

Effect of Shear Rheology on PVDC and PE Blend Permeation Behavior

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SYNOPSIS

The morphology of an immiscible polymer blend is dependent on the flow properties of the components and the deformation fields to which the mixture is exposed. The barrier properties of an immiscible blend is dependent on the barrier properties of the components and the morphological structure of the blend. Therefore, the resulting permeation rate of these blends is dependent on the rheology of the component materials. Conversely, the morphology of these blends can be studied by measuring permeation rates of a probe molecule. The oxygen permeation rate of vinylidenechloride copolymers blended with polyethylene changes abruptly over a small composition range. In the absence of significant extensional flow fields, this change is due to a phase inversion, and its position in the composition range is dependent on the shear rheology of the components.

INTRODUCTION

The barrier properties of a two-phase polymeric material can be highly dependent on the structure. This is especially true if the components themselves differ greatly in permeability. For a melt-mixed polymer blend, the rheological and interfacial properties of the components coupled with the flow fields determine the morphology. Since the permeation rate is affected strongly by the structure, there is a significant dependence of the permeation rate on the rheology of the component materials. In this work, oxygen as the permeant through the vinylidenechloride copolymer (co-VDC) and polyethylene (PE) blend system is studied. These two polymers differ by 2 orders of magnitude in the rate of oxygen permeation.

The permeation rate is largely influenced by the polymer that composes the continuous phase. Also, the size and shape of the dispersed phase has significance influence. If the high barrier polymer forms the continuous phase, percolation paths can exist where relatively little of the high barrier material need be traversed. The extent to which this occurs

depends on the relative volume, size, geometry, and orientation of the dispersed phase. Since the resulting transmission rate of this type of structure follows a reciprocal additivity function, small areas of these percolation paths significantly affect the overall permeation rate. The inverse structure, where the low barrier polymer comprises the continuous phase, is also affected by the geometry of the dispersed phase. What is needed to make a significant permeation rate change is a lamellar structure oriented perpendicular to the diffusion path. A tortuous path thus exists, decreasing the permeation rate. In either case the steady-state permeation properties of the blend are bounded by the series and parallel limiting structures. These limits can be visualized by a two-layer structure. In the series case the permeation path is perpendicular to the interface, and parallel in the parallel case.

EXPERIMENTAL

Blending

The blends were made using a single screw, 10 : 1, *L/D* 2-in. diameter extruder. Steam heating was used to obtain a 175°C flat extrusion profile. The co-VDC was first mixed with 2 wt % tetrasodium pyrophosphate and 1% epoxidized soybean oil. This

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mixture was pelletized as it exited the extruder. These co-VDC pellets were then tumble blended with the polyolefin and reextruded. The additives, short extruder, and steam heat, as opposed to electric heat, all contributed to the extrusion stability necessary for a blending study requiring multiple extrusions.

Rheology

The shear viscosity of the materials was obtained using an extrusion-fed slit rheometer. It consists of a 1-in wide die fed by a $\frac{3}{4}$ -in. 24 : 1 extruder. Three slit heights of 0.026, 0.051, and 0.076 in. are used to extend the range of shear rate measurement. Barrel temperature set points were 165, 175, and 175°C for zones 1 to 3. The die set point was 175°C. The extruder speed is varied within the range of 10–150 rpm. At each speed the extruder is run until the die pressures stabilize and then a sample is collected over a 1-min time period. The mass output rate was used with the melt density to calculate the volumetric output rate. An average pressure reading taken over the same time period is used for the shear stress calculation. A Rabinowitch correction is performed and the resulting shear rate and viscosity data is reported. Within the ranges of shear rate and viscosity measured in this work, repetitive viscosity measurements of the same polymer will fall within

a $\pm 3\%$ window. A more extensive description of this rheometer can be found elsewhere.¹

Oxygen Permeation Rate

Permeation rates were measured using a MoCon Oxtran 1050. Low barrier blends were measured directly at 23°C. Due to the long times involved for steady-state permeation to occur with high barrier samples at 23°C, measurements are made at 40, 50, and 60°C and an Arrhenius extrapolation is made to obtain a 23°C result. The relative humidity was 70% during the measurements. An example of this extrapolation is shown in Figure 1 for a blend of 83 vol % 70,000 M_w co-VDC and 35 MI low-density polyethylene. Results for two separately molded samples are included. The extrapolated oxygen permeation rates for the two samples at 23°C are 0.298 and 0.302 $\text{cm}^3 \text{ mil}/100 \text{ in.}^2 \text{ day atm}$. The reproducibility of oxygen transmission rate using this technique is typically better than $\pm 2\%$.

Compression-molded films were used for the permeation measurements. The sample was pressed between chrome-plated steel plates with polyethyleneterephthalate film between the sample and steel plate. The steam-heated platens were at a set point of 180°C. The sample was held at 1000 lb total ram force for 1 min during the warm-up step. The force was then increased to 40,000 lb and held for 2 min. The platens were then water-cooled to about 50°C,

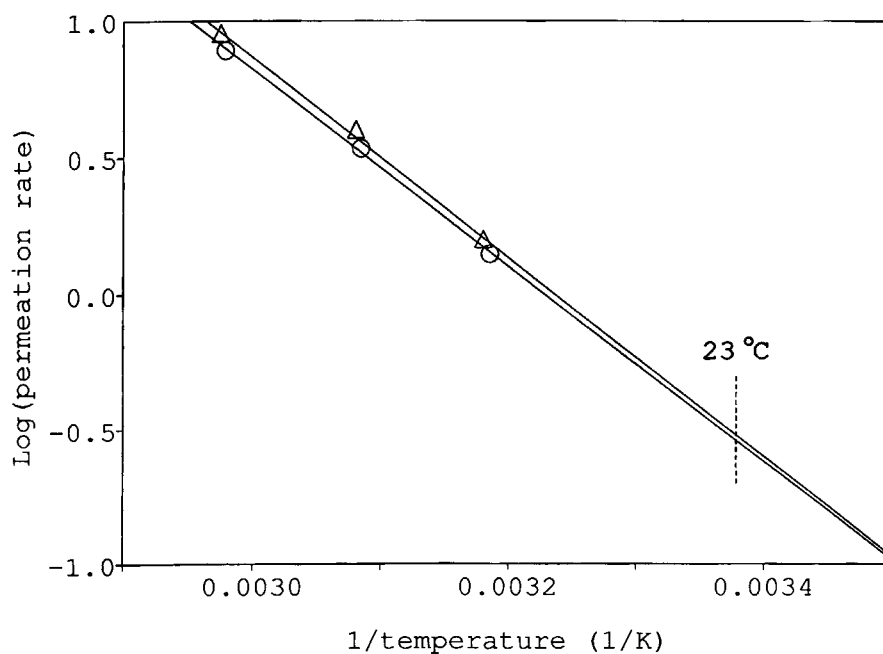


Figure 1 Arrhenius extrapolation of high barrier blend to 23°C.

which occurred in about 3–4 min. The resulting molded film had an area of approximately 40 in.²

RESULTS AND DISCUSSION

Rheology measurements of the components at 175°C are shown in Figure 2. The co-VDC is an 80,000 M_w , 15 wt % vinyl chloride copolymer. Four polyethylenes were used: three low-density resins with MI of 2, 4, and 12 and a high density of 95 MI. At 100 s⁻¹ the viscosity ratios of PE/PVDC range from about 0.1 to 0.8 (the co-VDC rheology is for the resin with the tetrasodium pyrophosphate and epoxidized soybean oil). These resins were then blended as described above at various composition ratios. Polyethylene-co-ethylacrylate is used as a compatibilizer. The amount of acrylate copolymer is 20% based on polyethylene. This is necessary to decrease the phase size under the rather gentle mixing conditions that were used to make the blend. In addition, the films made for the permeation measurements have greater strength and are easier to handle due to the greater interphase adhesion.

The results of the oxygen permeation rate measurements from compression-molded films are shown in Figure 3. A nonsymmetrical S shape is seen for the transmission rate versus composition function. This S shape is due to the phase inversion that

takes place because of the composition shift from the high composition fraction polyethylene blends to the high co-VDC blends. This basic shape has been seen for many analogous blend systems. Shur and Ranby have reported results of polyvinylchloride (PVC) blended with polyethylene-co-vinylacetate (EVA),² polyacrylonitrile-co-butadiene (NBR),³ chlorinated polyethylene (CPE),⁴ and polyacrylonitrile-co-butadienecostyrene (ABS).⁵ In the PVC/EVA case, permeation rate versus composition data were shown. The shape is very similar to the present work, and the previous authors attributed the S shape to a phase inversion. No rheology data of the components were given. However, it was stated that the EVA had a much higher flow rate than the PVC, although no mention of a relationship between this and the position of the phase inversion was given.

Data were also shown for a blend of PVC with a 65% vinylacetate copolymer. This was reported to be a miscible blend, and the composition versus permeation rate data did not have the S shape.

For PVC/NBR³ blends, the data are somewhat more difficult to analyze in the view of miscibility versus immiscibility. This is because within the acrylonitrile range studied, at least semimiscibility existed. The CPE/PVC⁴ blends are interesting to compare because in this work it is stated that the CPE increases in viscosity with chlorine content. Composition versus permeation rate graphs look similar to Figure 3. The S curves are indicative of

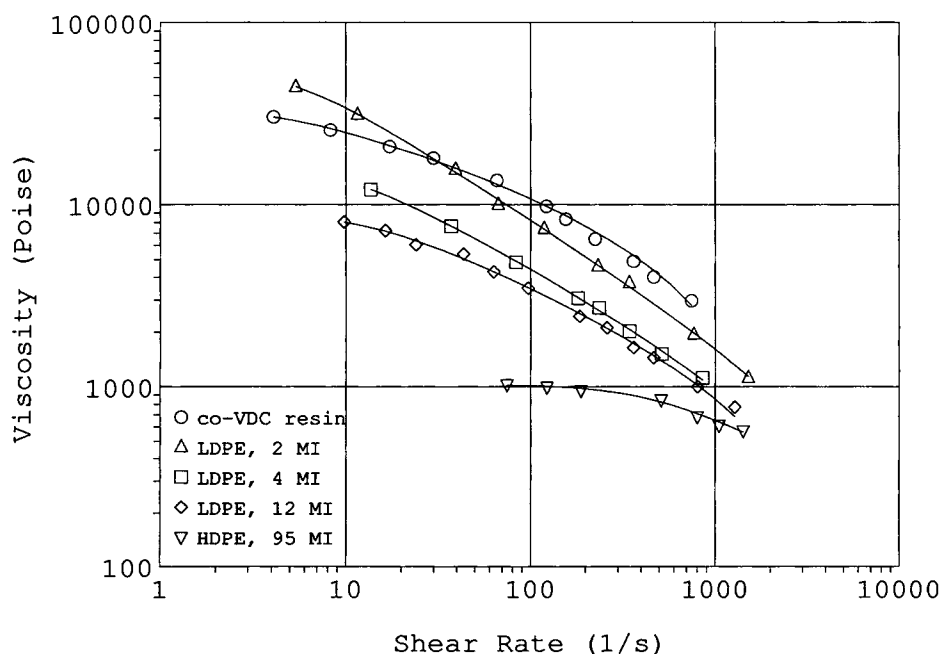


Figure 2 Shear rheology curves of co-VDC/PE blend components.

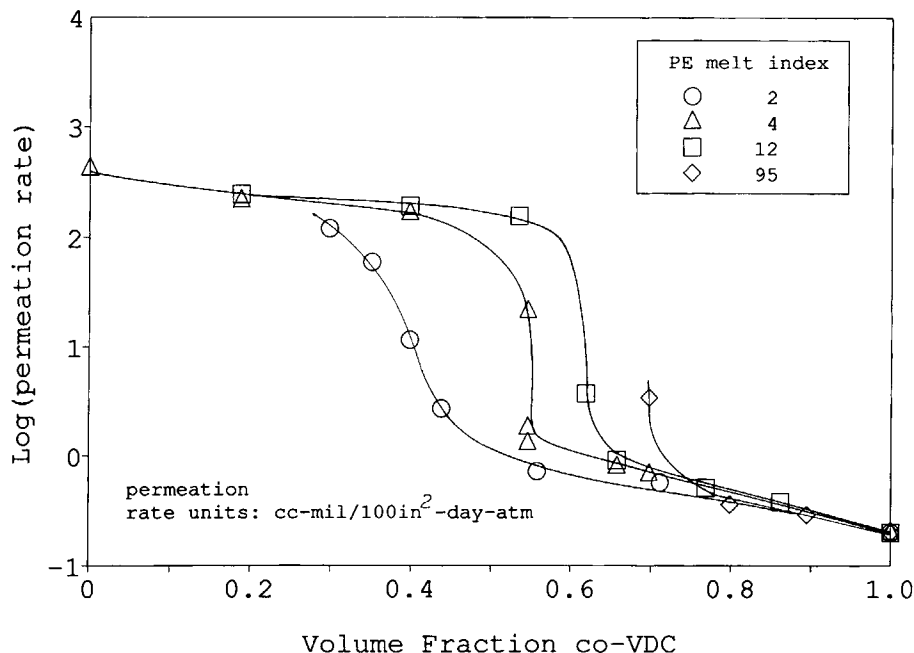


Figure 3 Oxygen permeation rate as a function of PE viscosity and level. The volume percent is calculated from densities measured at 23°C. Permeation rate is in units of cm^3 mil/100 in.² day atm.

the phase inversion shift toward higher CPE contents with increasing CPE viscosity. This is consistent with our results. However, the issue is somewhat clouded because the permeation rate of the CPE alone decreases significantly with increasing chlorine content. Thus, through the chlorine content, the CPE permeation rate and viscosity are coupled. This is probably why no comments were made as to the effect of the viscosity on barrier. In the PVC/ABS⁵ study, somewhat S-shaped curves are seen; however, like the PVC/ABS work, semimiscibility makes it difficult to draw conclusions based on a two-phase model of pure A and B components.

Subramanian and Mehra⁶ studied the transport of toluene through a nylon/PE blend. An S-shaped function is seen for the composition dependence of a well-mixed blend. As expected, structures with the same compositions but with a laminar-layered structure (diffusion perpendicular to the lamellar surface) more closely resemble the series case. Sax and Ottino⁷ derived relationships for the diffusion of a permeant through a semirandom two-phase structure. The shapes of the curves correspond well to the experimental data from the many studies.

In the current work the phase inversion composition range is mainly dependent on the flow properties of the two polymers. Interfacial energies are assumed to be similar since only the type of poly-

ethylene is changing and all polymers are in the melt state when the morphology is formed. An analogous explanation for the inversion occurring at higher PE content with higher molecular weight can be used as for molecular weight segregation during flow. A quasi-thermodynamic description has been given for the experimental results of finding lower molecular weight species near the wall during the shear flow of PE.⁸ At zero shear all polymer chain segments have a constant free energy. Under steady-state laminar flow, a shear gradient is induced. This results in an elastic deformation that increases the free energy over that of the equilibrium state. Short chains entangle less than long chains, and therefore the short chain free energy change is less in the imposed shear field. In a two-phase blend, the potential for increasing the elastic deformation is greater for the continuous phase. Given that the co-VDC phase has not changed, if a lower molecular weight polyethylene is substituted, it will have a tendency to remain the continuous phase until a higher co-VDC concentration is reached. Therefore the shift in the permeation rate function for the co-VDC/PE blends is due mainly to the change in PE molecular weight since the phase inversion is controlled by the flow properties of the components. The permeation rate shift is not due to differences in barrier properties of the components or miscibility considerations.

Shown in Figure 4 is a schematic of this function with the parallel and series layer cases added for comparison. At high polyethylene levels the structure is a polyethylene continuous matrix with dispersed spheroid-shaped PVDC particles. Up to where the inversion occurs, the transmission rate is little affected by the dispersed high barrier phase. The tortuosity is, however, a slight factor even for the nearly spherical particles. This can explain some of the deviation of the data from the parallel model in the high permeation rate region. In order to discuss the nonspherical nature of the particles, Figure 4 also contains a function derived from a filled polymer model. This model⁹ assumes spherical impermeable particles. A comparison of the data with this model gives evidence of a deviation from spherical shape for at least some of the particles. If one assumes the particles are disks with an L/D ratio of greater than 1, a better fit to the initial data results. Using the following relationship:¹⁰

$$P_{(\text{filled})} = \frac{P_{(\text{unfilled})} \times \text{Vol}_{(\text{polymer})}}{1 + (L/2D) \times \text{Vol}_{(\text{filler})}}$$

The best fit to the first three data points of Figure 4 is obtained with an L/D of 3.5. The somewhat disklike geometry of the co-PVDC phase probably results from the last processing step, the compression molding. To obtain a film with no holes, the

pellets are piled in the middle of the mold. This results in a large amount of biaxial extensional flow during the compression, some of which is retained in the cooled and crystallized sample.

In high co-VDC level compositions, the oxygen transmission is similarly only slightly affected by the presence of the PE phase. A small deviation from the series model is seen due to a few high permeation rate paths present. These arise from random fluctuations in the two-phase structure where a group of particles are in relative close proximity in the permeation direction. Although few in number, their effect is significant due to the reciprocal additivity of permeation rate for this type of morphology.

Figure 5 shows morphological map of PVDC/PE blends from this study. The filled circle is used to signify a blend with an oxygen permeation rate of less than $1 \text{ cm}^3 \text{ mil}/100 \text{ in.}^2 \text{ day atm}$. The open circle is used for blends with values higher than these. If we instead choose $10 \text{ cm}^3 \text{ mil}/100 \text{ in.}^2 \text{ day atm}$ for the delineation value, the results would be almost the same due to the slope of the permeation rate function shown in Figure 3. The blends discussed so far, in addition to some others, are represented in Figure 5. The additional data are all from co-VDC/PE blends; however, different components were used. Other co-VDC resins used were a 70,000 M_w , 11% vinyl copolymer and three methacrylate copolymers. The molecular weight of the vinylidene

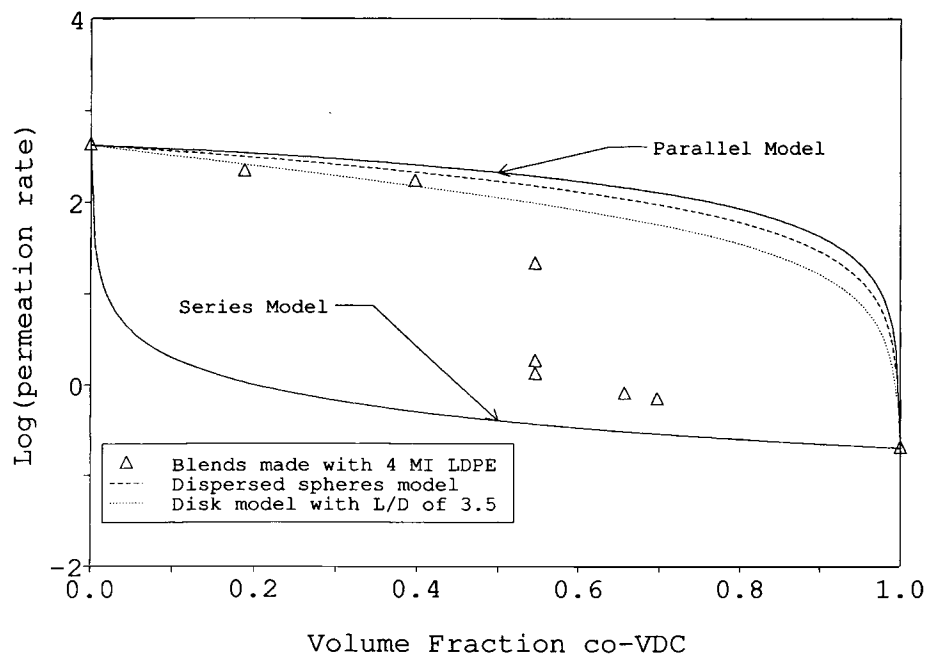


Figure 4 Comparison of data for the 4 MI LDPE blends with various two-phase permeation models.

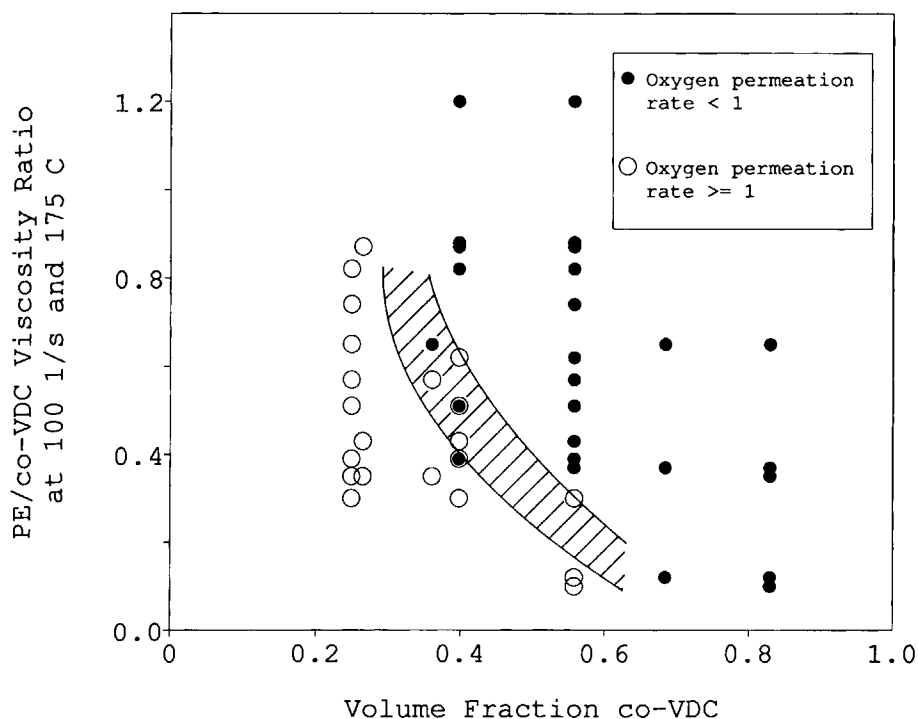


Figure 5 Phase inversion boundary as determined by the oxygen permeation behavior of the blend.

chloride methyl acrylate copolymers were 55,000, 90,000, and 110,000 with 6, 6 and 4 wt % comonomer contents, respectively. Two more LDPEs were used, with 8 and 35 melt flow rates. The appropriate position of the phase inversion region is shown by the grid. Essentially, the oxygen molecule has been used to probe the structure. When measured this way, the inversion does occur over a band due to the previously mentioned percolation and tortuosity cases. In this band other factors such as the elasticity of the components, minor variations in interfacial energy, or the flow fields can play a large role in determining the resulting permeation rate.

CONCLUSIONS

When two immiscible polymers with widely differing barrier behaviors are blended, the permeation rate as a function of composition is almost discontinuous due to the phase inversion. This is true when a lamella-type structure is not present. Within the ranges of co-VDC and PE investigated in this study, the viscosity ratio of the components is of main importance to the position of the inversion. At compositions with the dispersed phase being the high barrier component, the diffusion behavior is close to the parallel model. Deviations from the model are due to tortuosity, especially if extensional flow-cre-

ated geometries remain in the blends. When the high barrier component is the continuous phase, the series model is more closely followed with deviations due to high permeation rate paths composed of close proximity dispersed phase.

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