

Solution Viscosities of Ethylene–Propylene Copolymers in Oils

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Synopsis

Viscosities were obtained on oil solutions of ethylene–propylene copolymers with 58–80 mol % ethylene. For amorphous copolymers, intrinsic viscosities and equivalent hydrodynamic volumes showed little variation from –10 to 50°C. They decreased precipitously at low temperature for a partially crystalline copolymer with 80 mol % ethylene. The data can be explained by postulating that more ethylene and resulting crystallinity lead to ordered domains in solution at low temperatures, giving rise to additional contraction of the copolymer above that expected for a totally amorphous material.

INTRODUCTION

One of the important industrial applications of ethylene–propylene copolymers (EPs) is as viscosity index (VI) improvers to extend the temperature range over which motor oils can function. For best effectiveness, at low temperature the increase in oil viscosity brought about by the VI improver should be as small as possible to avoid undue thickening of the product, and increase as the temperature rises to counteract the loss of oil viscosity caused by thermal expansion. EPs useful as VI improvers are high molecular weight linear copolymers, with the two monomers generally distributed along the chains in a random manner. Typically, they contain 60 or more mol % ethylene and range in molecular weight (\bar{M}_w) from about 100,000 to 350,000. In spite of the wide use of these EPs, no information has been published on the effect of composition and structure on their key viscometric properties related to performance in service. To help fill this void, we are now reporting on the effect of ethylene to propylene ratio and crystallinity on their viscosities in oils at –10 to 50°C.

RESULTS

Characterization of Materials

The properties of the EPs used in this work are summarized in Table I. The copolymers with 58–70 mol % ethylene were amorphous while that with 80 mol % ethylene contained a small amount of crystallinity. Weight average molecular weights ranged from about 148,100 to 321,500 and polydispersity from 2.9 to 4.1. The mean number of ethylene units in sequences of three or more, the

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TABLE I
Molecular Characteristics of Ethylene-Propylene Copolymers

VI improver	GPC		NMR			FTIR	DSC	Crystallinity (%)	
	$\bar{M}_w \times 10^{-3}$	$Pd = \bar{M}_w/\bar{M}_n$	Ethylene (mol %)	\bar{N}	$En \geq 3$	CH_2/CH_3	T_m (°C)	DSC	X-ray
EPA1	148.1	2.9	60	4.2	0.35	2.04	—	Trace	—
EPA2	251.6	3.5	58	3.9	0.30	2.08	—	Trace	—
EPB1	191.9	3.4	70	4.8	0.56	5.05	—	Trace	—
EPC3	321.5	4.1	80	6.1	0.65	7.50	43	7.4	5.2

fraction of ethylene sequences containing three or more ethylenes and the ratio of CH_2 to CH_3 units all increased with the amount of ethylene. The compositions of the two oils used for the solutions are shown in Table II. SNO-100 and N-100 Pale were, respectively, typical paraffinic and naphthenic base stocks. The N-100 Pale thus contained about 71% naphthenic components as compared to 54 for the SNO-100. It also contained smaller amounts of saturated paraffins and aromatics.

Viscosities

Figures 1 and 2 show the relative viscosities of the copolymers in SNO-100 at 20 and $-10^\circ C$. At $20^\circ C$, the most important variable affecting relative viscosities was molecular weight. EPC3, with the largest \bar{M}_w , had the highest viscosity at all concentrations and EPA1, with the smallest \bar{M}_w , the lowest. At $-10^\circ C$, the situation was very different. The amorphous copolymers with 58–70% ethylene were still lined up in the expected order but EPC3 was now the

TABLE II
GC-MS Data of Base Stocks

Constituents	SNO-100	N-100 Pale
Saturated paraffins (%)	26.12	14.25
Naphthenic (%)		
1-Ring	17.27	17.55
2-Rings	14.12	16.32
3-Rings	9.76	13.98
4-Rings	11.42	14.37
5-Rings	1.40	8.74
Total	53.97	70.96
Aromatics (%)		
Monoaromatics	12.90	8.30
Diaromatics	3.60	3.60
Triaromatics	0.80	0.90
Total	17.30	12.80
Others (%)	2.61	1.99

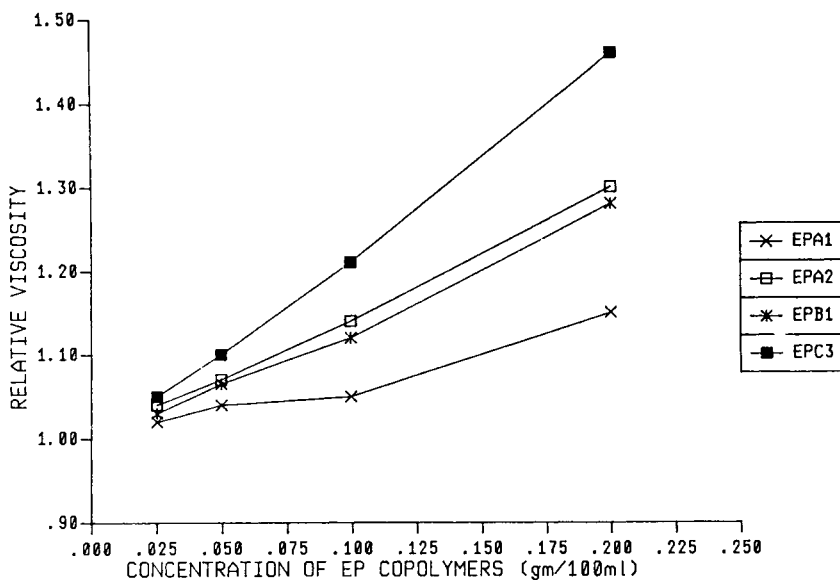


Fig. 1. Relative viscosities of EP copolymers in SNO-100 base oil at 20°C.

least viscous. Identical results were obtained in the N-100 Pale. These data clearly demonstrate that copolymer structure and composition had a major effect on solubility at -10°C , overriding the effect of molecular weight.

To determine the region where this viscosity-temperature inversion occurred, we obtained intrinsic viscosities of all copolymers in both oils at -10 – 50°C by the customary extrapolation to zero concentration of plots of reduced solution

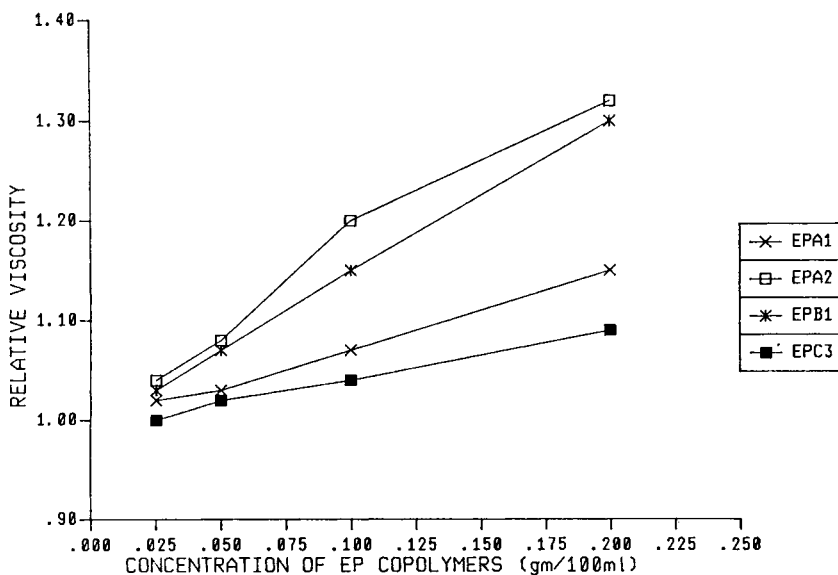


Fig. 2. Relative viscosities of EP copolymers in SNO-100 base oil at -10°C .

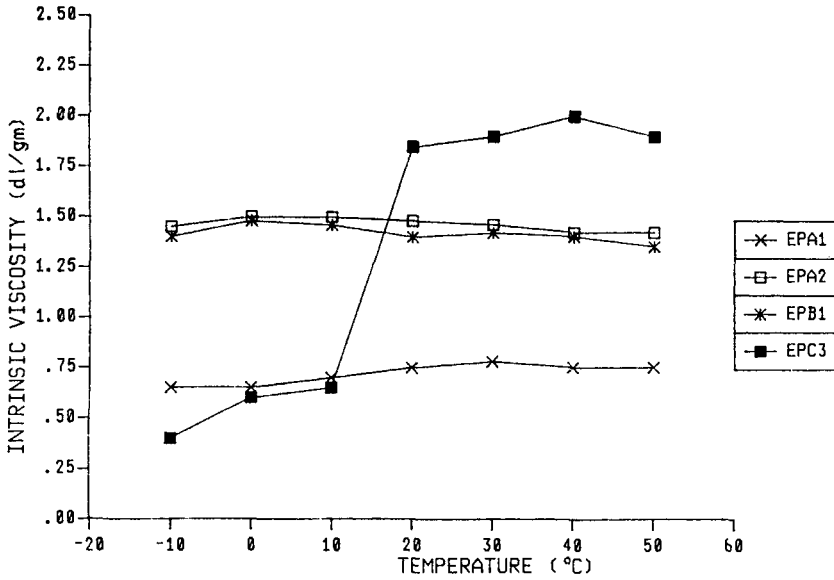


Fig. 3. Intrinsic viscosities of EP copolymers in SNO-100 base oil at various temperatures.

viscosities vs copolymer concentrations.¹ These were then plotted against temperature. As seen in Figures 3 and 4, the intrinsic viscosities of the EPs with 58–70% ethylene hardly changed with temperature. In the case of the EPC3 with 80% ethylene, on the other hand, the viscosities decreased precipitously between 10 and 20°C in SNO-100 and –10 and 10°C in N-100 Pale. Huggins constants for the copolymers in both oils are shown in Figures 5 and 6. They

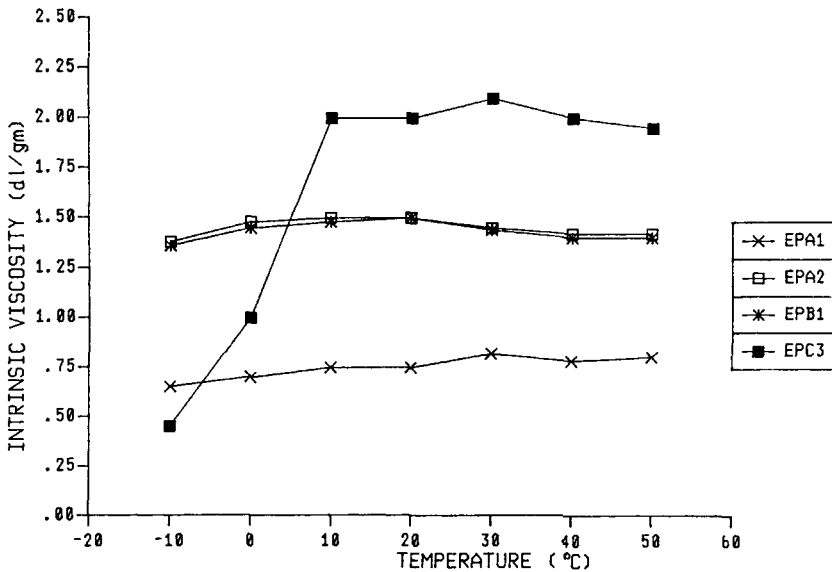


Fig. 4. Intrinsic viscosities of EP copolymers in N-100 Pale base oil at various temperatures.

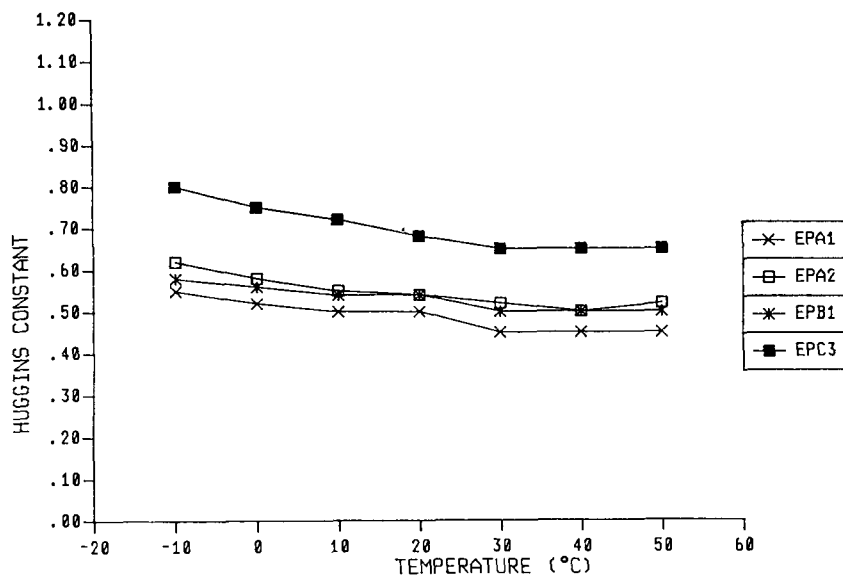


Fig. 5. Huggins constants for EP copolymers in SNO-100 base oil at various temperatures.

change very little for the amorphous EPs and decrease with increasing temperature for the crystalline one.

DISCUSSION

Previous work in our laboratory with pure hydrocarbon solvents showed that the solubility of the EP copolymers discussed in this paper was quite sensitive

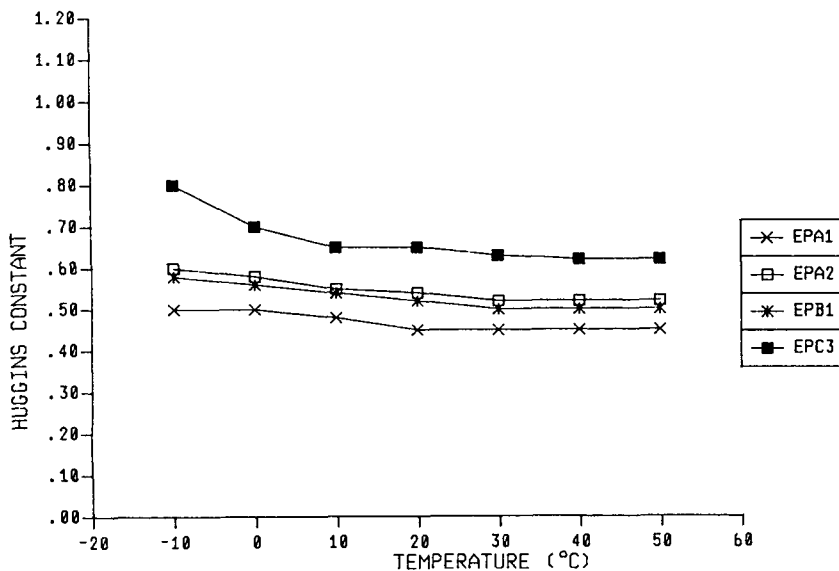


Fig. 6. Huggins constants for EP copolymers in N-100 Pale base oil at various temperatures.

to structural variations of the solvent.² It was, therefore, somewhat surprising that the viscosity of all samples differed so little in the two oils. Apparently, much bigger differences in solvent composition than found in different types of oils are required for an effect on solubility.

The viscosity behavior observed in the two oils, including the sudden decrease in $[\eta]$ at low temperature for the partially crystalline EPC3, was similar to that which we found in pure hydrocarbons which were not particularly good solvents for these copolymers. The drastic decrease in $[\eta]$ is symptomatic of a rapidly deteriorating solvent quality, resulting in a concomitant decrease in solvent-polymer interaction and contraction of the polymer coil in solution. In contrast, $[\eta]$ changed very little with temperature for the amorphous materials, indicating that polymer-solvent interaction remained essentially constant.

This can be seen clearly in Table III which shows the temperature dependence of the equivalent hydrodynamic volumes, V_e , for all copolymers. They were calculated using the expression $V_e = \bar{M}_w[\eta]/\nu N$, where ν is the shape factor, assumed to be 2.5 for spheres, and N is Avogadro's number.³ As the table shows, there was a drastic decrease in V_e values for the crystalline EPC3 between 10 and 20°C in the SNO-100 and between -10 and 10°C in the N-100 Pale oil. For the amorphous copolymers, V_e changed only slightly as the temperature fell from 50 to -10°C.

The only related work we are aware of was carried out by Arlie et al.⁴ and Maderek and Wolf.⁵ Arlie et al., who obtained intrinsic viscosities for one copolymer with 57 mol % ethylene and presumably amorphous in two base oils, one hydrogen refined and the other solvent refined, reported that $[\eta]$ values decreased slightly between 0 and 50°C. The values in the hydrogen refined oil were about 15-20% lower than in the solvent refined one. Overall, the results reported by Arlie et al. thus gave the same general picture for amorphous copolymers in oils as we obtained. We surmise that compositional differences between their base oils were larger than between our oils, thus accounting for

TABLE III
Equivalent Hydrodynamic Volumes V_e of EP Copolymers in SNO-100 and N-100
Pale Base Oils at Various Temperatures

$V_e \times 10^{18} \text{ cm}^3/\text{molecule}$							
(°C)	-10	0	10	20	30	40	50
<i>SNO-100</i>							
EPA1	6.40	6.40	6.80	7.40	7.65	7.40	7.40
EPA2	24.25	25.10	25.10	24.75	24.40	23.75	23.75
EPB1	17.85	18.85	18.60	17.85	18.10	17.85	17.20
EPC3	8.50	12.80	13.90	39.50	40.60	42.70	40.60
<i>N-100 Pale</i>							
EPA1	6.40	6.90	7.40	7.40	8.05	7.65	7.85
EPA2	23.00	24.75	25.10	25.10	24.40	23.75	23.75
EPB1	17.35	18.50	18.85	19.10	18.35	17.85	17.85
EPC3	9.60	21.35	42.70	42.70	44.80	42.70	41.65

the different $[\eta]$ values in the two oils. Maderek and Wolf obtained intrinsic viscosities of an EP with 60 mol % ethylene in an undefined oil between 40 and 100°C. Their $[\eta]$ values rose rapidly to a maximum at about 70°C and then declined almost equally fast. We are unable to advance a reason for the difference between their results and those obtained by us and Arlie et al.

We hypothesize that in solution EPs with small amounts of crystalline material form partially ordered domains or quasicrystalline regions at the temperature at which a more crystalline copolymer would precipitate. These regions are kept in solution by the more soluble mixed EP sequences and short ethylene sequences incapable of organizing into ordered structures. A somewhat similar suggestion has been made by Filiatrault and Delmas.⁶ These ordered domains result in localized volume contractions, which decrease the hydrodynamic volumes of the copolymer chains and reduce viscosity. It appears that these partially ordered structures are quite stable since the copolymers remain in solution and do not precipitate. This is the situation with the EP with 80% ethylene. The copolymers with 58–70% ethylene are quite soluble, and the temperature at which partially expanded chains collapse sufficiently for the material to precipitate is below the temperature range covered by this study.

EXPERIMENTAL

The EP copolymers used in this work were prepared by conventional Ziegler-Natta polymerization using a soluble catalyst composed of an alkylaluminum halide and a vanadium-salt; such copolymers are believed to be essentially linear, with very little branching.^{7,8} Weight average molecular weights, \bar{M}_w , and polydispersity indices, Pd, were obtained at 135°C in 1,2,4-trichlorobenzene by gel permeation chromatography using a Waters Associates 150-C ALC/GPC unit with five columns. The equipment was calibrated on 18 polystyrene standards with \bar{M}_w values between 3000 and 3,300,000. Crystallinities were determined on a Perkin-Elmer Model DSC-7 differential scanning calorimeter at a scanning rate of 10°C/min and using wide angle X-ray scattering measurements on a Scintag Pad V powder diffraction system. Ratio of ethylene to propylene, mean number of ethylene units in sequences of three or more, \bar{N} , and the fraction of ethylene sequences containing three or more ethylenes, $En \geq 3$, were obtained from C-13 NMR data in *o*-dichlorobenzene on a Varian VXR-300 spectrometer.^{9,10} Ubbelohde viscometers and a bath controlled to within $\pm 0.01^\circ\text{C}$ were used for viscosity measurements. Viscosities were run from -10 to 50°C at 10°C increments. Densities of the oils at the different temperatures were measured using a Mettler/Paar DMA 45 digital density meter and copolymer concentrations were corrected for change of oil density with temperature. Flow times for the oils were at least 100 s and no kinetic energy corrections were deemed necessary.¹¹ In related work we found experimentally that the effect of shear rate was negligible under the conditions of our measurements and it was unnecessary to correct for it. The two base stocks were used without a pour point depressant to avoid contribution of the latter to the viscosities of the solutions.

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Accepted January 5, 1990