

Transport of Small Molecules in Polyolefins. III. Diffusion of Topanol CA in Ethylene Polymers

ENIKŐ FÖLDES

Central Research Institute for Chemistry of the Hungarian Academy of Sciences,
H-1525 Budapest, P.O. Box 17, Hungary

SYNOPSIS

Transport properties of Topanol CA, [1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butyl-phenyl)-butane], were studied in low-density polyethylene (LDPE), in a blend of low-density and linear low-density polyethylenes (LDPE/LLDPE) and in ethylene vinyl acetate copolymer (EVA). The rate of diffusion (D) was evaluated on the free-volume theory basis. A linear relationship was obtained between $\ln D$ and the reciprocal fractional free volume of the noncrystalline phase of the polymers. Solubility of the additive is higher in EVA than in polyethylene. Compatibility of Topanol CA with ethylene polymers is poor, the measured solubility values depend on the experimental conditions and thermal history of the additive source. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Because stability of polymers determines their lifetime, most of the commercially available materials are protected against degradation by additives. Decrease of the stabilizer effectiveness is a result of chemical reactions as well as physical loss of the additive.¹⁻³ The size of the stabilizers is considerably smaller than that of the macromolecules but they are fairly large compounds because their molecular mass exceeds 200 (generally between 220 and 1200). A great number of publications deal with permeation of gases and vapors in polymers;⁴⁻⁸ the literature concerning stabilizer transport is much more limited.² Moreover, the published results are not always consistent.

Systematic studies on the transport properties of antioxidants in ethylene polymers were started in our laboratories because of the contradiction of the data in the literature.⁹ Two articles were published^{9,10} emphasizing the necessity of a thorough characterization of the investigated materials to yield a feasible explanation for the obtained results.

Diffusion rate of antioxidants in polyolefins are mainly evaluated as a function of temperature, that

is, on the basis of the "activated state theory."⁸ It assumes that holes of different volumes are continuously formed and destroyed in a polymer due to thermal fluctuation. The rate of diffusion is an exponential function of reciprocal temperature. Ethylene polymers have a relaxation transition (α -transition) between 20 and 100°C that results in a change of the thermal expansion coefficient.¹¹⁻¹⁴ Therefore, specific volume, that is, hole formation, is not a linear function of temperature in this range. The "free-volume theory"¹⁵⁻¹⁷ was applied successfully in our recent study¹⁰ for evaluating the diffusion rate data of an antioxidant in these systems. The free-volume concept describes the penetration rate of small molecules as a probability function of hole formation in the polymer independently from temperature.

Temperature dependence of the diffusion rate and solubility of Topanol CA in low-density polyethylene (LDPE) was measured by Moisan,¹⁸ and Billingham and his coworkers¹⁹ gave solubility data in LDPE and polypropylene at two different temperatures. In this work transport properties of Topanol CA were studied in three different ethylene polymers; moreover the physical structure of the additive and the polymers were also characterized as a function of thermal history. Diffusion rate was measured at different temperatures and the results were treated on

the free-volume theory basis. Different methods were used for determining solubility.

EXPERIMENTAL

Materials

Topanol CA antioxidant (T-CA) (provided by ICI Ltd.) is 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)-butane, a condensation product of 3-methyl-6-*tert*-butyl phenol and crotonaldehyde, $M_w = 545$. According to the supplier the commercial material contains maximum 15% toluene, and the melting point is minimum 181°C. For the diffusion measurements toluene was evaporated from the as-received stabilizer. Additive sources were prepared by mixing 5 wt % T-CA with additive-free LDPE and ethylene vinyl acetate copolymer (EVA) in a Brabender twin-screw compounder at 150°C, and subsequently compression molding them twice at 150 and 130°C, respectively, in an argon atmosphere into 1-mm thick plates.

Transport properties of T-CA were studied in LDPE, in a blend of 60 wt % LDPE and 40 wt % linear low-density polyethylene (LDPE/LLDPE), and in ethylene vinyl acetate copolymer with 3 mol % vinyl acetate content (EVA-9) (LDPE: Tipolen PB 2212, TVK, Hungary; LLDPE: Tipelin FA 381, TVK, Hungary; EVA-9: Evatane 1020 VN3, ATOCHEM). Characterization of the polymers is given in a previous study.¹⁰ For the experiments, the polymers were formed into 70–90 μm films by blown-film extrusion.

Methods

Volatility of the additive was determined in air by two methods. The as-received material was stored in an atmospheric oven at different temperatures and weight loss was measured as a function of time. Thermogravimetric analysis was performed at a rate of heating of 10°C/min using the TG 50 Thermobalance of a Mettler TA 3000 Thermal Analyzer system.

Densities of the additive and the polymers were measured in sunflower oil as a function of temperature between 25 and 80°C.

Melting and crystallization properties of the materials were determined by DSC measurements (DSC-30 unit of the Mettler system) using 10°C/min rate of heating and cooling.

Diffusion measurements were carried out according to the system described by Roe et al.²⁰ Fifty ad-

ditive-free polymer films were placed between two additive sources, put into a diffusion cell, compressed by 2 N/mm², and stored in a vacuum oven at controlled temperature for a time shorter than the additive could reach the middle of the film stack. Additive concentration of the films was determined by UV spectroscopy. The measured values were plotted as a function of penetration depths, the diffusion coefficient and an “extrapolated solubility” were calculated.

For “equilibrium solubility” measurements six additive-free films were placed between two additive sources, and long experimental times were applied to reach equilibrium concentration.

RESULTS AND DISCUSSION

Characterization of Additive

Toluene content of the as-received additive and its rate of evaporation were determined at different temperatures. As seen in Figure 1, the investigated material contained about 10 wt % toluene that evaporated relatively fast even at room temperature. At 80°C weight loss close to equilibrium was reached in 1 h. By thermogravimetric analysis 68°C was obtained as the starting temperature of toluene evaporation, and 10.4% weight loss was measured up to 230°C, indicating good heat stability of the additive.

Density of the toluene-free additive was measured after complete dissolution in sunflower oil. A linear relationship was obtained as a function of temperature between 25 and 80°C (Fig. 2).

T-CA is a polymorphous material, its morphology depends strongly on the preparation conditions and thermal history. The former effect is reflected in the

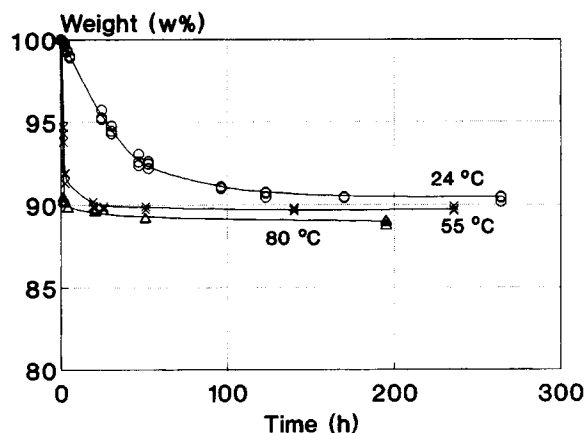


Figure 1 Weight changes of T-CA as a function of time at different temperatures.

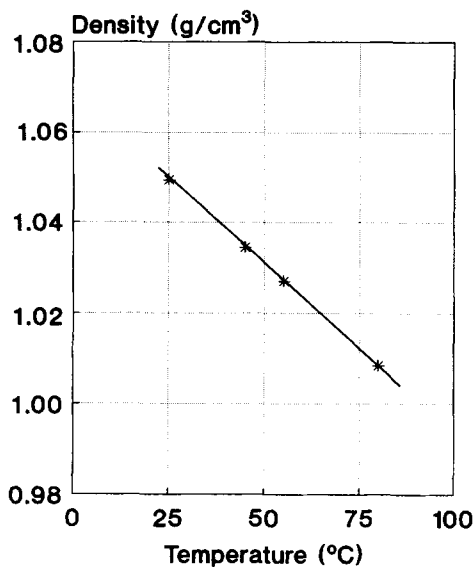


Figure 2 Temperature dependence of the density of T-CA measured in sunflower oil.

melting properties of the virgin material. Melting endotherms of two different batches obtained at different times are compared in Figure 3. Two melting peaks were obtained in one case and three in the other at different temperatures. These results suggest that the additive crystallizes in different forms in the presence of toluene. Evaporation of the solvent results in a recrystallization process. The final morphology is affected by the temperature of solvent evaporation seen in Figure 4, where endotherms of

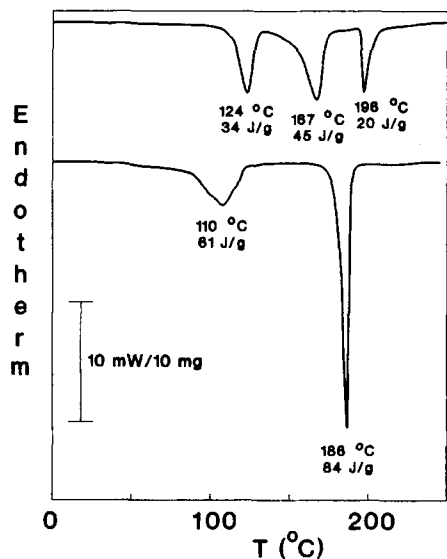


Figure 3 Heat capacity changes of T-CA of different batches measured by DSC. Rate of heating: 10°C/min.

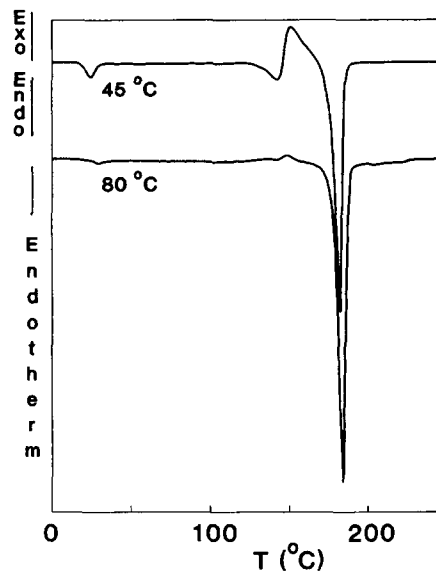


Figure 4 Effect of annealing at different temperatures on the heat capacity changes of T-CA. Rate of heating: 10°C/min.

the material annealed at 45 and 80°C are presented. Melting characteristics of the sample annealed at higher temperature indicate a more homogeneous crystalline structure.

Effect of thermal history was also studied by cooling the melted toluene-free additive at different rates and annealing it subsequently for different times. After fast cooling (quenching or 10°C/min

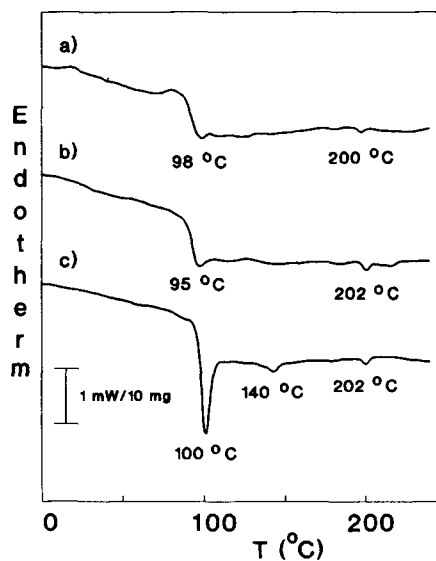


Figure 5 Heat capacity changes of T-CA: (a) quenched from melt; (b) annealed at 45°C for 48 h after quenching; (c) annealed at 45°C for 670 h after quenching. Rate of heating: 10°C/min.

Table I Characteristics of Investigated Polymers

Polymer	Temperature (°C)	Density, ρ (g/cm ³)	$\alpha_{c,\Delta H}$	v_a (cm ³ /g)	α'_a
EVA-9	45	0.909	0.325	1.145	0.703
	55	0.900	0.300	1.155	0.727
	80	0.875	0.225	1.181	0.801
LDPE	45	0.909	0.430	1.174	0.608
	55	0.902	0.415	1.181	0.623
	80	0.883	0.370	1.202	0.669
LDPE/LLDPE	45	0.914	0.505	1.183	0.535
	55	0.909	0.490	1.190	0.552
	80	0.889	0.440	1.214	0.604

cooling rate) the material did not crystallize. Heat capacity changes of the sample melted at 200°C for 5 min, quenched in liquid nitrogen, then annealed at 45°C are shown in Figure 5. The quenched sample has a glass transition around 98°C and a very small melting peak at 200°C. The latter transition must be originated from the unmelted stable crystals. After long annealing time the overheating peak above the glass transition, characteristic for a more stable glass,^{21,22} increases and some crystal formation can also be traced from the small melting peak at 140°C. Similar changes were obtained at 55 and 80°C. Annealing at 80°C resulted also in some discoloration of the material hinting at a degradation process. This suggests that T-CA is less stable thermally than expected from the results of the thermogravimetric measurements.

Characterization of Polymers

A detailed description on the characterization of the investigated polymers was given in a previous pub-

lication.¹⁰ Temperature dependence of the crystalline mass fraction ($\alpha_{c,\Delta H}$) was determined by DSC. Partial integration was used to calculate $\alpha_{c,\Delta H}$ from the melting endotherm. As the diffusion of additive is restricted to the noncrystalline phase of the polymer, specific volume (v_a), and volume fraction (α'_a) of the disordered phase were calculated from the measured density (ρ) and crystallinity data. It was assumed that

1. ethylene polymers consist of an impermeable crystalline and a permeable disordered phase;
2. acetate groups are rejected from the crystallites;
3. density of the crystallites are independent of the ethylene polymer type.

The results are given in Table I. A linear relationship was found between $\alpha_{c,\Delta H}$ and v_a in the measured temperature range.¹⁰

Fractional free volume (f_a) of the noncrystalline phase were calculated by

Table II Fractional Free Volume of Ethylene Polymers and Diffusion Coefficient of T-CA

Polymer	Temperature (°C)	f_a (cm ³ /g)	$D \times 10^8$ (cm ² /s)
EVA-9	45	0.102	1.51
	55	0.112	2.72
	80	0.145	11.60
LDPE	45	0.106	1.75
	55	0.113	2.51
	80	0.135	7.10
LDPE/LLDPE	45	0.098	1.13
	55	0.105	1.35
	80	0.129	6.05

$$f_a = \alpha'_a(v_a - v_o)/v_o \quad (1)$$

where v_o is the occupied specific volume of the polymer at 0 K. $v_o = 1.0 \text{ cm}^3/\text{g}$ was used for the calculation.^{23,24} The results are given in Table II. It was shown¹⁰ that f_a versus temperature plot of LDPE and EVA-9 is not linear between 25 and 80°C because of some structural changes of the polymers (α -relaxation transition).

Diffusion and Solubility of T-CA in Ethylene Polymers

Diffusion measurements were carried out at 45, 55, and 80°C. The additive concentration in the polymer layers, $c(x, t)$, measured after t diffusion time were plotted as function of penetration depths, x .

Results showed that the original toluene content of the additive does not influence the measured $c(x, t)$ values. It can be explained by the rapid evaporation of the solvent at the preparation temperature of the additive source. On the other hand, thermal history of the complete additive source has a considerable effect (Figs. 6, 7). The additive source annealed at elevated temperature for some time (or at room temperature for a longer period) before the experiment resulted in a significant decrease of the

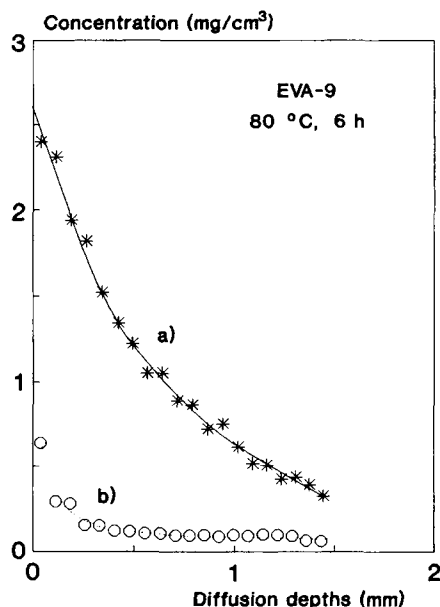


Figure 6 Concentration distribution of T-CA in EVA-9 measured at 80°C after 6 h. Additive source (a) as prepared and (b) annealed at 80°C for 2 h before the measurement.

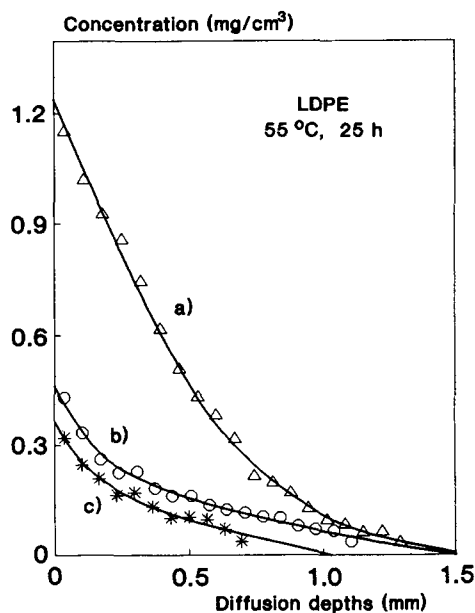


Figure 7 Effect of thermal history of the additive source on the concentration profile measured in LDPE at 55°C after 25 h. Additive source (a) as prepared; (b) annealed at 80°C for 5 min then quenched in ice water; (c) annealed at 80°C for 2 h then cooled slowly.

measured concentration values. It is caused by structural changes of the additive source, which is a metastable solution after preparation.² During annealing the stabilizer separates from the polymer matrix and recrystallizes, resulting in visible blooming. Similar effects were experienced when transport properties of Irganox 1010 were studied.⁹

The effect of the polymer type on the concentrations is represented by Figure 8, where $c(x, t)$ values measured after 20 h diffusion at 45°C are plotted as a function of penetration depths. In the ethylene vinyl acetate copolymer higher concentrations were obtained than in the other two polyethylenes.

From the measured $c(x, t)$ versus x functions the diffusion coefficient, D , was calculated with the initial conditions that at the start of the experiment ($t = 0$) in the region $x < 0$ (in the additive source) the uniform concentration is $c = S$ (solubility in the additive source), and in $x > 0$ the concentration is zero. As the diffusion proceeds, the concentration distribution in $x > 0$ is given^{25,26} by

$$c(x, t) = (S/2)[1 - \text{erf}(x/K)] \quad (2)$$

and

$$K = 2\sqrt{Dt} \quad (3)$$

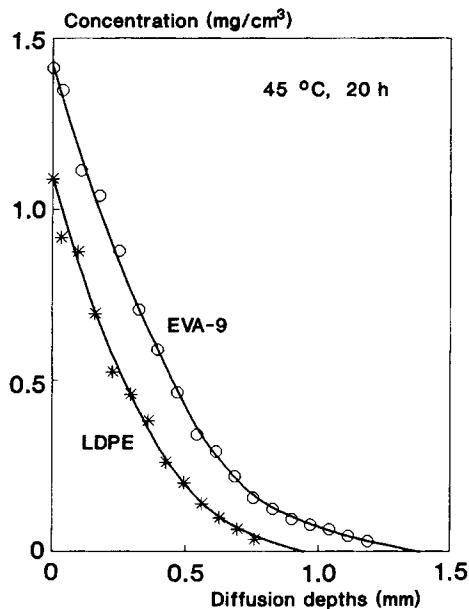


Figure 8 Concentration distribution of T-CA in LDPE and EVA-9 measured at 45°C after 20 h.

provided that concentration changes near the boundaries are negligible. This condition can be fulfilled by using the same polymers for the additive source and the film stack. For the calculations an interactive least-squares curve-fitting program was used.⁹ This calculating method also gives an extrapolated concentration at $x = 0$, which equals $c_0 = S/2$.

Diffusion coefficients calculated from the individual measurements had a larger scatter than those of Irganox 1076,¹⁰ but a smaller one than was experienced in the case of Irganox 1010. The average values are given in Table II.

According to the free-volume theory¹⁵⁻¹⁷ the diffusion coefficient can be expressed as

$$D = D_0 \exp(-A_D/f_a) \quad (4)$$

where D_0 and A_D depend upon the polymer type, and the size and shape of the penetrant. As it can be seen from Figure 9, the measured $\ln D$ values give a straight line as a function of reciprocal fractional free volume of the noncrystalline phase of the polymers. Parameters of eq. (4) were calculated and values of $D_0 = 2.20 \times 10^{-5} \text{ cm}^2/\text{s}$ and $A_D = 0.763$ were obtained.

According to the theory, A_D corresponds to the minimum hole size required for a displacement of the penetrating molecule.¹⁶ $A_D = 1.32$ was measured¹⁰ for Irganox 1076, which has a long-chain

structure of similar molecular mass ($M_w = 531$). Comparing A_D values of the two additives it can be concluded that the effect of fractional free volume changes is more enhanced with a linear molecule than that of a bulky one of the same molecular mass. This result can be attributed to the molar volume differences of the two compounds. Specific volume (v_{sp}) and changes of v_{sp} with temperature are larger for Irganox 1076 in the measuring range than those for T-CA (Fig. 10).

Solubility values of T-CA in ethylene polymers determined by equilibrium and extrapolating methods are summarized in Table III. Measuring time and technique are also given in the table.

The extrapolated solubilities are similar to those obtained by the equilibrium method after shorter experimental times. All results presented indicated that the additive suffers structural changes during annealing, which must be the explanation for the time dependence of the measured solubilities.

From the solubility data given in Table III we can conclude that

1. T-CA has higher solubility in ethylene vinyl acetate copolymer than in polyethylene. It is attributed to the interaction of the polar groups. Solubility of the additive in LDPE and LDPE/LLDPE blend is so small even at elevated temperatures that the UV tech-

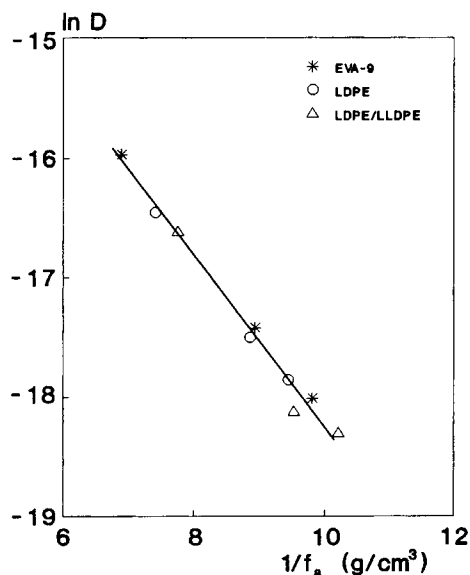


Figure 9 Relationship between the diffusion rate of T-CA and the fractional free volume of the noncrystalline phase of the polymer.

- nique gave more reliable results than the weight measurements.
- At 55 and 80°C the measured solubility values decreased with increasing experimental time. In LDPE and LDPE/LLDPE, similar solubilities were obtained between 45 and 80°C. This latter result cannot be attributed to the measuring technique because the weight measurements did not provide higher solubilities either.
 - The thermal history of the additive source strongly influences the measured concentrations. Annealing of the additive source at 80°C before the experiment results in a drastic decrease of the measured solubilities compared to those obtained by a freshly prepared additive source (see values for LDPE, 45°C, 200 h in Table III).

Structural changes of the LDPE-base additive source was proved by DSC measurements. The heat capacity changes of the freshly prepared blend of 5 wt % T-CA with LDPE revealed an endothermic peak only in the polymer melting range; that of the annealed sample also gave a small peak at 161°C (Fig. 11). It originates from the separated and recrystallized stabilizer. When the additive was mixed with EVA, this effect could not be traced by DSC. However, the lack of a separate melting peak does not prove complete dissolution because the additive

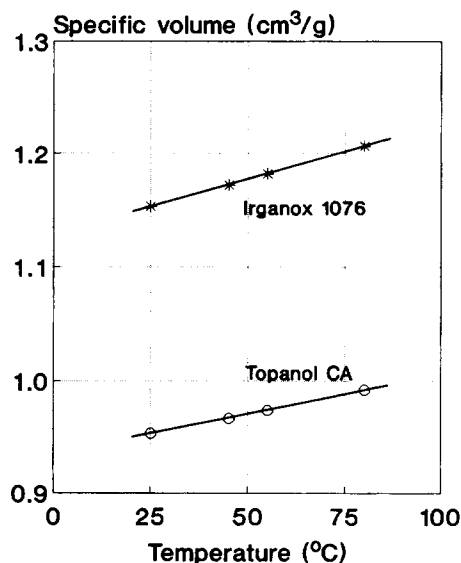


Figure 10 Temperature dependence of specific volume measured in sunflower oil.

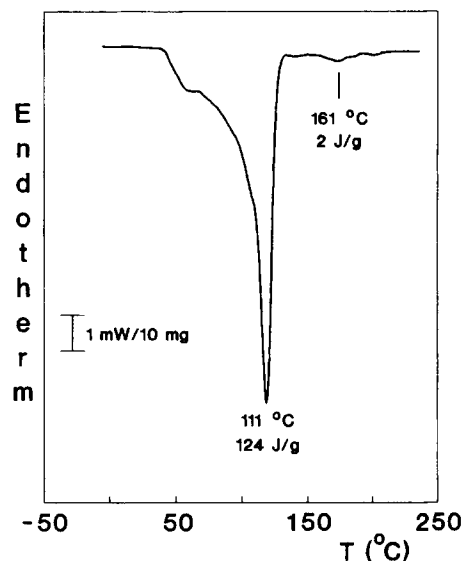


Figure 11 Melting endotherm of 95 wt % LDPE and 5 wt % T-CA blend annealed at room temperature for 6 months. Rate of heating: 10°C/min.

is polymorphous and the melting peaks of the components can overlap each other.

Summarizing the results of the solubility measurements, the conclusion can be drawn that compatibility of T-CA with ethylene polymers is poor. Using a freshly prepared additive source for the studies, that is, when a metastable solution is contacted with a stack of additive free polymer films, diffusion and phase separation processes compete. At elevated temperatures additive separation and recrystallization is fast, and their rate exceeds that of the dissolution and diffusion; therefore, the measured concentration values change with experimental time and depend also on the thermal history of the additive source.

CONCLUSIONS

In this work physical properties of T-CA and transport of the additive in three different ethylene polymers were studied.

The investigated antioxidant is polymorphous, its morphology strongly depends on thermal history. Although this additive is not volatile under 200°C, it shows some discoloration at 80°C hinting at some chemical changes.

The rate of diffusion of the additive in LDPE, LDPE/LLDPE blend, and EVA was determined at

Table III Solubility of T-CA in Ethylene Polymers

Polymer	Temperature (°C)	Solubility (mg/cm ³)	Determination [Time (h), Method]		
EVA-9	45	4.0	200, ^a UV		
		9.2	500, ^a UV		
	55	15.0	300, ^a weight		
		10.0	500, ^a weight		
		11.0	7 ^b		
	80	27.0	200, ^a weight		
LDPE	45	2.4	200, ^a UV		
		0.3	200, ^{a,c} UV		
		2.6	500, ^a UV		
		2.8	25 ^d		
	55	2.2	100, ^a UV		
		0.8	300, ^a UV		
		0.8	500, ^a UV		
		2.5	20 ^d		
	80	1.8	200, ^a UV		
		2.6	5 ^d		
		LDPE/LLDPE	45	1.5	200, ^a UV
				2.1	500, ^a UV
55	1.3		100, ^a UV		
	0.7		210, ^a UV		
80	0.7		500, ^a UV		
	1.3		100, ^a UV		
		1.4	200, ^a UV		

^a Equilibrium measurement.

^b EVA-base additive source, data calculated by eq. (2).

^c Additive source annealed at 80°C for 2 h before the experiment.

^d LDPE-base additive source, data calculated by eq. (2).

different temperatures. The results were evaluated as a function of the fractional free volume of the noncrystalline phase of the polymer in an Arrhenius plot. It was found that the diffusion rate of Topanol CA is less dependent on the free volume changes of the polymer than that of Irganox 1076, which has a long linear chain and similar molecular mass.

Solubility of Topanol CA in ethylene polymers is small, although it dissolves in EVA more readily than in polyethylene due to interaction of the polar groups. The measured solubility data depend not only on temperature but also on the measuring technique, the time of the experiment, and thermal history of the additive source. It is attributed to the physical changes of the material during the experiments and annealing.

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REFERENCES

1. J. Y. Moisan, in *Polymer Permeability*, Chap. 4, J. Comyn, Ed., Elsevier, London, 1985, p. 119.
2. N. C. Billingham, in *Oxidation Inhibition in Organic Materials*, Vol. 2, Chap. 6, J. Pospíšil and P. P. Klemchuck, Eds., CRC Press, Boca Raton, FL, 1990, p. 249.
3. J. Luston, V. Pastusáková, and F. Vašš, *J. Appl. Polym. Sci.*, **47**, 555 (1993).
4. H. B. Hopfenberg, Editor, *Permeability of Plastic Films and Coatings to Gases, Vapors, and Liquids*, (Polymer Science and Technology, Vol. 6), Plenum Press, New York, 1974.
5. D. W. Van Krevelen and P. J. Hoftyzer, *Properties of Polymers, Their Estimation and Correlation With Chemical Structure*, Part IV, Chap. 18, Elsevier, Amsterdam, 1976, p. 403.
6. C. E. Rogers, in *Polymer Permeability*, Chap. 2, J. Comyn, Ed., Elsevier, London, 1985, p. 11.
7. W. J. Koros, Editor, *Barrier Polymers and Structures*,

- ACS Symposium Series 423, American Chemical Society, Washington, D.C., 1990.
8. W. J. Koros and M. A. Hellums, in *Encyclopedia of Polymer Science and Engineering. Supplement Volume*, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Eds., Wiley, New York, 1989, p. 724.
 9. E. Földes and B. Turcsányi, *J. Appl. Polym. Sci.*, **46**, 507 (1992).
 10. E. Földes, *J. Appl. Polym. Sci.*, **48**, 1905 (1993).
 11. P. Hedvig, *Dielectric Spectroscopy of Polymers*, Chap. 4, Akadémiai Kiadó, Budapest, 1977, p. 196.
 12. R. S. Stein, T. Kyu, S. Hu, and T. Masaoka, *Polym. Prepr.*, **24**, 117 (1983).
 13. R. H. Boyd, *Polymer*, **26**, 323 (1985).
 14. Y. P. Khanna, E. A. Turi, T. J. Taylor, V. V. Vickroy, and R. F. Abbott, *Macromolecules*, **18**, 1302 (1985).
 15. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
 16. H. Fujita, *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1961).
 17. A. Peterlin, *J. Macromol. Sci. Phys.*, **B11**, 57 (1975).
 18. J. Y. Moisan, *Eur. Polym. J.*, **16**, 979 (1980).
 19. N. C. Billingham, P. D. Calvert, and A. S. Manke, *J. Appl. Polym. Sci.*, **26**, 3543 (1981).
 20. R.-J. Roe, H. E. Bair, and C. Gieniewski, *J. Appl. Polym. Sci.*, **18**, 843 (1974).
 21. B. Wunderlich, *Macromolecular Physics*, Vol. 2, Chap. 7, Academic Press, New York, 1976, p. 363.
 22. M. J. Richardson, in *Development in Polymer Characterisation*, Vol. 1, Chap. 7, J. V. Dawkins, Ed., Applied Science, London, 1978, p. 205.
 23. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
 24. A. K. Doolittle and D. B. Doolittle, *J. Appl. Phys.*, **28**, 901 (1957).
 25. W. Jost, *Diffusion in Solids, Liquids, Gases*, 3rd printing, Academic Press, New York, 1960.
 26. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975.

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