

# Fat-simulating and accelerating solvents for polyolefins and *MWD* of solvent extracts of polyethylenes

Shu-Sing Chang, Walter J. Pummer and John R. Maurey  
*Polymer Science and Standards Division, National Bureau of Standards,*  
*Washington, DC 20234, USA*  
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Migration kinetics of straight-chain oligomers and antioxidants from several polyolefins at different temperatures into various solvents have been studied by radioactive tracer techniques. Anhydrous ethanol appears to be a well suited food-oil or liquid-fat simulant for extracting different types of migrants from polyolefins. Pure and mixed triglycerides are also good oil or fat simulants, but the triglycerides offer no simpler analytical procedures than the use of oil or fat themselves. *n*-Octanol may also be considered as a reasonable oil or fat simulant; however, its action depends somewhat on the choice of migrants. The accelerating action of *n*-heptane over that of oil or simulants is quantitatively demonstrated. The accelerating effects are greater for migration systems with lower diffusion coefficients. The diffusion coefficients for migration into *n*-heptane are about 20 times greater than the diffusion coefficients into ethanol or oil for otherwise identical migration systems yielding diffusion coefficients of about  $10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> into oil or ethanol. For systems yielding diffusion coefficients into oil or ethanol of about  $10^{-12}$  cm<sup>2</sup> s<sup>-1</sup>, the corresponding diffusion coefficients into *n*-heptane are about 1000 times greater. The molecular weight distributions (*MWDs*) of the *n*-heptane and ethanol extracts of polyolefins have been analysed. *n*-Heptane can not only accelerate the migration of the individual migrant but also remove oligomer species that are slightly soluble or present at low levels in the oil or simulant extracts.

**Keywords** Antioxidant; diffusion; migration; oligomer; polyolefin; simulating solvent

## INTRODUCTION

Polymeric food packaging materials are essential in modern life to preserve and to aid in the distribution of food. At present, the consumption of polymers in food packaging is estimated to be in excess of  $2 \times 10^{12}$  g or  $4 \times 10^9$  lb annually in the US alone<sup>1</sup>. Thus, the per capita consumption is approximately 10 kg annually. About two-thirds of these materials are made of polyolefins, i.e. high- and low-density polyethylenes, and polypropylenes. Therefore, it is important to know the amount of any fraction of these polymers or their processing additives which migrate into food during its packaging, storage and usage. The migration levels combined with consumption factors are used together to calculate an estimated daily intake level which would be taken into consideration to determine the safe concentration level of the particular indirect or unintentional food additive in the polymer<sup>2</sup>.

Accelerated tests are generally performed by means of accelerating solvents rather than by elevating temperatures. Under the specified conditions of the Food and Drug Administration guidelines for indirect food additive petitions<sup>3</sup>, the amount of material that migrates into fatty food or food oil is estimated by dividing the *n*-heptane extractability by a factor of 5. This procedure would overestimate the extraction level of a migrant which is sparingly soluble in food oil or slowly diffuses out of the polymeric material. On the other hand, these guidelines tend to underestimate the extraction level of a migrant

which may be completely extractable by the food within its shelf-life.

The solvents tested in this research include alcohols, water, ethanol-water mixtures, *n*-alkanes, pure and mixed triglycerides as well as food oil. *n*-Octanol and a synthetic mixture of triglycerides, HB307\*,<sup>4</sup> have also been used as oil accelerating or simulating solvent. *n*-Octanol is more popular in the biological field, while HB307 is often used in Europe.

We have found, from some 250 extraction experiments with various solvents as described in several National Bureau of Standards Interagency/Internal Reports (NB-SIR), cf. ref. 5, on the migration of oligomers and low molecular weight additives in polyolefins, that anhydrous ethanol may be considered as a successful simulating solvent for liquid food oil in the temperature range of interest for food packaging, storage and utilization. Although pure triglycerides, such as tributyrin and tri-octanoin, and synthetic triglyceride mixtures, such as HB307, may also perform successfully as fat simulants, the analytical problems associated with the determination of the migration levels in fats or oils themselves will also exist in these simulating solvents. We present here a summary

\* Certain commercial materials and equipment are identified in this paper to specify the experimental procedure adequately. This identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

of the findings pertinent to the selection of simulating solvents for liquid food oils and a quantitative description of the accelerating action of n-heptane over that of food oils and oil simulants. The effect of the accelerating solvents in extracting the oligomer fraction of polyolefins are demonstrated by analysing the molecular weight distributions of the extracts.

## EXPERIMENTAL

Commercially available n-alkanes, antioxidants and solvents were used directly without further purification. It is believed that the purities of the materials used in this work generally exceed 96%. The water content of the anhydrous ethanol was determined to be in the range 0.04–0.1%, as determined by the Karl–Fischer method, depending upon the degree of occasional exposure to the laboratory atmosphere during a period up to one year.

The two polyethylenes used were taken from original polymer stocks from which National Bureau of Standards–Standard Reference Materials (NBS–SRM) 1475, linear polyethylene (LPE) whole polymer, and 1476, branched polyethylene (BPE) whole polymer, were characterized<sup>6–8</sup>. The weight- and number-average molecular weights for the LPE or high-density polyethylene are 52 000 and 18 300, and those for the BPE or low-density polyethylene are about 100 000 and 24 000, respectively. The polypropylene samples were prepared from a commercial food-packaging-grade isotactic polypropylene of weight-average molecular weight 290 000.

Thin sheets of polyolefin sample with radioactive additives were prepared in the following manner. An appropriate amount of a solution of n-octadecane, n-dotriacontane, or BHT (3,5-di-*tert*-butyl-4-hydroxytoluene) doped with their <sup>14</sup>C-labelled counterparts to yield sufficient activities was mixed with polymer granules or precipitated polymer powder. The mixture was dried with large glass beads in a rotary evaporator and then hot pressed into plaques of 0.025–0.07 cm thickness. Plaques of two concentrations of n-C<sub>18</sub>H<sub>38</sub>, 0.01 and 1%, were prepared to monitor the influence of the oligomer concentration. The concentration of n-C<sub>32</sub>H<sub>66</sub> in the plaques was about 1%. The concentration of BHT in the plaques was of the order of 0.001–0.01%. Most of the finished plaques have a specific activity about 5 μCi per gram of polymer. The specific activity of these original <sup>14</sup>C-labelled compounds are of the order of 10–20 Ci mol<sup>-1</sup>.

Individual strips of the plaques were placed in special extraction vials with 15–20 ml of solvent in a temperature-controlled aluminium block on a reciprocating shaking table. Aliquots of 0.2–0.5 ml were taken with a time schedule from less than 1 min after the initiation of the experiment until equilibrium extraction or partition was achieved. During the extraction process, some low molecular weight material from the polymer, other than the specific additive, may also be extracted by the solvent. Depending on the migrant, migrant concentration, polymer, polymer thickness, solvent and temperature, the experiments required from a few hours to more than a year to reach equilibrium. The radioactivity of the aliquots was determined by liquid scintillation counting techniques sensitive to 10 pCi of the activity.

Diffusion coefficient is estimated by fitting the data to a generalized solution<sup>9</sup> solving for the case of diffusion between a plane sheet 'p' of thickness 2l and a stirred

liquid 's' of finite volume V<sub>s</sub>:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_n^2} \exp(-q_n^2 T)$$

where  $\alpha = M_{s\infty}/M_{p\infty} = kV_s/V_p$ ,  $k = C_{s\infty}/C_{p\infty}$ ,  $T = Dt/l^2$  and  $q_n$  are the non-zero positive roots of  $\tan q_n = -\alpha q_n$ . Detailed computation for this series is outlined elsewhere<sup>5</sup>.

In most cases, the migration behaviour shifted from a low initial value of diffusion coefficient to a higher value. These increases were caused by solvent absorption or swelling of the polymer. The diffusion coefficients cited here are the apparent maximum values achieved when the polymer plaque was saturated by the solvent. Thus, the reported values yield upper bound migration levels.

## RESULTS AND DISCUSSION

Within the limited temperature range of food utilization and storage, the simulating solvent (or type of food) is the single most important parameter affecting both the ultimate amount of extracted migrant and the diffusion coefficient of the migrant, acting through its solubility of the migrant and its swelling action upon the polymer. The equilibrium amount of a migrant extractable into a system with a finite solvent-to-polymer volume ratio is governed by the partition coefficient or the respective solubilities of that migrant in the solvent and in the polymer. When the system is far from equilibrium, the amount migrated is determined by the diffusion coefficients and associated parameters, such as the time of extraction and the thickness of the sample.

More refined correlations may be obtained by specifying more parameters, such as the type of migrants, migrant concentration in the polymer, type of polymer and temperature. However, in the following sections we are only concerned with the major influence exerted by the solvents irrespective of all other factors that also affect migration. By correlating diffusion coefficients in various solvents to those in one of the solvents, e.g. corn oil or ethanol, while keeping all other parameters constant, it is possible to reduce the large spread of observed diffusion coefficients, of the order of 10<sup>7</sup>, to within a factor of 5 or less.

The diffusion coefficients for migration of n-C<sub>18</sub>H<sub>38</sub>, n-C<sub>32</sub>H<sub>66</sub> and BHT from polyethylenes and polypropylene into various solvents at different temperatures are listed in Tables 1 to 4. The diffusion coefficients at 60°C are listed in a separate column, in order to facilitate easier comparison. In Figures 1 and 2, diffusion coefficients for migration into simulating or accelerating solvents are plotted against reference values, corresponding to those for migration into either corn oil or ethanol for otherwise identical conditions (migrant, migrant concentration in the polymer, polymer and temperature). For each particular sample, the diffusion coefficients for extractions by any of the various solvents may be inferred from the diffusion coefficients for extractions by the reference solvent, shown along the abscissa. The diagonal line would indicate a 1:1 relationship of the corresponding diffusion coefficients. The most significant correlations found are for the use of pure triglycerides and alcohols as food oil simulants and for the quantitative indication of

Table 1 Diffusion coefficients ( $D \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) of  $n\text{-C}_{18}\text{H}_{38}$  migrating from polyolefins into different solvents

Solvent	$t$ ( $^{\circ}\text{C}$ )	Migrant concentration in polymer (%)			
		0.01		1	
		LPE	LPE	BPE	PP
Ethanol	24		0.026		
	30		0.018	0.058	0.0092
	60	0.11	0.52	3.4	0.50
Corn oil	30	0.00044	0.013	0.17	0.0027
	60	0.11	0.48	3.4	0.21
Tributyryn	30			0.044	0.0044
	60			2.2	0.26
Trioctanoin	30	0.00062	0.016	0.19	
	60	0.12	0.58	4.0	
HB307	40			0.20	
	60			2.5	
n-Heptane	24	0.23	1.7		
	30	0.37	2.0	4.9	5.6
	60	8.5	12	64	42

Table 2 Diffusion coefficients ( $D \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) of  $n\text{-C}_{32}\text{H}_{66}$  migrating from polyolefins into different solvents

Solvent	$t$ ( $^{\circ}\text{C}$ )	LPE	BPE	PP
Ethanol	30	0.0015	0.0023	0.0014
	60	0.058	0.29	0.23
Corn oil	30	0.00012	0.00034	0.00024
		0.030	0.20	0.063
Tributyryn	30		0.00084	0.00098
	60		0.21	0.13
Trioctanoin	30	0.00025	0.00031	
	60	0.43	0.24	
HB307	40		0.0037	
	60		0.29	
n-Octanol	30		0.00065	0.00025
	60		0.35	0.047
n-Heptane	30	0.069	0.083	1.4
	60	27	17	23

Table 3 Diffusion coefficients ( $D \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) of BHT migrating from polyolefins into different solvents

Solvent	$t$ ( $^{\circ}\text{C}$ )	LPE	BPE	PP
Ethanol	30	0.0019	0.038	0.00062
	60	0.066	1.0	0.096
Corn oil	30	0.0011	0.029	0.00073
	60	0.050	0.83	0.032
Tributyryn	30	0.00073	0.034	0.00055
	60	0.049	0.85	0.070
HB307	40		0.13	
	60		0.96	
n-Octanol	30	0.010	0.052	
	60	0.15	1.4	
n-Heptane	30	2.8	5.1	1.7
	60	12	37	17

Table 4 Diffusion coefficients ( $D \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) of BHT migrating from polyethylene plaques moulded at high temperatures

Solvent	$t$ ( $^{\circ}\text{C}$ )	LPE	BPE
Ethanol	30	0.00073	0.026
	60	0.026	0.79
Corn oil	30	0.0011	0.017
	60	0.047	0.57
Trioctanoin	30	0.0014	0.020
	60	0.065	0.67
n-Heptane	30	1.6	4.2
	60	7.5	31

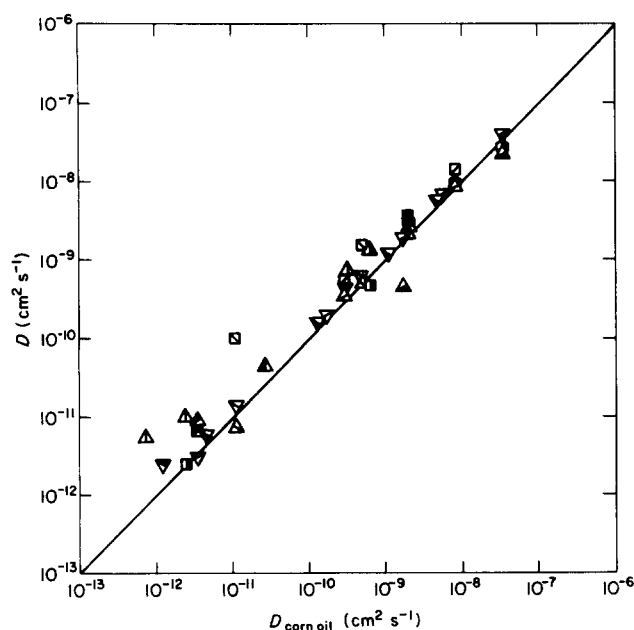
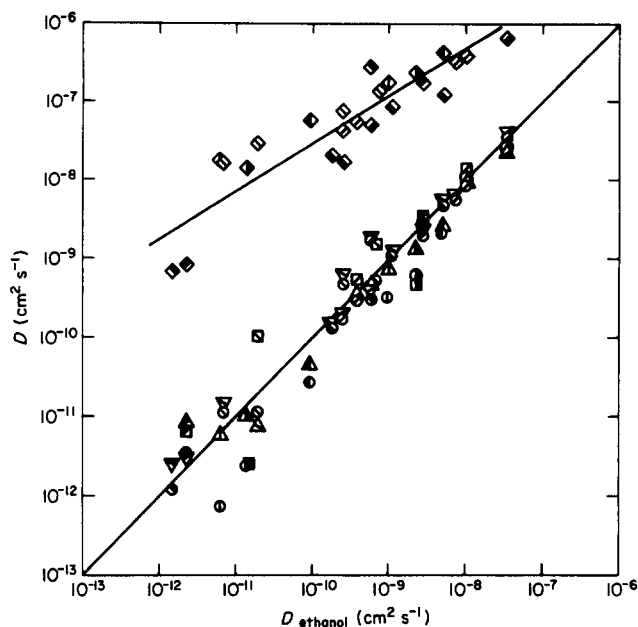


Figure 1 Diffusion coefficients for migration into simulating solvents versus those for corn oil. Simulating solvent:  $\Delta$ , tributyryn;  $\nabla$ , trioctanoin;  $\circ$ , HB307;  $\square$ , n-octanol. Polymer:  $\backslash$ , linear polyethylene;  $/$ , branched polyethylene;  $|$ , polypropylene. Migrant: left/lower shading,  $n\text{-C}_{18}\text{H}_{38}$ ; right/upper shading,  $n\text{-C}_{32}\text{H}_{66}$ ; unshaded, BHT



**Figure 2** Diffusion coefficients for migration into various solvents versus those for ethanol. Simulating solvent: ○, corn oil; △, tributyrin; ▲, trioctanoin; ○, HB307; □, n-octanol; ◇, n-heptane. Polymer: ●, linear polyethylene; /, branched polyethylene; |, polypropylene. Migrant: left/lower shading, n-C<sub>18</sub>H<sub>38</sub>; right/upper shading, n-C<sub>32</sub>H<sub>66</sub>; unshaded, BHT

the accelerating action of the accelerating solvent, n-heptane.

As shown in *Figure 1*, the diffusion coefficients of the migrants (n-octadecane, n-dotriacontane, or BHT) moving from the polyolefins (LPE, BPE, PP) into either tributyrin, trioctanoin, or the synthetic triglyceride mixture (HB307) at either 30° or 60°C are all of the same magnitude as the corresponding diffusion coefficient obtained from corn oil extractions. Diffusion coefficients from the simulating solvent experiments are, in general, slightly higher than those for corn oil extractions. For all cases studied, diffusion coefficients with trioctanoin are not quite twice those with corn oil. With a few exceptions at low diffusion coefficient values and one case with n-C<sub>18</sub>H<sub>38</sub> in BPE, diffusion coefficients for trioctanoin extractions are also within 2.5 times those for corn oil extractions. The synthetic triglyceride mixture (HB307) gives almost identical results as corn oil at 60°C. n-Octanol behaves like corn oil in removing n-C<sub>32</sub>H<sub>66</sub> from polypropylene, but generally acts as a slightly accelerating solvent, especially in removing BHT from LPE.

By using ethanol as a reference solvent, the diffusion coefficients in other simulating solvent extractions (triglycerides and n-octanol) scatter more evenly on both sides of the 1:1 diagonal lines, as shown in *Figure 2*. With a few exceptions, diffusion coefficients for corn oil experiments are somewhat lower than for ethanol. Therefore, ethanol may be considered as a food oil simulating solvent with a slight accelerating action. With only one exception, diffusion coefficients for tributyrin extractions are slightly lower than those for ethanol. Most of the diffusion coefficients with trioctanoin are almost the same as those for ethanol, with a few cases being slightly higher. Diffusion coefficients with n-octanol may either be greater or smaller than those with ethanol, and are probably

strongly dependent on the migrant involved. The maximum observed deviation is about a factor 7 at low diffusion coefficient values, which corresponds to a factor of about 2.5 in the amount migrated when the diffusion kinetics govern the migration.

The accelerating action of n-heptane is clearly demonstrated in *Figure 2*. The diffusion coefficients of the migrants moving into n-heptane are all well above those for migration into various triglycerides and alcohols for otherwise identical test specimens and experimental conditions. The accelerating action is greater at lower diffusion coefficients. The diffusion coefficients with n-heptane are 20 times higher than those of the simulating solvents under conditions producing the highest observed diffusion coefficients near 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup> in oil. This accelerating factor increases to about 1000 for low diffusion coefficients with simulating solvents, at about 10<sup>-12</sup> cm<sup>2</sup> s<sup>-1</sup>. These factors correspond to an increase of the amount migrated by a factor of 4.5 to 30, respectively, when the amount migrated is far from the equilibrium level and is governed by the diffusion kinetics alone.

From the above observations, either ethanol or triglycerides (pure or mixed) may be used successfully on most occasions as food oil simulants, regardless of their dissimilarities in viscosity, solvation power for the migrants, and swelling power for the polymers. The use of pure saturated triglycerides as simulating solvents for food oils or fatty foods will only offer the advantages of well defined composition and long-term chemical stability. The synthetic mixed triglycerides may also provide these advantages over the natural mixed triglycerides, i.e. the food oils. Any difficulties or analytical procedures associated with the analysis of the additives in oils will be similar in all cases involving triglycerides. Therefore, the use of pure or mixed triglycerides as simulating solvents for food oils will not simplify the procedures applied to the use of the food oils themselves as extracting solvents. From a rather limited database, n-octanol may also be considered as a fat simulant, although the variability among different migrants is more distinct.

The polyolefins absorb from 5 to 15% of their weight in n-heptane, depending largely on the crystallinity of the polymers. The polymers absorb from 2 to 5% of their weight in corn oil or triglycerides and much less than 1% of their weight in ethanol. The agreement among the diffusion coefficients with ethanol and triglycerides seems to indicate that the amount of solvent absorbed or the degree of swelling of the polymer alone is not sufficient to determine the diffusion coefficient. However, the kinetics of migration seem to indicate a definite influence exerted by solvent absorption or swelling, as evident in the migration curves from which *D* values are derived<sup>5</sup>.

The accelerating action of n-heptane compared to that of ethanol (and that of triglycerides), coupled with the differences in the solubilities of oligomers of polyolefins in the various simulating solvents, has dramatic effects on the total extractability of oligomers from polyolefins. We, therefore, subjected large quantities (50 g) of the original polymer stocks (used to prepare SRM 1475 (LPE) and SRM 1476 (BPE)) to extraction by either 500 ml of ethanol or n-heptane at 70°C for 160 days, with occasional shaking. By assuming a minimum diffusion coefficient of about 10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup> for n-C<sub>32</sub>H<sub>66</sub> and a pellet radius of 0.1 cm, the reduced time  $T = Dt/l^2$  is 1.4. Thus, according to the generalized solution for the

diffusion equation, the extractions should be at least 95% complete. The results of the 160-day extractions are listed in Table 5. For each of the two polymers, about 6–8 times as much of the oligomer fraction of the polymer was extracted by n-heptane than by ethanol.

The extracts were then subjected to gel permeation or size exclusion chromatographic analysis to determine their molecular weight distribution, as summarized in Table 6 and shown in Figure 3 for linear polyethylene extracts and in Figure 4 for branched polyethylene extracts, respectively. The molecular weight scales were calibrated by analysing five NBS polyethylene standard reference materials, three n-alkanes of carbon numbers C<sub>10</sub>, C<sub>20</sub> and C<sub>44</sub> and test mixtures containing known amounts of n-alkanes from C<sub>6</sub> to C<sub>44</sub>. The molecular weight scale for branched polyethylene is only approximately correct; however, it should be sufficiently accurate for comparative purposes.

The extracts from the linear polyethylene show ordinary symmetrical distributions with peak molecular weights centred at about 300 for ethanol and at about 800 for n-heptane extracts. Such results are expected from the practice of molecular weight fractionation by solvents of different solubility power. On the low molecular weight side, e.g. near n-C<sub>18</sub>H<sub>38</sub> or below, there is a large enough solubility or even total miscibility of the oligomer fraction in either solvent that almost all of the low molecular weight fraction will be dissolved by the extraction processes, c.f. label A in Figures 3 and 4. The solubility of n-alkane in the solvent decreases progressively with the increase in the n-alkane or oligomer molecular weight. This causes an observable equilibrium partitioning of the higher molecular weight n-alkane or oligomer to occur between the polymer and the extracting solvent. This partitioning has been confirmed for n-C<sub>32</sub>H<sub>66</sub> by both extraction and absorption experiments with ethanol. Not only is the extractable amount at equilibrium,  $M_{\infty}/M_0$ , reduced for larger molecules, but the diffusion coefficients for larger molecules also drop significantly. Therefore, at a specific finite time before reaching equilibrium partition, the fractional amount of the extractable,  $M_t/M_{\infty}$ , of higher molecular weight species extracted is much less than that of lower molecular weight species. Thus, the combination of the effects of solubility, partitioning and

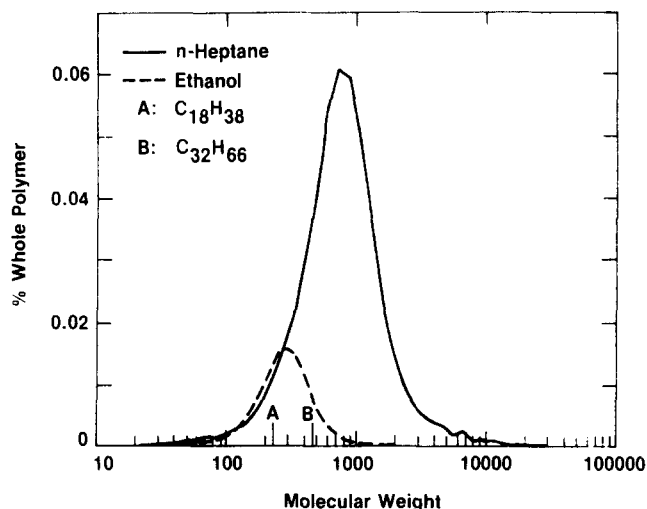


Figure 3 Molecular weight distribution of 70°C ethanol (---) and n-heptane (—) extracts of linear polyethylene

diffusion would produce the shape of the molecular weight distribution curve beyond the peak molecular weight extracted.

A similar comparison of the two extracting solvents for branched polyethylene is seen in Figure 4. The skewed curves are most probably due to shortcomings in the size versus molecular weight calibration, which was based on n-paraffins and linear polyethylene fractions. The peak of apparent molecular weight extracted is about 350 for ethanol and about 3200 for n-heptane extracts.

### CONCLUSION

Ethanol may be considered as a reasonable simulating solvent for liquid food oil or fat in removing oligomers and other processing aids from polyolefins. Not only are the diffusion coefficients of the migrants migrating from the polyolefin samples into ethanol similar in magnitude to that into food oils and triglycerides, but even the equilibrium amounts of extraction, as determined by the

Table 5 Extractions of polyethylenes by ethanol and n-Heptane at 70°C for 160 days

Solvent	Amount extracted (wt%)	
	LPE (SRM 1475)	BPE (SRM 1476)
Ethanol	0.08	0.23
n-Heptane	0.47	1.8

Table 6 Molecular weight distributions of ethanol and n-Heptane extract of polyethylenes

Solvent	$M_n:M_w$	
	LPE (SRM 1475)	BPE (SRM 1476)
Ethanol	250:310	310:410
n-Heptane	560:1020	620:3000

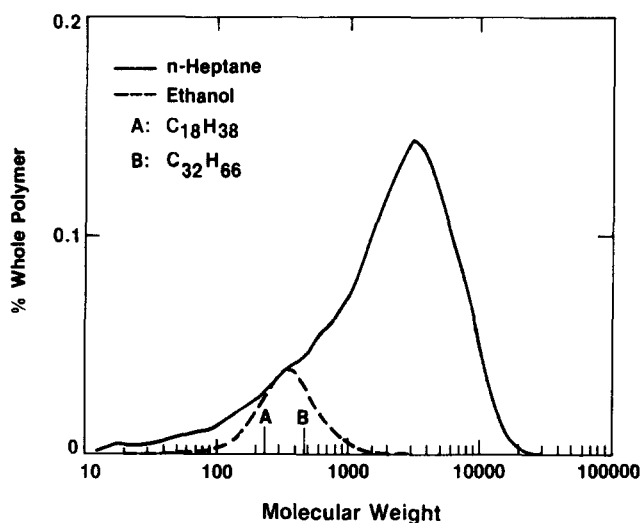


Figure 4 Molecular weight distribution of 70°C ethanol (---) and n-heptane (—) extracts of branched polyethylene

equilibrium partitioning of the migrant between the solvent and the polymer, are also similar in magnitude.

The oligomers have finite solubilities in the polymers. For the lower molecular weight oligomer, n-C<sub>18</sub>H<sub>38</sub>, it is miscible with the triglycerides at temperatures above its melting point of 28.0°C. Therefore, n-C<sub>18</sub>H<sub>38</sub> is totally extractable by triglycerides at temperatures above 30°C. The solubilities of n-C<sub>18</sub>H<sub>38</sub> in ethanol are 13 and 29% at 30° and 60°C, respectively<sup>10</sup>. These solubilities are sufficiently high that, at a solvent/polymer volume ratio of 40, more than 98% of n-C<sub>18</sub>H<sub>38</sub> may be extracted from any of the polyolefins. The amount of migrant extractable at equilibrium is calculated as:

$$\frac{M_{s\infty}}{M_{p0}} = \frac{\alpha}{1 + \alpha}$$

where

$$\alpha = \frac{M_{s\infty}}{M_{p\infty}} = \frac{C_{s\infty} V_s}{C_{p\infty} V_p} = k \frac{V_s}{V_p}$$

The variables *M*, *C* and *V* denote the mass of migrant, the concentration of migrant and the volume, respectively. The first subscript, *s* or *p*, indicates either the solvent of polymer. The second subscript ∞ indicates an infinite time or an equilibrium. The partition coefficient *k* can be approximated by the ratio of the solubilities of the migrant in the solvent over that in the polymer.

For the higher molecular weight oligomer, the solubility decreases rather sharply. At a few degrees below the melting point of 69°C,<sup>10</sup> the solubilities of n-C<sub>32</sub>H<sub>66</sub> in n-heptane, ethanol and triglycerides are all finite. The solubilities of n-C<sub>32</sub>H<sub>66</sub> at 60°C are 77% in n-heptane, 0.7% in ethanol and about 2% in the triglycerides. At 30°C, the solubilities are 5% in n-heptane, 0.008 in ethanol and about 0.02% in the triglycerides. Although the solubilities of n-C<sub>32</sub>H<sub>66</sub> are higher in the triglycerides than in ethanol, they are still of the same order of magnitude. The solubilities in n-heptane are almost two orders of magnitude higher than in the triglycerides or ethanol. Therefore, for all practical purposes ethanol may behave rather similarly to the triglycerides. Kinetically, the slightly higher diffusion coefficient for migration into ethanol allows a shorter time to reach equilibrium. However, the higher solubility in the triglycerides allows a little more of the migrant to be extracted at equilibrium.

The accelerating solvent n-heptane can not only accelerate the diffusion process during extractions but also

remove more of the migrants at equilibrium partition. It can also remove high molecular weight species of oligomers that may hardly be present in ethanol extracts. The total weight fraction of oligomers extracted by n-heptane is about 6–8 times greater than that extracted by ethanol (Table 5). This factor is of the order of magnitude of 5, which is used in the FDA guidelines to correct for the accelerating action of n-heptane over food oil. However, the major difference between n-heptane and ethanol, which behaves very much like oil or oil simulants, is caused by different amounts of the higher molecular weight species being removed by the solvents. Below the molecular weight of 300–350, the same amount of oligomers (total extraction) may be extracted from polyolefins by any of these solvents. Therefore, the accelerating factor of 5 used in the guidelines for migrant extractions by n-heptane compared to food oil may be applicable to the gross oligomer weight fraction extracted from polyolefins but is clearly not applicable for the migration of individual species.

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