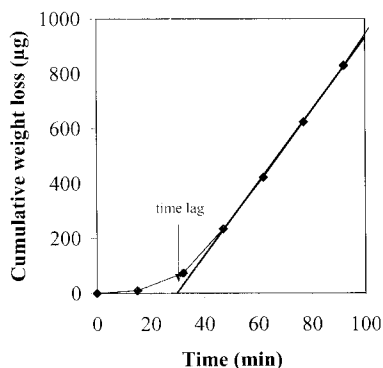


Figure 2 Cumulative weight loss vs. time of a toluene solution permeating through a 400 μm PEHD film at 60°C.

desorbed in each cycle, one obtains the permeation flow. At the end of the analysis, the bottle is weighed, which allows us to perform an analysis yield between the masses detected and the total loss of mass.

Figure 2 gives the evolution of the mass of escaping vapor cumulated for a 400- μm HDPE film exposed to pure toluene at 60°C. One typically observes two phases: a transient phase, and a stationary phase. In the latter phase, the quantity of escaping vapor varies linearly with the time. The intersection of the straight line of the stationary phase with the time axis corresponds to the "time lag." It is directly related to the diffusion coefficient.⁷ Starting from the slope of the straight line of the stationary phase, one can determine the permeability flow that one will express in $\text{g}/\text{m}^2 \cdot 24 \text{ h}$. To unify our measurements, the permeation flow will be expressed for a thickness of 1 mm (the films have thicknesses between 100 and 400 μm). For this, the rule of proportionality between the flow and the inverse of the thickness is used as derived from the diffusion law⁷ (checked experimentally in this range of thickness). It should be noted that during the analysis a slight overpressure exists inside the bottle that deforms the surface of the polymer film. Thus, the effective surface of the film increases. Because this surface increase must be taken into account in the expression of the permeability flow, the real permeability surface is calculated by a measure of the deflection of the spherical deformation cap. By comparing the permeability measurements obtained by this method and the conventional measurements (reversed-dish gravimetric method) on different polymers, we were able to ensure ourselves simultaneously of the impermeability of the cell and the validity of the results obtained.

When the liquid in contact with the polymer film is a mixture, the composition of the escaping vapor can be analyzed thanks to the separation achieved in the chromatography column. Thus, for a methanol/toluene mixture, the evolution of the masses of toluene and methanol having crossed the polymer film can be

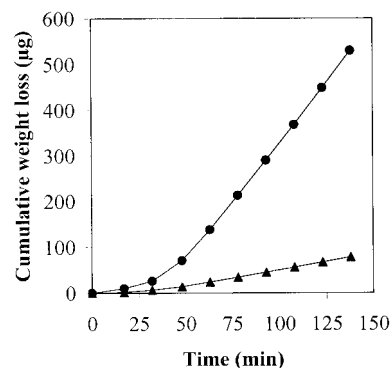


Figure 3 Cumulative weight loss vs. time for toluene (●) and methanol (▲) when a toluene/methanol solution (50/50 by weight) is permeating through a 400- μm PEHD film at 60°C.

determined precisely by one and the same experiment. For example, Figure 3 shows the evolution of the masses of methanol and toluene vapor having crossed a 400- μm HDPE film in contact with an equal-mass mixture of these two solvents at 60°C. One notes in particular that the methanol flow is a great less than that of toluene. From these curves, on each of the components, the "time lag" can be determined, and once the permanent phase is reached, their respective permeation flows can be obtained.

RESULTS AND DISCUSSION

Influence of the composition of the mixture

According to the methodology described above, films of PA12, PVDF, HDPE, and EVOH were placed in contact at 60°C with solutions of different compositions of a methanol/toluene mixture and the permeability flows of the methanol and the toluene, and thus the total permeability flow, were measured. The val-

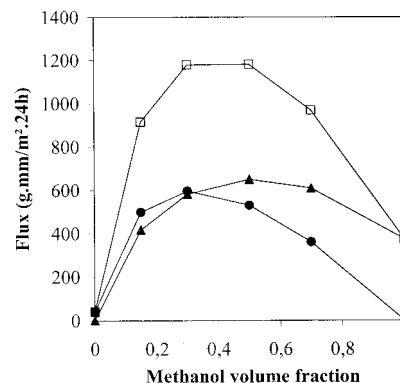


Figure 4 Permeation flux for toluene (●), methanol (▲) and total permeation flux (□) vs. methanol volume fraction when a methanol/toluene mixture permeates through a 100- μm PA12 film.

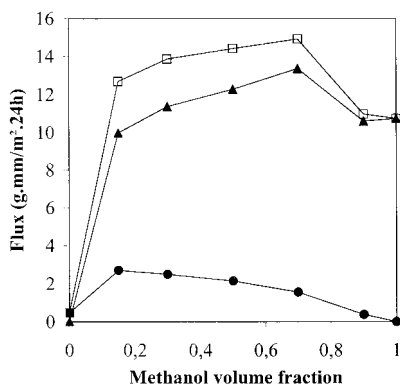


Figure 5 Permeation flux for toluene (●), methanol (▲) and total permeation flux (□) vs. methanol volume fraction when a methanol/toluene mixture permeates through a 100- μm PVDF film.

ues of the flows are reported respectively in Figures 4, 5, 6, and 7 as a function of the volume fraction of methanol of the solution in contact with the film.

As Figure 4 demonstrates, the permeability flow of the pure methanol across the PA12 is substantially greater than that of the pure toluene, which reflects the better affinity of this polymer for methanol compared to toluene. In the mixtures, these flows are systematically superior to the simple linear combination of the flows of each of the solvents when they are alone. Adopting the usual terminology,⁸ one speaks of a "positive synergy" between the solvents. In particular, it is very interesting to see that as soon as one introduces a small fraction of methanol into the toluene, the permeability flow for the toluene increases significantly. At intermediate concentrations (volume fractions of methanol between 0.15 and 0.70), the total flow exceeds by more than a factor of two the flow obtained for the pure methanol. This bell curve for the total permeability flow, typical for a "positive synergy," has been reported many times in the literature for various polymer/solvent 1/solvent 2 systems.⁹⁻¹¹ Notably, this measurement confirms that estimating the permeation flow of a mixture based on knowledge of the flows of each of the components taken separately is not straightforward.

The PVDF is a substantially better barrier to the mixture than the PA12 (Fig. 5), because the permeability flows of the two compounds are lower by close to 2 decades. As for the PA12, the flow of pure methanol is higher than the flow of pure toluene, and one observes a strong positive synergy between the permeability flows of the two solvents. A maximum toluene flow is obtained when one introduces 15% of methanol in the mixture, and the flow of methanol constitutes the majority even though the mixture is rich in toluene. The methanol flow then remains almost constant beyond this content.

A completely different behavior than that of the PA12 and the PVDF can be observed for the HDPE,

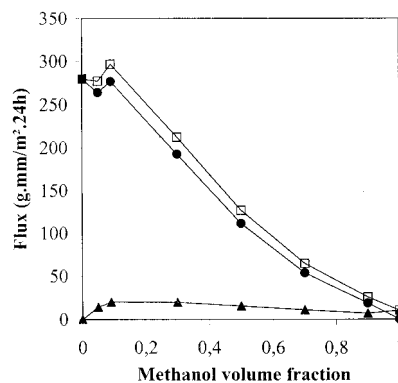


Figure 6 Permeation flux for toluene (●), methanol (▲) and total permeation flux (□) vs. methanol volume fraction when a methanol/toluene mixture permeates through a 400- μm PEHD film.

because the permeability flow for pure toluene is substantially higher than that of pure methanol (Fig. 6). This difference reveals the better compatibility of HDPE with toluene than with methanol, contrary to the PVDF and the PA12. In addition, in the case of HDPE, we do not observe any increase of the total flow for the intermediary concentrations. The toluene flow decreases as a function of the methanol content in the mixture essentially linearly with the volume fraction. A slight concavity of this flow curve can nevertheless be observed for the compositions that are low in methanol (volume fraction <0.1). At this composition, the methanol flow reaches a maximum as well. There is still a "positive" synergy here because the flow at this maximum exceeds the value of the flow for pure methanol.

Finally, EVOH behaves towards the solvents in a manner contrary to that of HDPE (Fig. 7). The large flows are recorded for the compositions rich in methanol (which reflects a better chemical affinity of EVOH

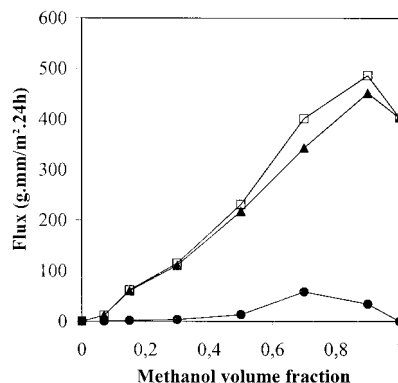


Figure 7 Permeation flux for toluene (●), methanol (▲) and total permeation flux (□) vs. methanol volume fraction when a methanol/toluene mixture permeates through a 100- μm EVOH film.

with methanol than with toluene), and the maximum of the total flow is found for the composition methanol/toluene 90/10. The curve of the toluene flow shows an interesting feature: its maximum is located for the composition 70/30 with a value that is 2500 times greater than the flow of pure toluene (respectively 0.023 and 58.5 g · mm/m² · 24 h)!! This reflects once again a "positive" synergy between the two solvents. Similar flow curves have already been encountered in the literature with other polymer/solvent 1/solvent 2 systems.^{9,12,13} When the mixture becomes less rich in methanol, the total flow varies linearly with the composition. The flow of toluene is very low compared to the flow of methanol, even though the mixture is rich in toluene. One finds here confirmation of the fact that EVOH is an excellent barrier to hydrocarbons, and to toluene in particular.

Thus, the study of the permeation of the methanol/toluene mixture across these four films highlighted in each of the cases a "positive" synergy phenomenon between the two solvents, which manifests itself differently depending on the type of polymer. As had been studied previously, this synergy between the two solvents is explained essentially by the dependence of the solubility of the mixture as a function of its composition and is thus explained by the existence of solvent 1/solvent 2, solvent 1/polymer, and solvent 2/polymer interactions.^{8,14-16} In this particular case of a permeation of a binary mixture across a polymer membrane, there exists a correlation between the synergy obtained between the flows of the two solvents and the sign of their Flory-Huggins interaction coefficient χ_{AB} .^{15,16} If the solvents do not like one another ($\chi_{AB} > 0$), the polymer matrix will "overswell" upon contact of the mixture compared to the contact with the pure solvents (i.e., the solubility of the mixture is greater than that of the pure solvent), because these latter would prefer to be in contact with the polymer than in contact with one another. As the concentration of the two solvents in the polymer matrix is higher compared to the pure solvents, the permeation flows will be proportionally higher and the synergy between the permeation flows will be of the "positive" type. Conversely, if the solvents have good chemical affinities with one another ($\chi_{AB} < 0$), the polymer matrix will "deflate" upon contact of the mixture compared to the contact with the pure solvents (i.e., the solubility of the mixture is less than that of the pure solvent), because these latter prefer to be in contact with one another than in contact with the polymer. As the concentration of the two solvents in the polymer matrix is lower than compared to the pure solvents, the permeation flows will be proportionally lower and the synergy between the permeation flows will be of the "negative" type. Because, according to the literature, the Flory-Huggins interaction coefficient between methanol and toluene at 65°C is $\chi_{MT} = 2.01$,¹⁷ this

explains why the synergy between their permeation flows was found to be "positive" in the case of the four polymer films studied.

Moreover, the changes of concentration in the membrane of one of the components due to the presence of another compound also induces changes in the transport mechanisms, which is translated by an increase or a decrease of the diffusion coefficients.⁸ These kinetic differences are very well illustrated by the measurements of the time lag issuing from the weight curves of the different films, because the time lags are inversely proportional to the diffusion coefficients.⁷ As Table I shows, for a given solvent, the time lag (and thus the diffusion coefficient) can vary in a relation of 1 to 5 as a function of the concentration of the solvent. Thus, there exist many cases where a solvent diffuses more quickly when it is mixed with another (e.g., toluene or methanol in PA12, or toluene in PVDF), which can be set parallel with the increase of solubility of the mixture compared to the pure solvents when $\chi_{AB} > 0$. In addition, even if it only gives orders of magnitude, this time-lag analysis allows one to demonstrate which of the two solvents diffuses more

TABLE I

| PA12 | | |
|--------------------------|------------------------|-----------------------|
| Methanol weight fraction | Methanol time lag (mn) | Toluene time lag (mn) |
| 0.00 | | 27.60 |
| 0.09 | 3.23 | 8.31 |
| 0.28 | 4.17 | 8.04 |
| 0.48 | 4.76 | 7.68 |
| 0.68 | 5.04 | 10.08 |
| 0.79 | 5.04 | 11.50 |
| 0.89 | 4.66 | 12.00 |
| 1.00 | 4.26 | |
| HDPE | | |
| Methanol weight fraction | Methanol time lag (mn) | Toluene time lag (mn) |
| 0.00 | | 30.5 |
| 0.08 | 27.2 | 34.1 |
| 0.28 | 31.3 | 37.0 |
| 0.48 | 30.6 | 37.0 |
| 0.66 | 26.2 | 37.8 |
| 0.89 | 18.5 | 27.7 |
| 1.00 | 6.9 | |
| PVDF | | |
| Methanol weight fraction | Methanol time lag (mn) | Toluene time lag (mn) |
| 0.00 | | 6.55 |
| 0.14 | 31.59 | 29.13 |
| 0.28 | 29.14 | 23.45 |
| 0.48 | 27.86 | 20.00 |
| 0.68 | 24.87 | 15.28 |
| 0.89 | 20.76 | 5.80 |
| 1.00 | 15.31 | |

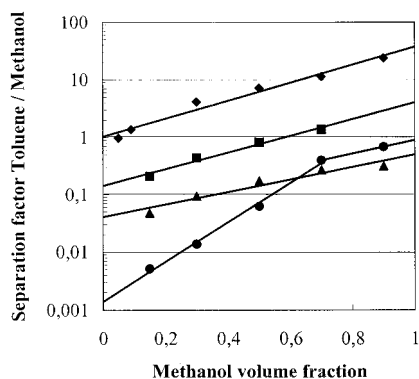


Figure 8 Toluene/methanol separation factor vs. methanol volume fraction for PA12 (■), PVDF (▲), PEHD (◆) and EVOH (●).

quickly in the polymer matrix and “opens the meshes” for the other solvent that diffuses proportionally more quickly than when it is pure. As Table I shows, even if it is the minority compound of the mixture, methanol diffuses more quickly than toluene in PA12 and HDPE, and the opposite occurs in PVDF, where methanol appears to diffuse more slowly than toluene. In particular, it is interesting to note that toluene diffuses four times more quickly in the PA12 when it is mixed with a small quantity of methanol.

Analysis of the partition coefficient of the mixture

Within the framework of the pervaporation of a binary mixture across a polymer film, the partition coefficient is generally defined by:

$$\alpha_{AB} = \frac{J_A/J_B}{\phi_{A0}/\phi_{B0}}$$

where ϕ_{i0} is the volume fraction of the solvent i in the initial mixture, and J_i is the flow of the solvent i across the polymer film.⁸ Thus, when this partition coefficient is greater (less) than 1, the membrane allows solvent A (B) to pass more easily than solvent B (A).

Starting from the measurements of the permeability flows of the preceding paragraph, it is easy to determine the toluene/methanol partition coefficient for each composition of the mixture in a given type of mixture. This latter is reported in Figure 8 for each of the four polymers. We can notably confirm that the HDPE allows toluene to pass more easily, contrary to EVOH and PVDF. Only the PA12 demonstrates little selectivity, because the partition coefficient is close to 1. As Figure 8 also shows, the logarithm of the partition coefficient demonstrates a linear dependency as a function of the volume fraction of one or the other of the compounds. Only the EVOH appears to display a more atypical behavior with two straight lines of dif-

ferent slopes. This is most certainly due to the existence of specific interactions between the hydroxy functions of this polymer and methanol. Moreover, the slopes of the straight lines that correspond to the PA12, the HDPE, the PVDF and the start of the slope of the EVOH are on the same order, respectively 3.3, 3.6, 2.5, and 2.7. Only the film of EVOH presents a value that is very different in the second part of the curve. Thus, the partition coefficient of the four polymer films is an exponential function of the composition of the mixture, which is in agreement with most of the experimental observations.^{10,11,18} In addition, recent theoretical developments have shown that, in the case of the permeation of a binary mixture across an elastomer membrane, $\log(\alpha_{AB})$ expressed as a function of ϕ_{B0} is a straight line with the slope χ_{AB} .^{15,16} By transposing this theoretical result obtained on elastomer membranes to thermoplastic polymer films above their T_g (one this assimilates crystals to reticulation points), which is the case at 60°C for each of the polymers considered here, it is possible to evaluate the Flory-Huggins interaction coefficient between methanol and toluene at 3.02 on average, which is an acceptable order of magnitude. It is not possible to obtain a better agreement between theory and experiment because the systems studied (elastomers and semicrystalline thermoplastic polymers) present several notable differences, but we can, nevertheless, retain that it is indeed, because of a positive Flory-Huggins interaction coefficient between methanol and toluene that the synergy between the flows of these two solvents is positive, regardless of which polymer is studied.

CONCLUSION

This article presents an experimental technique, based on gas chromatography, which makes it possible to obtain in a single experiment the permeation flows of each of the compounds of a binary mixture of miscible solvents across a polymer film. More specifically, we were interested in the mixture methanol/toluene as a “binary” model of a complex gasoline to understand the selectivity brought about, in front of these solvents, by the nature of the polymer. Thanks to these experiments, we were able to demonstrate the strong “positive synergy” that exists between the flows of methanol and toluene when they are mixed, in comparison to the flows of the solvents taken separately, that is, the total flow of the methanol and the toluene is greater than the weighted average of the flows of the solvents alone and the flow of one of the compounds can be greatly superior when it is mixed than when it is alone. On this point, the most striking example is that of toluene, which has an extremely low permeability across EVOH, but can see this value grow by three orders of magnitude when it is mixed with methanol! This phenomenon was notably highlighted

on four polymer films of very different kinds (PA12, PVDF, HDPE, EVOH), and in light of recent theoretical developments, we can consider that this property is general.^{15, 16} This “positive synergy” is notably manifested by a sharp increase in the flow of toluene across a polymer, when the toluene is mixed with a small quantity of methanol, which is of some interest for the “fuel line” and gas tank applications. This “positive synergy” also sharply modifies the dynamic of diffusion of the solvents because, in general, the compound that diffuses most quickly “opens the meshes” of the polymer and induces a more rapid diffusion of the other compound. This is particularly evident for toluene across the PA12, because the former diffuses four times faster when it is mixed with a bit of methanol than when it is pure. Finally, we could relate this “positive synergy” to the evolution of the solubility of the mixture of solvents in the polymer film, and more specifically to the highly positive value of the Flory-Huggins interaction coefficient between methanol and toluene, $\chi_{MT} \approx 2$. This analysis was supported by the form of the selectivity curves for the different polymers towards the mixture of solvents, and by the numerical values that could be drawn from them in light of the recent theoretical developments.

In conclusion, these experimental data are very relevant for the understanding and prediction of the permeability behavior of polymers with respect to complex gasolines. For example, if ethanol replaces methanol, a similar behavior is to be predicted, because the Flory-Huggins coefficient between ethanol and toluene at 60°C is between 1.5 and 2.¹⁷ This work thus forms a necessary prelude to the design of multilayer polymer solutions for fuel line and gas tank applications. Indeed, by knowing the selectivity of the internal layer to the contact of the mixture, it is easy to determine the permeability of the second layer to the permeate selected by the first layer and so on, until the

last external layer. In light of the results presented earlier, the multilayer structures with alternating selectivity such as HDPE/EVOH or HDPE/PVDF are thus very interesting combinations for these applications to reduce gasoline emissions into the atmosphere.

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