Gas Permeation of Polymer Blends.   I. PVC/Ethylene–Vinyl Acetate Copolymer (EVA)*

YOUNG J. SHUR and BENGT RÅNBY, *Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden*

Synopsis

The transport behavior of O_2 and N_2 were studied for series of physical blends of PVC with EVA having different vinyl acetate (VAc) contents in the EVA (45 and 65 wt-%) and using different milling temperatures (160° and 185°C). The polymer blends were further characterized by dynamic mechanical measurements, density measurements, and x-ray diffraction. At higher VAc content in EVA and with higher milling temperature, the rate of permeation (P) and the rate of diffusion (D) decrease, and the activation energy of D (from Arrhenius plots) increases. Furthermore, the experimental density values of PVC/EVA-45 blends agree well with calculated values, assuming volume additivity of the two components, while those of PVC/EVA-65 blends are higher than the calculated densities. These results are interpreted as due to denser packing of polymer molecules and increased PVC–EVA interaction at higher VAc content and with higher milling temperature, indicating better compatibility between the blend components. The x-ray diffraction data give no evidence of crystallinity. Sharp increases in P and D values at about 7.5% EVA (by weight) are found for PVC/EVA-45 blends (in agreement with our previous work) but not for PVC/EVA-65 blends. This is interpreted as due to a phase inversion at increasing EVA content in the former blends but not in the latter blends. The dynamic mechanical measurements show that the PVC/EVA-65 blends milled at 160°C behave largely as semicompatible systems with maximum interaction between the two polymers at compositions of about 50/50 by weight.

INTRODUCTION

In earlier work from this laboratory, the gas transport behavior of PVC/EVA-45 blends has been studied and related to phase structure and compatibility of the two polymers.[1]

Permeability measurements are a useful method for phase studies of polymer blends, as pointed out by other authors.[2,3] The transport rate of permeant molecules is expected to be sensitive to changes in the micro and macrostructure of the polymer phases and related to the properties of the polymer chains, e.g., molecular mobility and phase interaction.

Despite the extensive work on gas permeation of homogeneous and regularly layered polymer systems, very few permeability studies of polymer blends have been reported. The mechanisms of permeant diffusion in polymer blends are more complex and more difficult to interpret than those for homogeneous or

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idealized systems. This is mainly due to (a) perturbation of the diffusion process due to the dispersed phase, (b) changes in number and size distribution of the holes due to interaction of the phases, and (c) complex transport mechanisms, e.g., interpreted as due to a "dual sorption mechanism." [4]

In the previous study of a series of PVC/EVA-45 blends,[1] with increasing EVA content a sharp increase in permeability and diffusivity was observed at 7–8% EVA by weight. This was interpreted as an effect of a phase inversion in the blends at this EVA content. Recently, Stallings et al.[5] have studied the transport behavior of a series of noble gases in poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene blends which are glassy and largely compatible. The diffusivity of argon and krypton but not of neon was found to be additive for the blends. The nonadditivity of neon diffusion was proposed to be due to the dual sorption process.[4]

The aim of the present work is to study the gas transport properties of PVC blends with a series of different polymers and correlate the data with the blend compatibility. In this paper the results for PVC/EVA blends are reported.

EXPERIMENTAL

Materials

The materials investigated were prepared by physical blending of PVC and EVA at the weight ratios of 100/0, 98/2, 96/4, 92.5/7.5, 85/15, 70/30, 50/50, 25/75, 10/90, and 0/100, using a steam-heated calender mill for 15 min at 160° and 185°C, respectively. The PVC powder and the common stabilizing additives used (organic Ba-Cd salts and Pb stearate, totally 3 parts per 100 parts of PVC + EVA) were first milled to a continuous slab. The EVA was then added and milled into the slab. Pieces of the slabs were pressed to sheets at 160°C for the measurements of permeability, density, dynamic mechanical properties and crystallinity.

The PVC sample used was suspension grade (Pevikon from KemaNord AB, Sweden) with $\bar{M}_w = 74,000$ and $d = 1.39$ g/ml at 25°C. The EVA samples used were of two grades: EVA-45 (Levaplan 450P from Bayer AG, W. Germany) containing 45% of VAc by weight and $\bar{M}_w = 170,000$ and $d = 0.985$; and EVA-65 (VAE 661 from Wacker Chemie AG, W. Germany) containing 65 wt-% of VAc and with $\bar{M}_n = 64,000$ and $d = 1.05$.

Measurements

The measurement of permeability for O_2 and N_2 was carried out on thin membranes (thickness about 0.05 mm) at 25° and 50°C, using an isostatic gas permeability meter (GPM-200 from Incentive AB, Sweden) based on the variation of thermal conductivity of the gas mixture in the test cell.

Measurements with an instrument based on the same principle and calculations of the permeability coefficients (P) have been described by Yasuda and Rosengren.[6] Helium was used as reference gas. The diffusion coefficients (D) were obtained from time-lag measurements in the direct recordings of gas composition.

The density measurements were carried out using a density gradient column (ASTM D1505-67) containing a toluene/carbon tetrachloride solution system having a density range of 0.87–1.59 g/ml at 25°C.

The measurements of dynamic mechanical loss tangent were made for the PVC/EVA-65 blends milled at 160°C using a direct-reading viscoelastometer (Rheovibron, Model DDV-II, Toyo Measuring Instrument Co., Japan) at 110 Hz and between −50° and 120°C.

The crystallinity measurements were made using a Philips recording x-ray diffractometer with CuK$_\alpha$ radiation at room temperature.

RESULTS AND DISCUSSION

The permeability measurements of the polymer blends show (Figs. 1 and 2) that with higher VAc content in EVA and higher milling temperature, (a) the values of P and D are lower, (b) the P and D values become more additive based on data for the two polymers, and (c) the P and D values show a sharp rise at 7.5% of EVA (by weight), mainly for PVC/EVA-45 blends milled at 160°C.

The permeability and diffusivity for O_2 and N_2 show lower values for the PVC blends with EVA-65 than with EVA-45, although the permeability of gases for EVA are reported to increase with increasing VAc content.[7]

The variation of VAc content in the EVA causes significant changes in the physical properties of EVA.[8] The compatibility with PVC is also increased. Hammer[9] has reported that PVC/EVA blends, milled at about 190°C, form two phase systems when the VAc content in EVA was below 50% by weight, while a single phase was formed at VAc contents of 65–70 wt-%. The improved compatibility with PVC may be due to the gradually increased polarity of EVA with higher VAc content. This would result in an expected better solubility of EVA in PVC, and vice versa.

The results under (a) and (b) indicate improved compatibility of the blends with increasing VAc content and higher milling temperature (Figs. 1 and 2). This is further supported by the different activation energies for diffusion (E_D) for oxygen and nitrogen as shown in Figures 3 and 4. The increase in the E_D values with increasing VAc content in the EVA polymer and with higher milling temperature also implies increased interaction of the two polymers due to increased mutual solubility. An increase in E_D as a result of improved compatibility may be interpreted as an effect of a decrease in mobility of the polymer chain segments due to PVC–EVA interaction.

A further indication in the same direction is given by the measured densities for the polymer blends (Fig. 5). For the PVC/EVA-45 blends, mixed and milled at 160°C, the experimental densities agree fairly well with the calculated values, assuming volume additivity and incompatibility of the two polymers. However, the PVC/EVA-65 blends have all higher measured densities than those calculated, both at low (160°C) and high (185°C) milling temperatures. The density differences (excess densities) are 0.02 and 0.03 g/ml, respectively, for 50/50 blends. These density differences cannot be explained as due to changes in crystallinity. X-ray diffraction measurements carried out for each blend have indicated that all samples are largely amorphous with crystallinity of less than 10%. It seems, therefore, reasonable to interpret the excess densities as due to closer packing (less voids) and/or better spatial arrangements of the polymer chains due to increased interaction between the two polymers.

The increased compatibility of the two polymers in the blends was also indicated from dynamic mechanical measurements for the PVC/EVA-65 blends
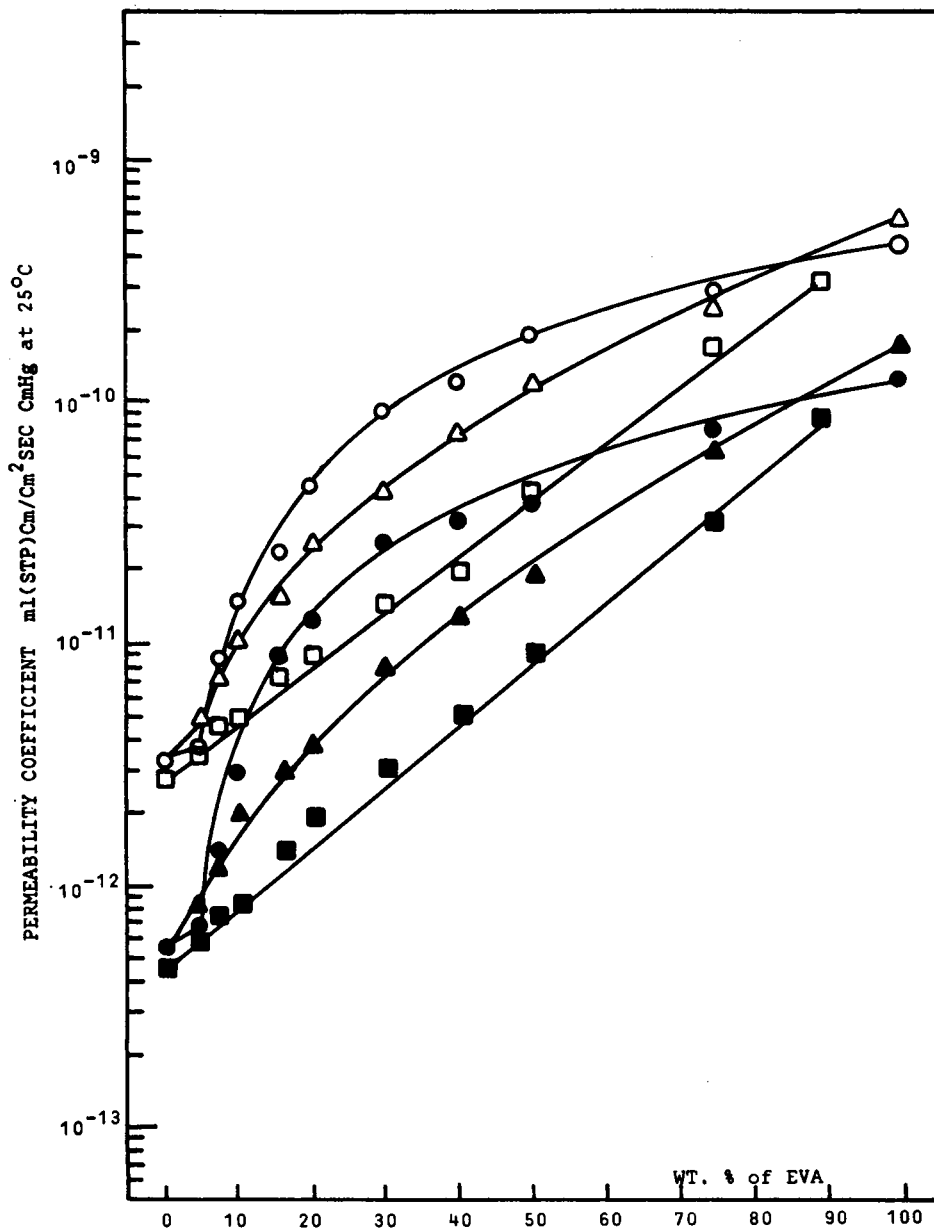
Fig. 1. Permeability coefficients as a function of blend composition in the polyblends.   For oxygen: (O) PVC/EVA-45, milled at 160°C; (△) PVC/EVA-65, milled at 160°C; (□) PVC/ EVA-65, milled at 185°C. For nitrogen: (●) PVC/EVA-45, milled at 160°C; (▲) PVC/ EVA-65, milled at 160°C; (■) PVC/EVA-65, milled at 185°C.

milled at 160°C (Fig. 6).   It has been reported that PVC/EVA-45 blends form incompatible systems at all compositions,[10,11] while PVC/EVA-65 blends milled at about 190°C form compatible systems.[9]   In our present study, the PVC/ EVA-65 blends milled at 160°C can be described as semicompatible systems from pure PVC up to compositions of 50/50 and then as compatible systems, i.e., they
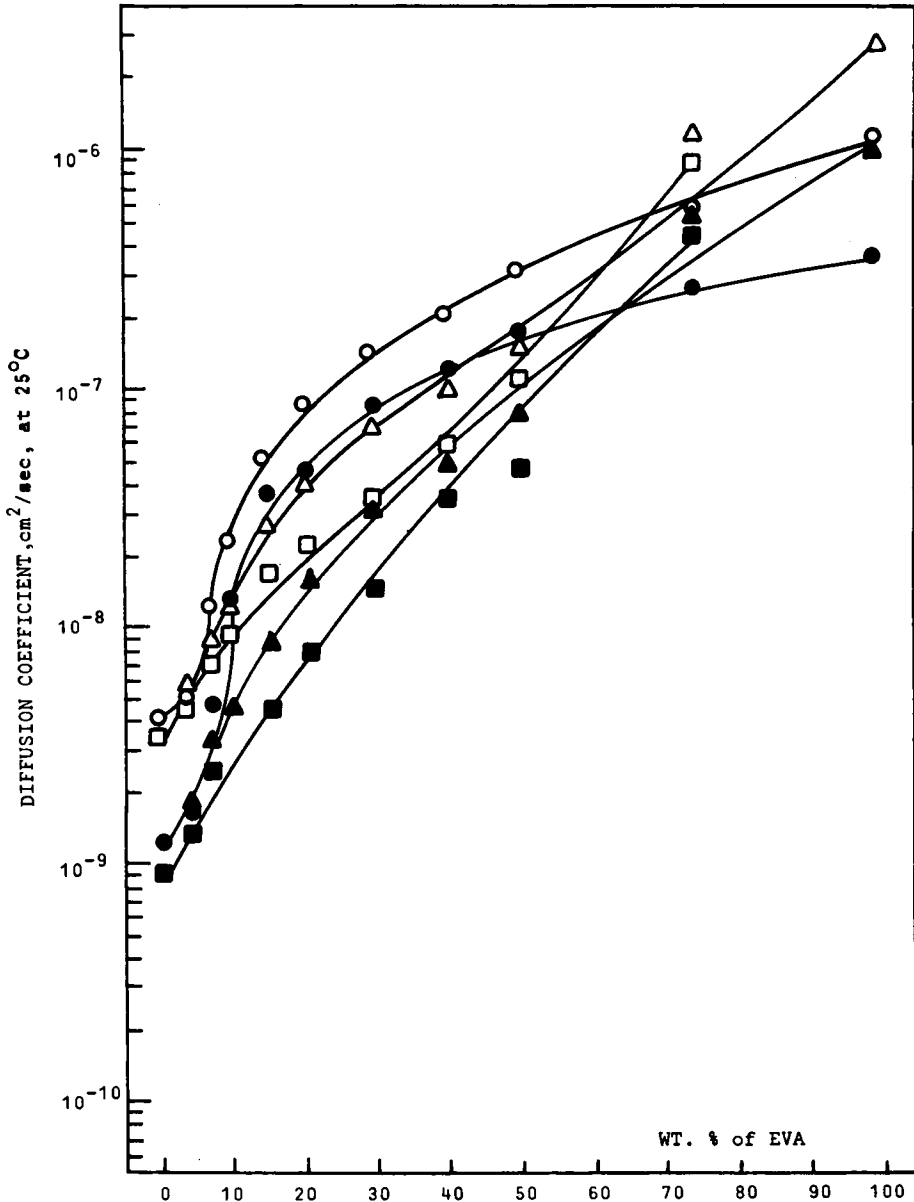
Fig. 2. Diffusion coefficients as a function of blend composition of the blends. For oxygen: (O) PVC/EVA-45, milled at 160°C; (△) PVC/EVA-65, milled at 160°C; (□) PVC/EVA-65, milled at 185°C. For nitrogen: (●) PVC/EVA-45, milled at 160°C; (▲) PVC/EVA-65, milled at 160°C; (■) PVC/EVA-65, milled at 185°C.

contain one pure (PVC) and one mixed (PVC + EVA) phase. In the dynamic mechanical measurements, the tan δ variation with temperature as a function of composition provides a qualitative picture of the interaction of the two mixed phases. Thus, the addition of EVA-65 up to 50 wt-% does not alter the *location* of the main relaxation maximum associated with PVC (at about +95°C). But the magnitude of the loss peak is changed, i.e., it is decreasing
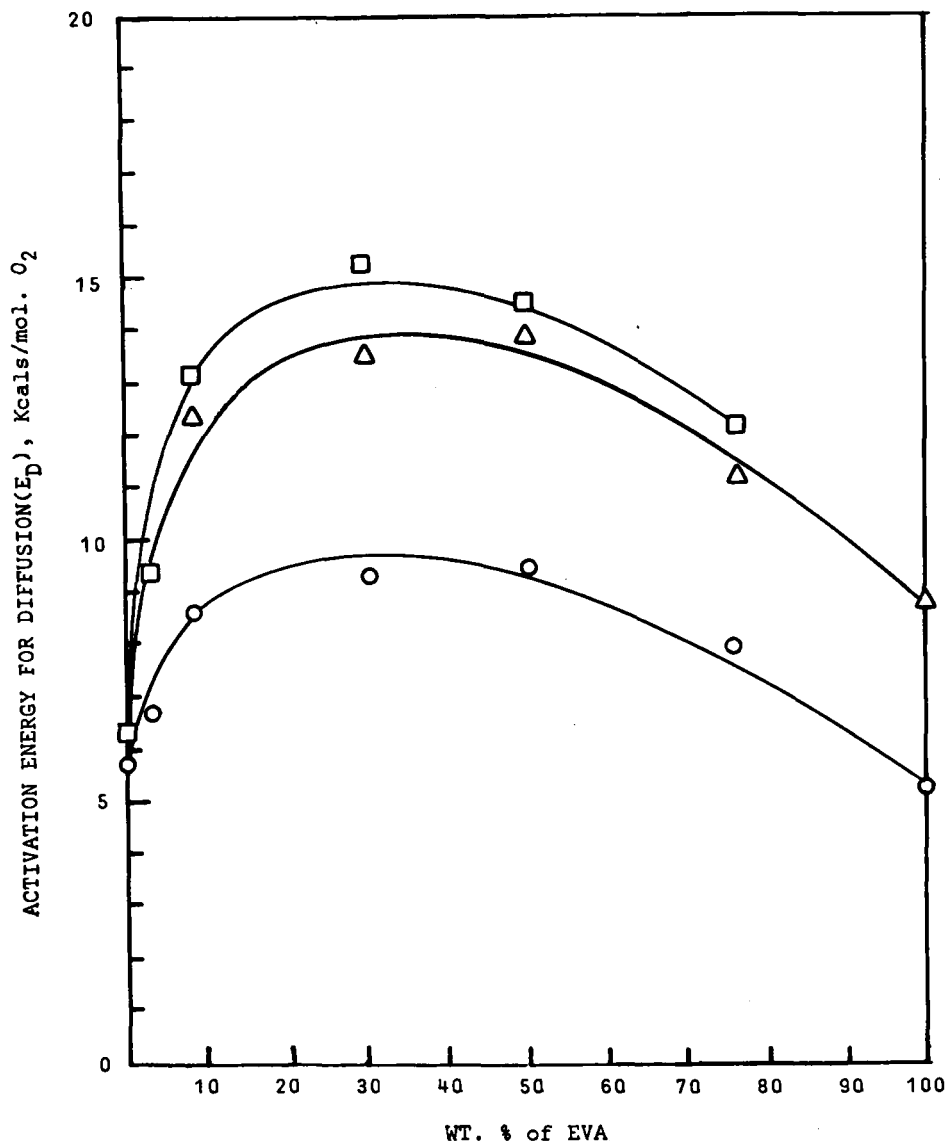
Fig. 3. Activation energy for diffusion vs. blend composition for oxygen in the blends: (O) PVC/EVA-45, milled at 160°C; (△) PVC/EVA-65, milled at 160°C; (□) PVC/EVA-65, milled at 185°C.

with increasing content of EVA-65. However, the low temperature loss peak thought to be associated with cooperative relaxation phenomena of the two polymers (located at about −15°C for pure EVA-65) is changing in location and magnitude over the whole composition range. This is interpreted to mean that the EVA added is partly associated with PVC, leading to a cooperative relaxation. At the same time, another part of the PVC phase relaxes independently. Starting with pure PVC, such a dual relaxation is observed for blend compositions up to 50/50. Thereafter, only cooperative relaxation is recorded in the tan δ curves. Similar results were obtained for the PVC/NBR-20 (acrylonitrile con-
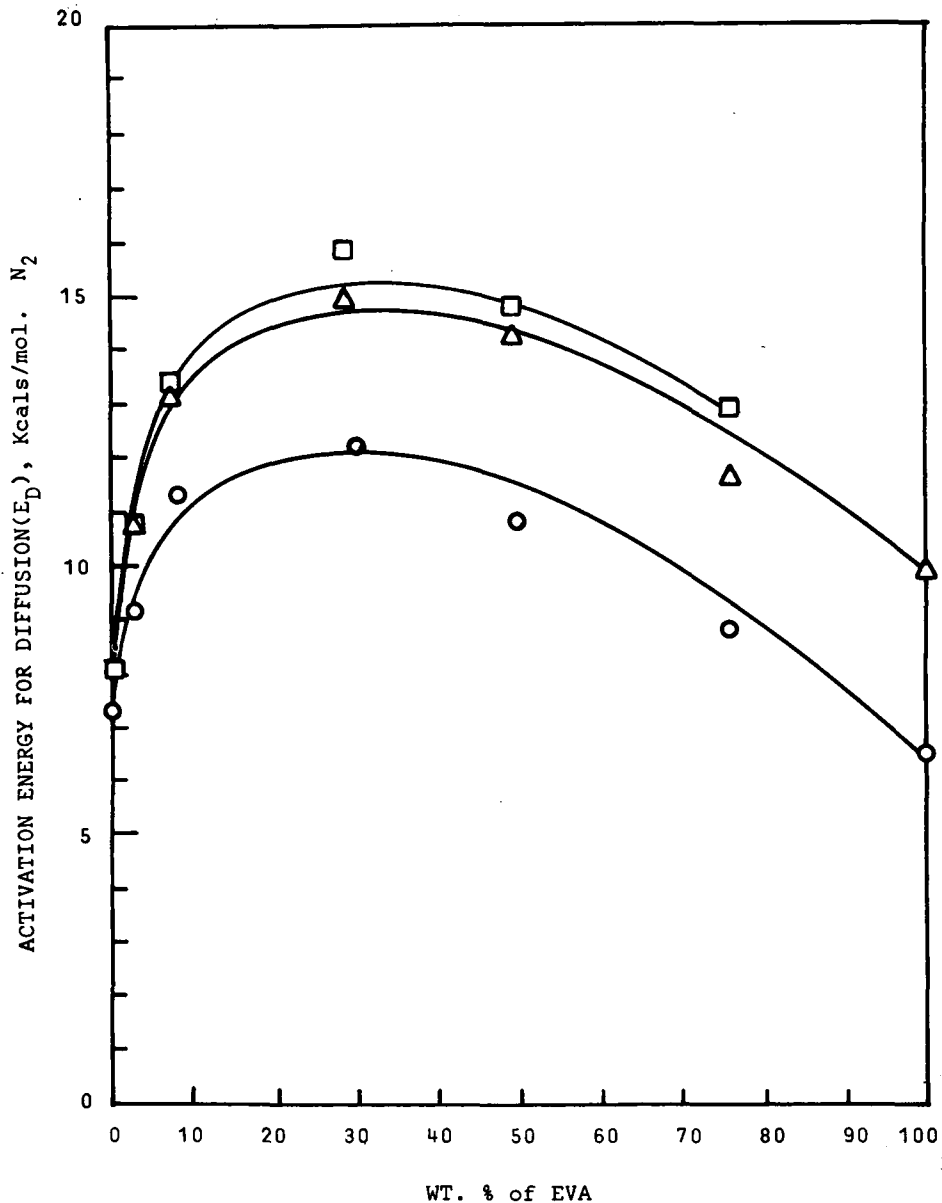
Fig. 4. Activation energy for diffusion vs. blend composition for nitrogen in the blends: (O) PVC/EVA-45, milled at 160°C; (△) PVC/EVA-65, milled at 160°C; (□) PVC/EVA-65, milled at 185°C.

tent 20%) system.[12] The PVC phase formed at low milling temperatures (~170°C) may be considered to contain two fractions, one having partly crystalline, unmelted particles (called phase I), and the other consisting of an amorphous fraction plus melted particles (called phase II). The cooperative relaxation with EVA is considered to occur mainly in phase II.

Using this model, three relaxation processes may occur: two associated with PVC and EVA, respectively, and a third related to the PVC/EVA mixed phase.
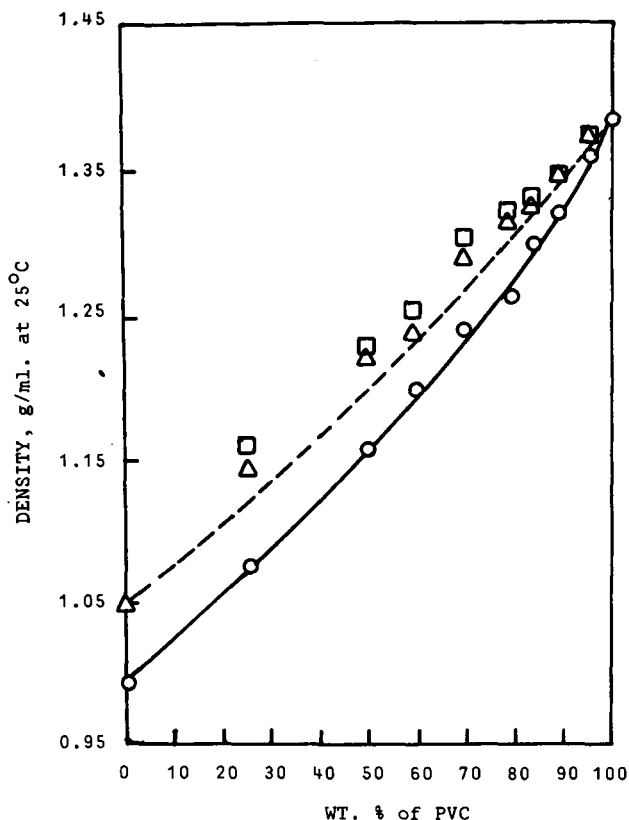
Fig. 5. Experimental and calculated densities of the blends vs. blend composition: (O) PVC/EVA-45, milled at 160°C; (△) PVC/EVA-65, milled at 160°C; (□) PVC/EVA-65, milled at 185°C; (———) calculated values for PVC/EVA-45; (- - -) calculated values for PVC/EVA-65.

At extreme blending ratios, there may be only one relaxation for PVC or EVA and the other for the mixed phase.   For higher degree of compatibility, only one relaxation for the mixed phase of the two polymers may occur, e.g., as in the case of PVC/EVA-65 blends milled at about 190°C.[9] With increasing milling temperature (≥180°C), the fraction of phase II indicating the level of compatibility is raised, implying that more PVC can be involved in the cooperative relaxation process.   This model is made probable by the morphologic studies of PVC milled at different temperatures.[13,14]   Hattori et al.[13] have observed by electron microscopy that the structure of PVC particles remains largely unchanged at extrusion temperatures up to 170°C.   However, from 180°C and higher, the particles gradually begin to loose their structure and form a continuous phase. Jyo et al.[14] have also shown that the original particle structure of PVC is not destroyed by milling at 155°C.   In contrast, the particle structure of EVA at the discussed temperature range (from 155° to 190°C) are easily changed, and the melt flow is also much higher than that of PVC.   It is, therefore, quite plausible that PVC and EVA are very difficult to blend into a homogeneous mixture unless there is strong molecular interaction.   Thus, EVA may behave as a lubricant between PVC particles at low EVA additions and then start to form a coherent phase with increasing EVA content in the blends.   This situation may be
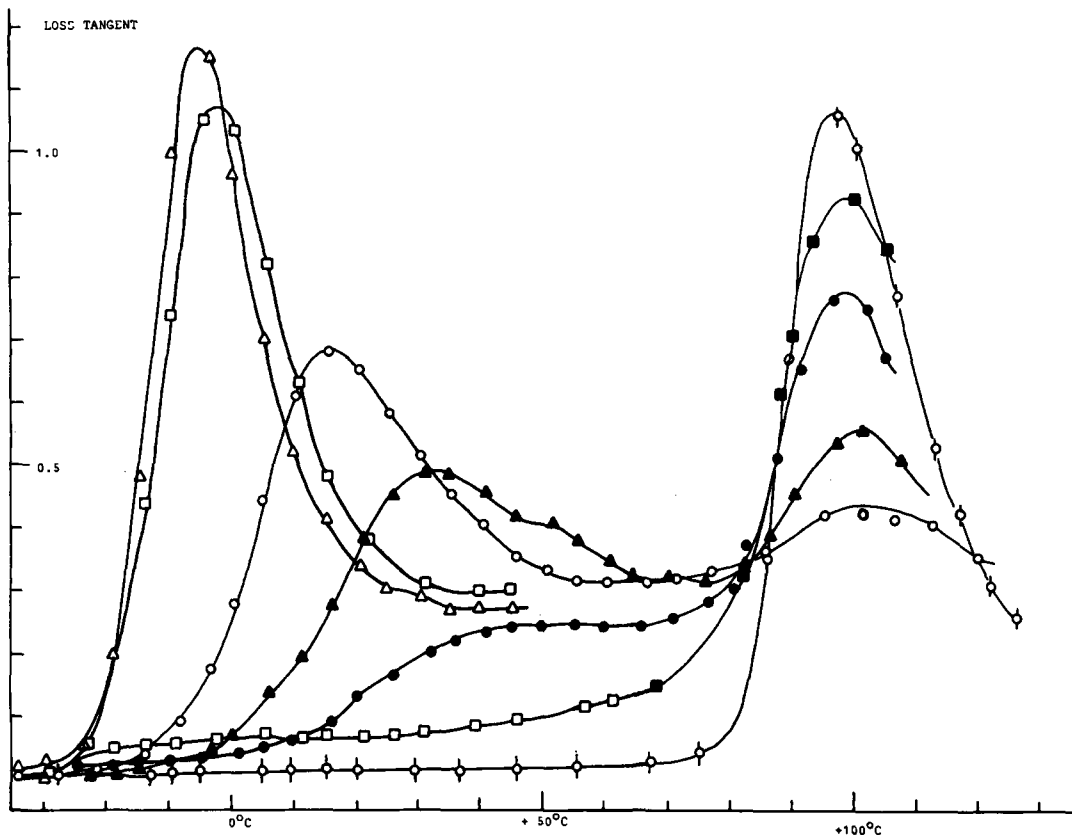
Fig. 6. Mechanical loss tangent of PVC/EVA-65 blends milled at 160°C as a function of temperature: (△) 10/90 (PVC/EVA-65); (□) 25/75; (○) 50/50; (▲) 70/30; (●) 85/15; (■) 92.5/7.5; (♢) 100/0.

changed when the VAc content in EVA and the milling temperature are increased. The increase in solubility of EVA in PVC with increasing VAc content and increasing melt index may reduce the mentioned expected lubricating behavior. Instead, a better interpenetration is expected into the PVC matrix which in addition may be looser at higher milling temperature. This general picture seems to agree with our results.

Only the PVC/EVA-45 blends milled at 160°C have a well-marked sharp increase in permeability and diffusivity at 7.5 wt-% of EVA-45. This agrees with earlier results[1] and is interpreted as a phase inversion: at very low EVA-45 content in the blends (≤ 7.5 wt-%), PVC is the continuous phase; and at higher EVA-45 content, EVA-45 is the continuous phase. However, no such phase inversion seems to take place for PVC/EVA-65 blends.

These studies are continued to further investigate the preliminary results obtained.

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