Viscosities of Ethylene–Propylene–Diene Terpolymer Blends in Oil

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SYNOPSIS

Viscosities were obtained on oil solutions of two ethylene–propylene–diene terpolymers (EPDMs) and their blends. For the amorphous terpolymer with 59 mol % ethylene, intrinsic viscosities were constant between −10 and 40°C. The viscosities decreased rapidly at low temperature for blends of this material with as little as 20 wt % of a slightly crystalline EPDM with 79 mol % ethylene. Dynamic viscosity measurements on 1.0% solutions of blends likewise gave considerably smaller values at low temperature than measurements on an amorphous EPDM of similar molecular weight. The data are in agreement with the view that longer ethylene sequences that crystallize in the bulk polymer can organize in oil into ordered domains that interfere less with flow than the disordered amorphous polymer regions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Previous work in our laboratory showed that small amounts of ethylene crystallinity in ethylene–propylene copolymers (EPs) significantly reduced the low temperature viscosities of these materials in poor hydrocarbon solvents, including oils, particularly at temperatures below about 10°C.[1-3] Thus, EPs with 80 mol % ethylene and small amounts of crystallinity had much lower viscosities than would have been expected on the basis of their molecular weights; this was not observed with amorphous materials containing 60 or 70% ethylene. Since polyolefins and their derivatives are widely used as additives in motor oils to enhance their viscosity characteristics, it was of obvious interest to determine the effect of blending partially crystalline and amorphous olefin copolymers. This paper describes our viscosity results on such ethylene–propylene–diene terpolymer (EPDM) blends in oil at −20–40°C.

MATERIALS

The properties of the EPDMs and their blends are summarized in Table I. Both terpolymers contained about 0.2 wt % diene. The EPDM with 59 mol % ethylene was amorphous while that with 79 mol % ethylene had 5.2% crystalline material. All blends had some crystallinity, which decreased progressively to less than 1% for the blend containing 20 wt % of the EPDM with 79 mol % ethylene. All melting points were about 43–44°C. Number average molecular weights ranged from 98,000 to 132,200. The N-100 Pale Oil used for this work was a typical naphthenic base stock with about 71% naphthenic components, 14% saturated paraffins, and 13% aromatics.[2]

RESULTS AND DISCUSSION

The intrinsic viscosities of the EPDMs and their blends in oil between −10 and 40°C are shown in Figure 1. Results on the two EPDMs were similar to those reported previously for amorphous and slightly crystalline EPs. The viscosity of the amorphous sample A was essentially temperature independent while that of the slightly crystalline C showed a precipitous decrease as the temperature was lowered. It is noteworthy that even as little as 20% of sample C in the blend B1 was sufficient to cause a substantial decrease in intrinsic viscosity at low temperature.

**Table I Molecular Characteristics of EPDMs and Blends**

	EPDM Samples		Blends		
	A	C	B1	B2	B3
Mol % ethylene	59	79	64	70	73
Wt % C in material	0	100	20	42	60
Iodine number	1.5	1.5	1.5	1.5	1.5
Crystallinity (%)	None	5.2	0.8	2.1	3.1
Melting point (°C)	None	43	43	44	43
$\bar{M}_n$	98,000	132,200	105,700	110,300	122,200
$\bar{M}_w/\bar{M}_n$	3.5	2.4	3.4	3.2	2.9

The effect of crystallinity on intrinsic viscosities of the two EPDMs and their blends at various temperatures is illustrated in Figure 2. While the intrinsic viscosities rose slightly with increasing crystallinity at 0 and 20°C, probably due to progressively higher molecular weights, [η] values fell substantially at −10°C as crystallinity increased, in spite of larger molecular weights.

The dynamic viscosities on 1.0% solutions obtained in a Haake Rotovisco Rotational Viscometer at 20 and −20°C are shown in Figures 3 and 4, respectively. At 20°C, the solution with sample C, with the most ethylene and greatest molecular weight, had the highest viscosity, followed by those of the other samples in decreasing order of crystallinity and ethylene content. At −20°C, the order was re-

versed: sample A, the amorphous material, gave the highest viscosity and sample C, the lowest. At 0°C, the results were similar to those at 20°C. These results are illustrated in Figure 5. At −10°C, the viscosities of all samples, with the exception of that of C, were extremely close. For reasons not clear at this time, sample C showed some gelation under shear, precluding comparable readings. Thus, as in the case of intrinsic viscosities, the Haake viscosity results confirmed that as little as 20% of sample C was effective in reducing viscosities of amorphous EPDMs at low temperatures.

While the reason is not yet completely clear for the sudden viscosity decrease of solutions of even slightly crystalline EPs and EPDMs as the temperature is lowered below 10–20°C, it appears to be re-
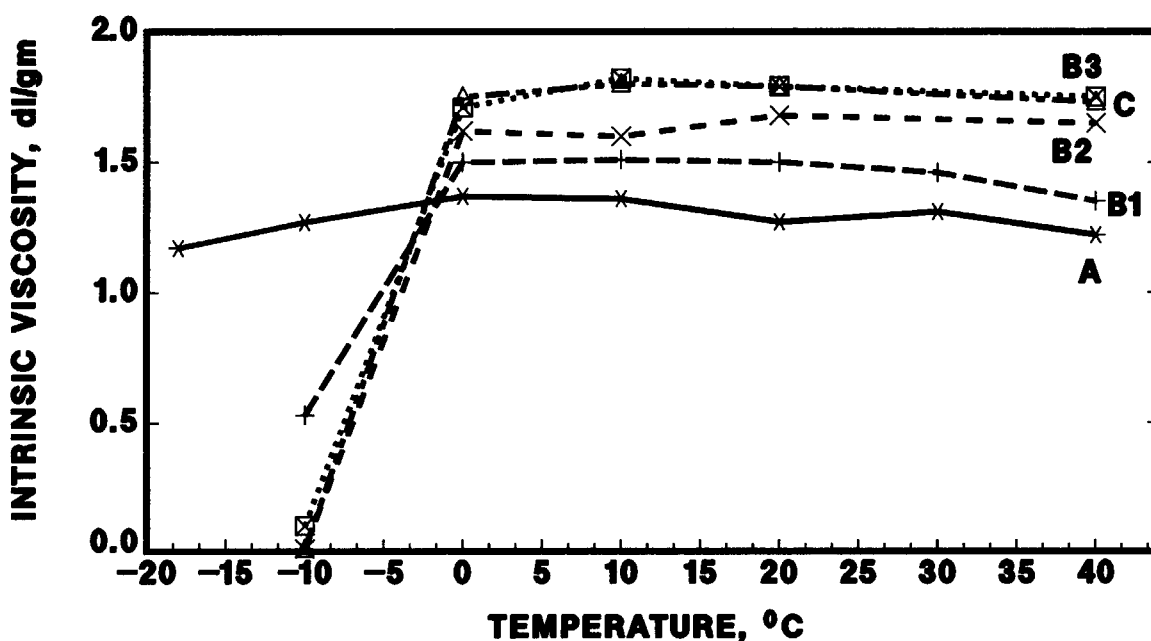
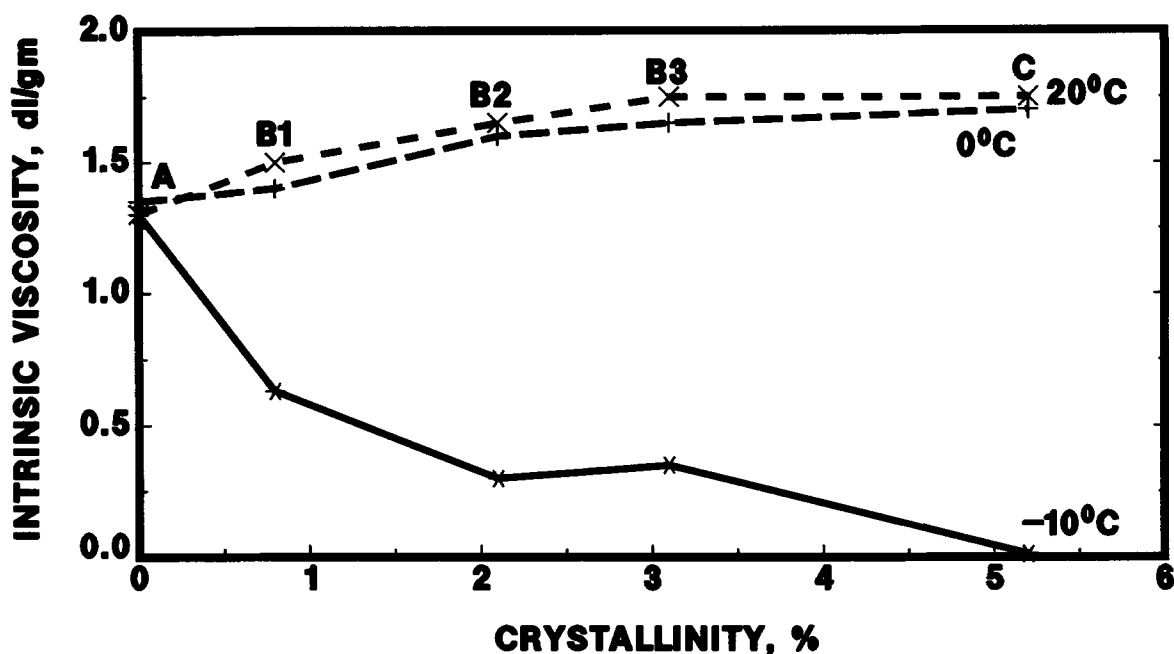**Figure 1** Intrinsic viscosities in N-100 Pale Oil.

Figure 2 Effect of temperature and crystallinity on intrinsic viscosities.

lated to the ability of macromolecules with longer ethylene sequences and small amounts of crystallinity to organize in poor solvents into partially ordered domains.[1-3] It was reported that when certain styrene-containing hydrocarbon block copolymers were dissolved in a poor solvent for one of the blocks, they could associate into micellar arrays with the cores composed of the less soluble blocks.[4-7] EPs . and EPDMs with about 80 mol % ethylene can be thought of as block copolymers with the crystallizable polyethylene segments comprising the less soluble blocks. The partially ordered domains formed from these blocks (which can crystallize in bulk) are kept in solution or suspension by the more soluble random-chain sequences of ethylene and propylene. The structure of these domains has not yet been elucidated: they could be micellar or quasicrystalline. These domains, which result in a reduction of random polymer entanglements and a concurrent increase in polymer mobility, are apparently formed in the temperature region where the sudden decrease in viscosity occurs.

The formation of these domains is supported by recent light-scattering results on an EP with 80 mol % ethylene in tetralin. It was found that in tetralin the EP formed aggregates and that their density increased as the temperature was lowered below 0°C, in contrast to results in a better solvent, methylcyclohexane, where it decreased.[8] The increased density is consistent with the formation of partially

ordered domains within the polymer aggregates. Previous work disclosed that the behavior of EP copolymers in oil was similar to that in tetralin.[2]

The results presented in this paper, particularly the dynamic viscosity data in Figures 3–5, show that the sudden viscosity decrease on cooling is related to the fraction of crystallizable ethylene blocks in the blends. Again, this is consistent with the formation of partially ordered domains. As the fraction of crystallizable ethylene blocks becomes smaller, the viscosity decreases less. Thus, the effect is most pronounced in the sample with 79 mol % ethylene and smallest in the blend with 64%. We find it rather surprising that this latter blend with only 20% of the high ethylene EPDM and 80% of amorphous material caused any decrease in solution viscosity at all. The only way we can rationalize it is that the combination of the small number of longer ethylene segments in the amorphous EPDM combined with the longer sequences of the partially crystalline EPDM is sufficient to create some of the structured domains responsible for the reduction in viscosity.

EXPERIMENTAL

The ethylene–propylene–diene terpolymers used in this work were prepared by conventional Ziegler–Natta polymerization using a soluble catalyst composed of an alkylaluminum halide and a vanadium
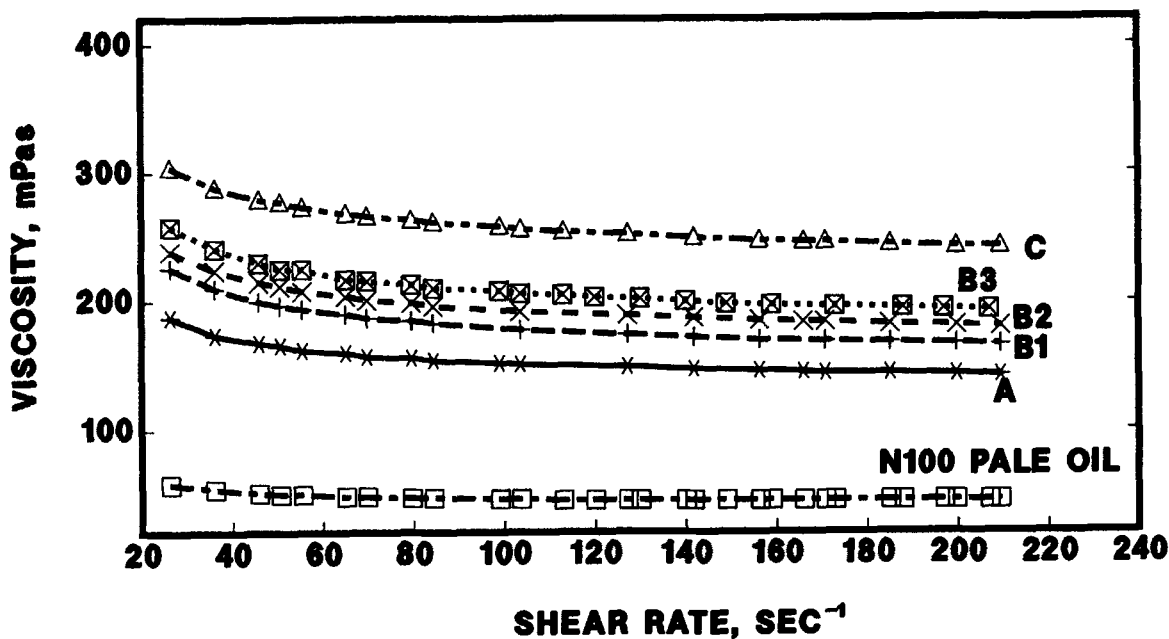
Figure 3   Dynamic viscosities of 1.0% polymer solutions in N-100 Pale Oil at 20°C.

salt; such copolymers are essentially linear, with very little branching. Diene concentration was estimated from iodine number measurements. Molecular weights and polydispersity indices, $\bar{M}_w/\bar{M}_n$, were obtained at 135°C in 1,2,4-trichlorobenzene by gel permeation chromatography on a Waters Associates 150-C ALC/GPC unit with four columns. The equipment was calibrated on eight polystyrene standards with M_w values between 4,000 and 3,100,000. Crystallinities on both the EPDMs and blends were determined on a Perkin Elmer DSC 7 differential scanning calorimeter at a scanning rate of 10°C/min and ratios of ethylene to propylene from C-13 NMR data in o-dichlorobenzene using a Varian VXR-300 spectrometer.[9,10]
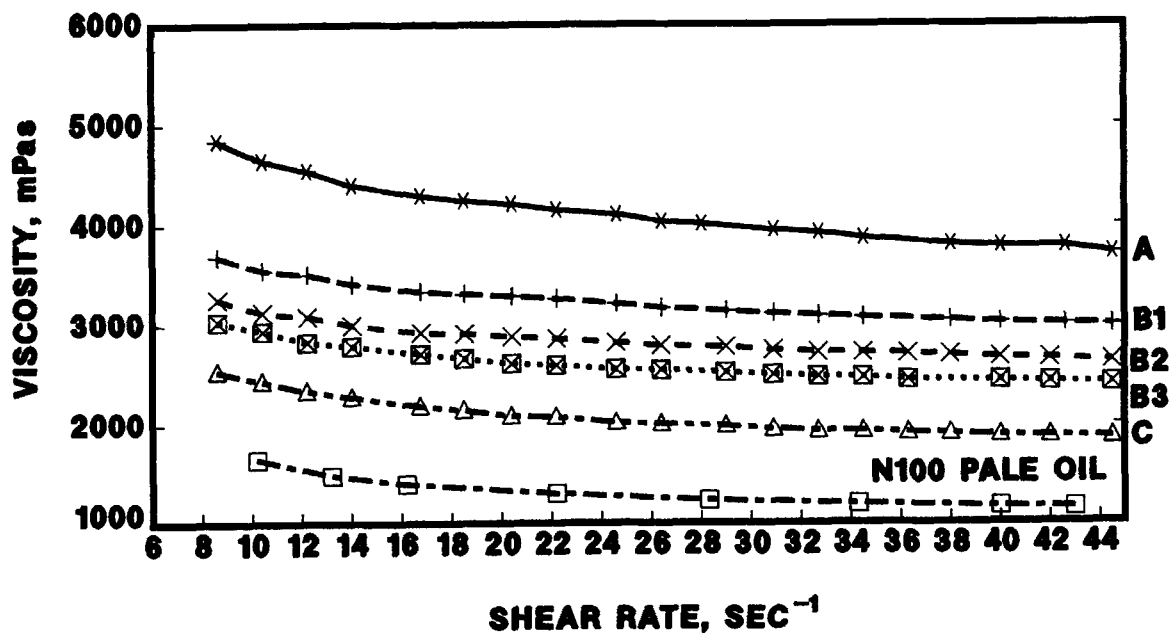
To prepare the blends, the two rubbers were cut

Figure 4   Dynamic viscosities of 1.0% polymer solutions in N-100 Pale Oil at −20°C.
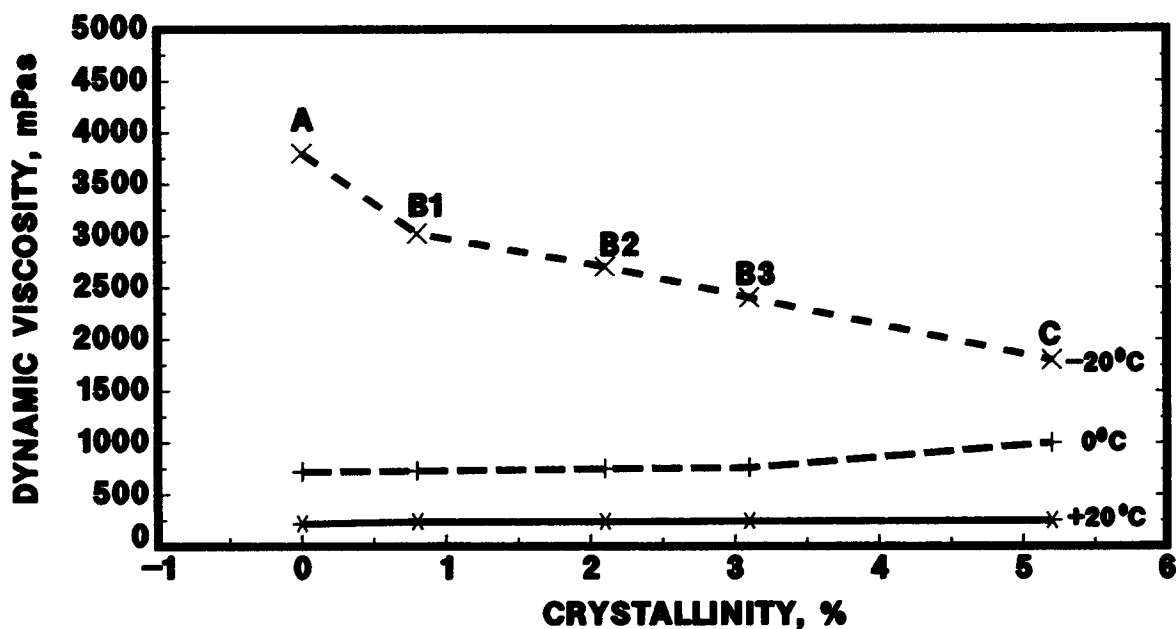
Figure 5 Dynamic viscosities as a function of temperature and crystallinity at a shear rate of 40 s^{-1}.

into $\frac{1}{2}''$ chunks, dissolved with stirring in hexane, and the solvent evaporated. This was done under nitrogen at 50°C.

Ubbelohde viscometers and a bath controlled to within +0.01°C were used for intrinsic viscosity measurements. Viscosities were run from −10 to 40°C at 10° increments. The details were the same as those described in previous work.[1,2] Measurements on 1.0 gm/dL solutions were obtained on a Haake Rotovisco Rotational Viscometer (Model RV-100) between 20 and −20°C at 10° intervals. Temperature was controlled to within 0.10°C.

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