

Physical Properties of Poly(ethylene adipate)/Low-Density Polyethylene Blends

S. S. IM,¹ T. J. KIM,¹ S. HAN,² T. J. MOON,² Y. C. BAE³

¹ Department of Textile Engineering, Hanyang University, Seoul 133-791, Korea

² Department of Materials Science, Korea University, Seoul 136-701, Korea

³ Department of Industrial Chemistry, Hanyang University, Seoul 133-791, Korea

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ABSTRACT: Mechanical and rheological properties of poly(ethylene adipate) (PEA)/low-density polyethylene (LDPE) blends were investigated. DSC results showed that there is no miscibility between PEA and LDPE. Tensile strength decreases with increasing PEA content, while the modulus increases. Elongation at break decreases with increasing PEA content. A rheological constitutive equation was used for describing and predicting the steady-state shear viscosity of PEA/LDPE blend. The suggested equation was successfully able to describe and predict viscosity of the blend as functions of shear rate and temperature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1745–1750, 1997

Key words: rheological properties; poly(ethylene adipate); rheological constitutive equation

INTRODUCTION

Conventional plastics are not easily degraded in the environment, due to their high molecular weight and hydrophobic character. In fact, scientists have traditionally sought ways to make them more resistant to heat, light, water, chemical attack, etc. Disposal of plastics, then, has become a major environmental concern, resulting in programs to reuse, incinerate, or convert these wastes.¹

Unlike plastic beverage bottles, certain disposables are not suitable for collecting and recycling; contaminated food packaging films and the like are not expected to have a long service life. Uncollectable litter such as merchandise bags are unsightly and pose a serious threat to wildlife. To

overcome these problems, plastics are being developed that degrade in the environment. There are two approaches to degradable plastics. One is to modify conventional materials by adding a degradability trait. The other is to synthesize items with resins that are inherently degradable. However, there is disagreement among scientists on whether traditional plastics such as polyethylene can ever completely biodegrade, even when blended with degradable additives. In spite of that, there has been an increase in the applications for biodegradable plastic products. Not only has there been a growth in the market segments for these materials, but some of these segments are growing into significant markets.

Although much work has been reported for properties of biodegradable polymers, the literature has given less attention to fundamental studies on those polymers. We cannot give a complete literature review here, but mention only a few relatively recent publications.

Correspondence to: Y. C. Bae.

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Bastiol, Bellotti, and Rallis² reported physical properties and melt processing results of starch-based polymer under steady-state shearing. They studied a peculiar microstructure involving a strong pseudoplastic behavior at high shear rates as well as yield stress at lower ones. Their proposed model explained fairly well the characteristics and viscoelastic behavior of this material based on hydrophilic and hydrophobic interactions between starch and vinyl-alcohol copolymers.

Chapman³ reported new applications and product improvements for biodegradable materials. Montaudo and co-workers⁴ studied the microstructure of the copolyesters formed in the exchange reactions which occur during the melt mixing of poly(ethylene adipate) (PEA) and poly(ethylene terephthalate) (PET). They observed that the copolyester initially formed in the exchange reaction is a block copolymer containing an excess of adipic units, as it should be expected if the reaction would proceed through the attack of PEA oligomers on the macromolecular PET chains.

In this article, thermal and tensile properties of PEA/low-density polyethylene (LDPE) blends was investigated. A unified simple rheological equation of state for the steady-state shear viscosity was used for describing and predicting the steady-state shear viscosity of PEA/LDPE blend.

EXPERIMENTAL

LDPE was obtained from Yugong Co. and used as received. Its melting point was reported to be $\sim 118^\circ\text{C}$. PEA was synthesized and its molecular weight, polydispersity, and melting point were 39,310, 1.59, and 44°C , respectively.

PEA and LDPE were manually mixed with PEA/LDPE compositions of 10 : 90, 25 : 75, and 30 : 70 by weight, and then blended in a two-roll mixer at 120°C for 5 min.

Thermal properties of blends were measured using DSC (SHIMADZU, DSC-50). The heating rate was $10^\circ\text{C}/\text{min}$, and the sample weight was ~ 5 mg.

Phase structures of blends were observed by using a scanning electron microscope (SEM, HITACHI S-2400) after etching a section of the blend sample with tetrahydrofuran to remove PEA.

Specimens for tensile test were compression molded at 145°C , 1500 psi for 5 min; dimensions of sample specimens used in this study were the

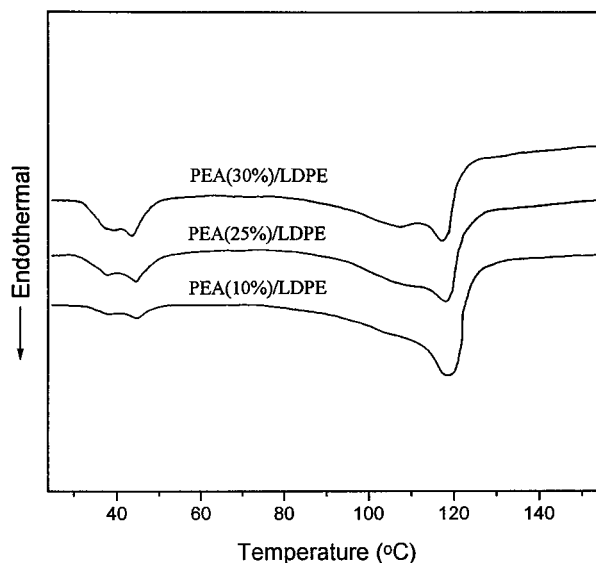


Figure 1 Melting temperatures of PEA/LDPE blends at the composition of PEA 10%, 25%, and 30%.

same as the type II specimens of ASTM D638. Tensile tests were performed by a UTM (Toyo Baldwin Co., UTM-4-100) using a crosshead speed of 20 mm/min. Steady-state shear viscosities of molten polymer blends were measured by using a capillary rheometer (Instron Co., Model 3211). Test temperatures were 160, 180, and 200°C .

RESULTS AND DISCUSSION

Thermal and Mechanical Properties

Figure 1 shows thermograms for PEA/LDPE blends. Because both melting endotherms are clearly resolved at various PEA compositions as shown in Figure 1, we conclude there is no compatibility between PEA and LDPE.

Figure 2 shows SEM micrographs of etched PEA/LDPE blends surface with various compositions. SEM micrographs of PEA/LDPE blends with 20% and 30% PEA composition show that PEA phases are evenly distributed in the matrix on the order of 2–3 μm in diameter. However, in the corresponding SEM micrograph of PEA/LDPE blend with 40% PEA composition, PEA phases are agglomerated in the matrix and unevenly distributed on the order of 5–15 μm in diameter.

In Figure 3, tensile strength is plotted against PEA composition. The tensile strength

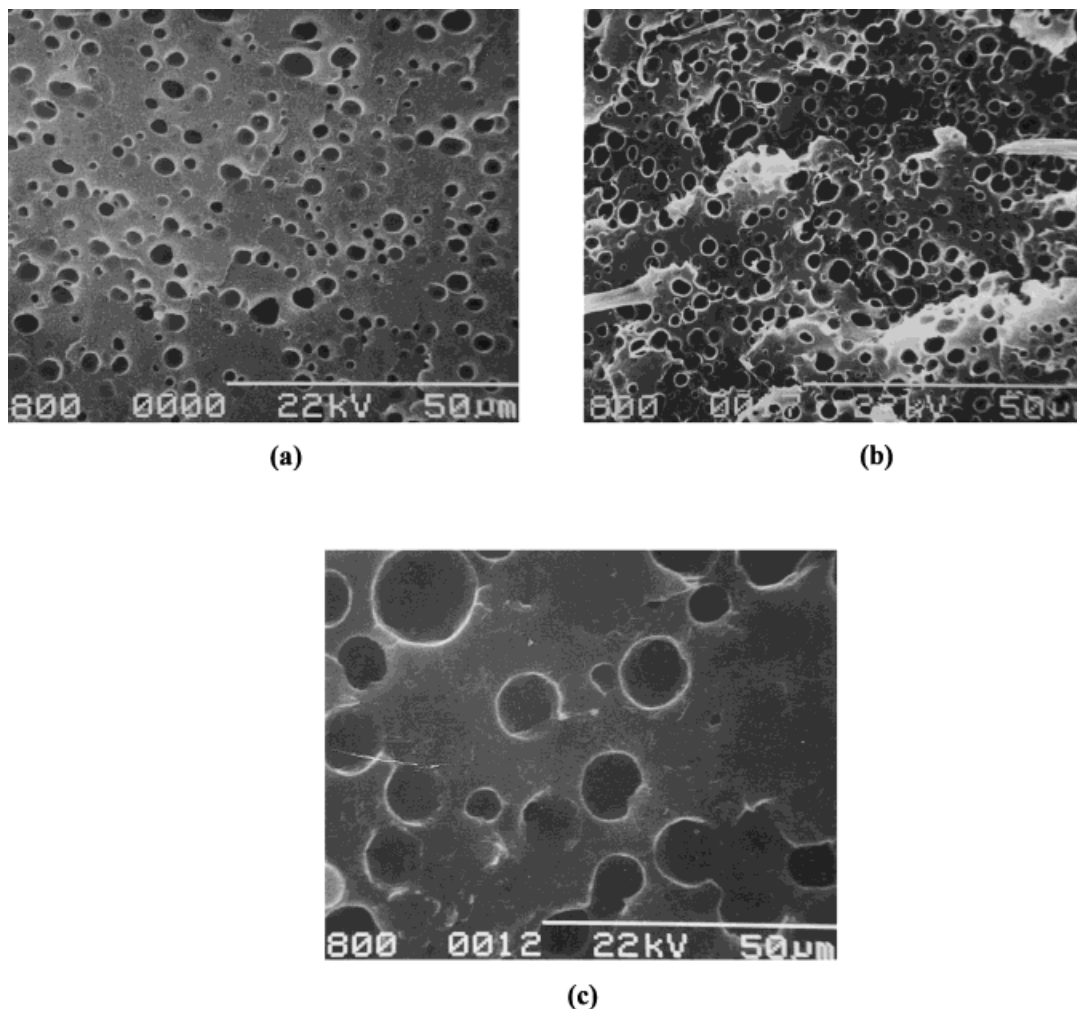


Figure 2 SEM photographs of PEA/LDPE blend taken after removing PEA by THF etching. The PEA composition is (a) 20%, (b) 30%, and (c) 40%.

of pure PEA is much lower than that of LDPE. Tensile strength of PEA/LDPE blend decreases with increasing PEA composition. This result is due to the incompatibility between PEA and LDPE, which can be estimated from results of DSC thermograms in Figure 1 and SEM photographs in Figure 2. Above 40% PEA composition by weight, tensile strength of the blend could not be measured due to the experimental difficulty.

The modulus of blend is plotted against PEA composition in Figure 4. The modulus of PEA is much higher than that of LDPE. In contrast to tensile strength, the modulus of blend remarkably increases with addition of small contents of PEA and it reaches a maximum value at $\sim 25\%$ PEA by weight. It is interesting that the

modulus of blend somewhat reflects positive synergism.⁵

Figure 5 shows the elongation at break with various PEA compositions. Elongation at break of LDPE is much higher than that of PEA and elongation decreases with increasing of PEA composition.

Rheological Equation of State for PEA/LDPE Blends

In the previous article,⁶ a unified rheological equation of state for the steady-state shear viscosity was derived based on thermodynamic principles. This constitutive equation for steady-state shear flow can be expressed in the form shown below.

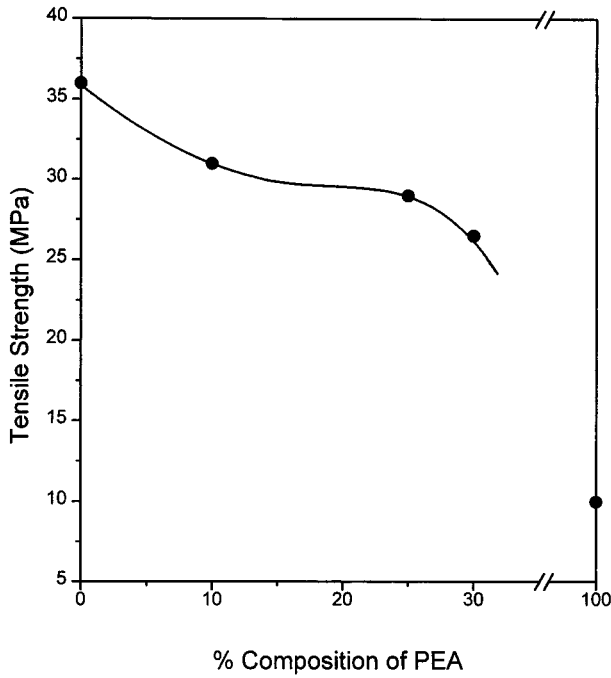


Figure 3 Variation of tensile strength with composition for PEA/LDPE blends.

$$\ln \eta = \ln \bar{K} + (n - 1) \ln \dot{\gamma} + \frac{Q}{RT} \quad (1)$$

In the above equations, \bar{K} is the material constant, n is the power-law index, Q is the activation energy for the given flow, R is a gas constant, and $n - 1$ is a function of temperature and is given by

$$n - 1 = \alpha + \frac{\beta}{T} \quad (2)$$

where α and β are constants.

Since eq. (1) is a thermodynamic equation of state, it follows that the thermodynamic criterion shown below is true.

$$J \equiv \frac{\partial^2 \ln \eta}{\partial(1/T)\partial \ln \dot{\gamma}} = \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma} \partial(1/T)} \equiv D \quad (3)$$

To prove eq. (1) is a state function experimentally, one needs to show the relationship in eq. (3) from experimental data.

It has been reported that the above rheological constitutive equation can be successfully described and predict the steady-state shear viscosity of polymer melts.⁶ In the following sections, the above rheological constitutive equation was

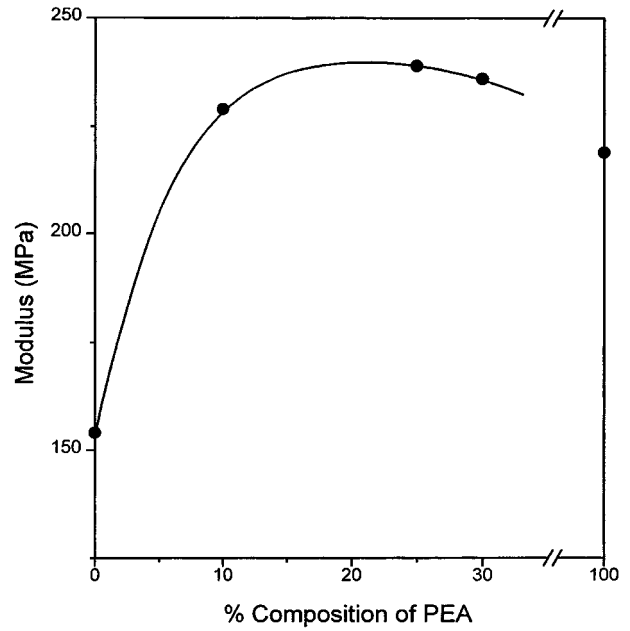


Figure 4 Variation of modulus with composition for PEA/LDPE blends.

used for describing and predicting the steady-state shear viscosity of PEA/LDPE blend.

As shown in Figure 6, steady-state shear viscosities of the PEA/LDPE (25% PEA composition) were plotted against temperature at various shear rates. Then, the value of $Q/R + \beta \ln \dot{\gamma}$ can

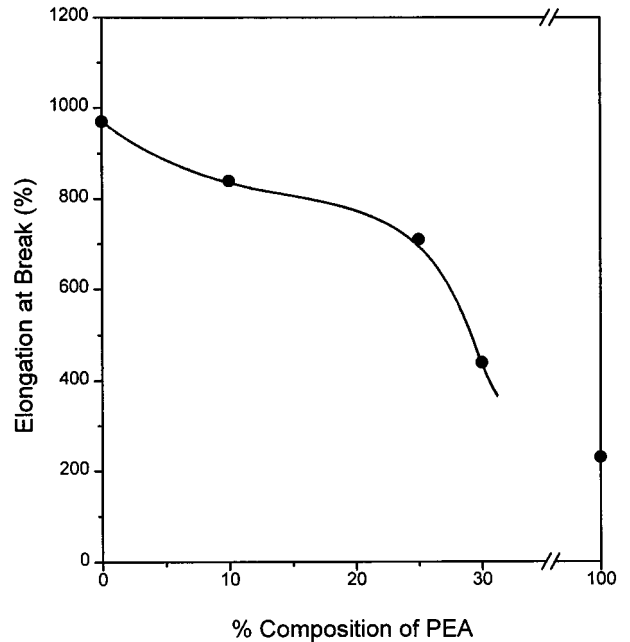


Figure 5 Variation of elongation at break with composition for PEA/LDPE blends.

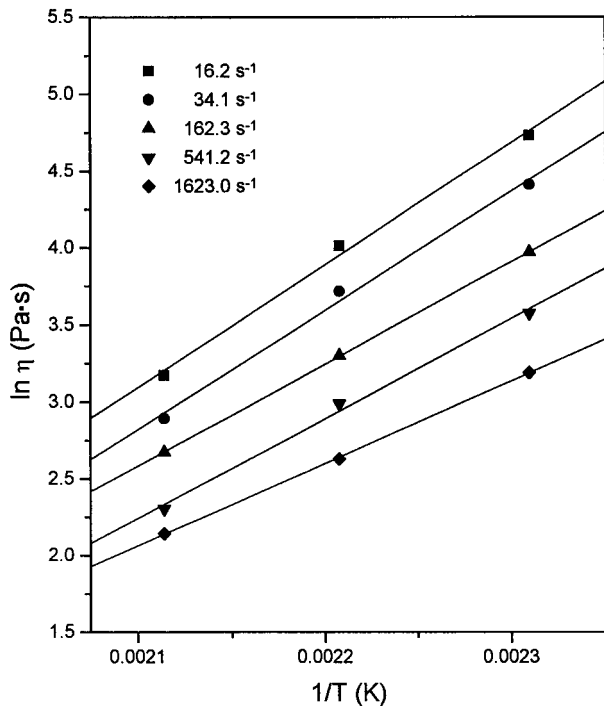


Figure 6 Variation of melt viscosity with temperature at fixed shear rate: (■) 16.2 s^{-1} ; (●) 34.1 s^{-1} ; (▲) 162.3 s^{-1} ; (▼) 541.2 s^{-1} ; (◆) 1623.0 s^{-1} .

be determined from the slopes of the plot in Figure 6. The values of $Q/R + \beta \ln \dot{\gamma}$ at various logarithmic shear rates were determined and plotted against $\ln \dot{\gamma}$ in Figure 7.

From eq. (3), the value of J for the PEA/LDPE blend can be determined from the slope of the plot in Figure 7, and calculated value was -540 .

Figure 8 shows that the steady-state shear viscosity was plotted against logarithmic shear rate at various temperatures. The values of $\alpha + \beta/T$ can be determined from the slopes of the plot in Figure 8. The values of $n - 1$ at various temperatures were determined and plotted against $1/T$ in Figure 9.

From eq. (3), D can be determined from the slope of the plot in Figure 9 and the value of D is -530 .

The difference between J and D is negligible, so eq. (3) satisfies the thermodynamic criterion. It shows that the rheological equation of state is a state function and that the steady-state shear viscosity of PEA/LDPE blend can be described by the rheological equation of state expressed in eq. (1).

When β is chosen by the mean value (-535) of J and D , the values of Q/R and α can be calcu-

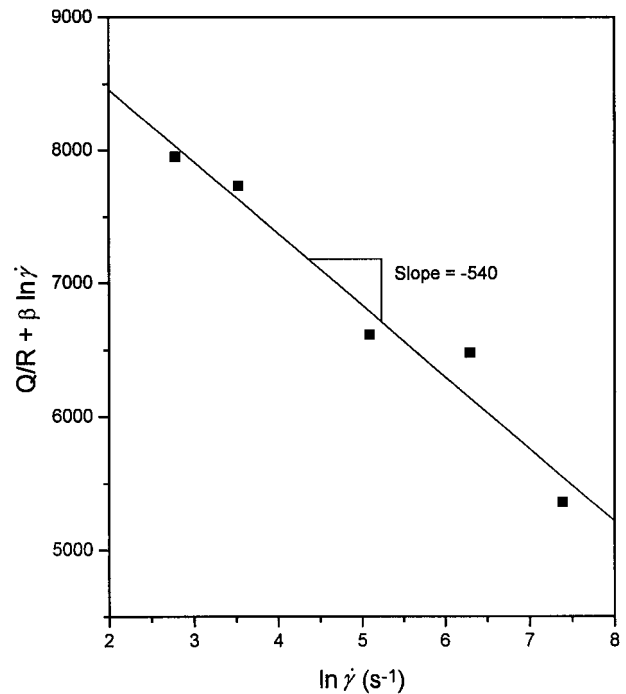


Figure 7 $Q/R + \beta \ln \dot{\gamma}$ versus $\ln \dot{\gamma}$.

lated based on results shown in Figure 7 and Figure 9, respectively.

Since the values of Q/R and material constant

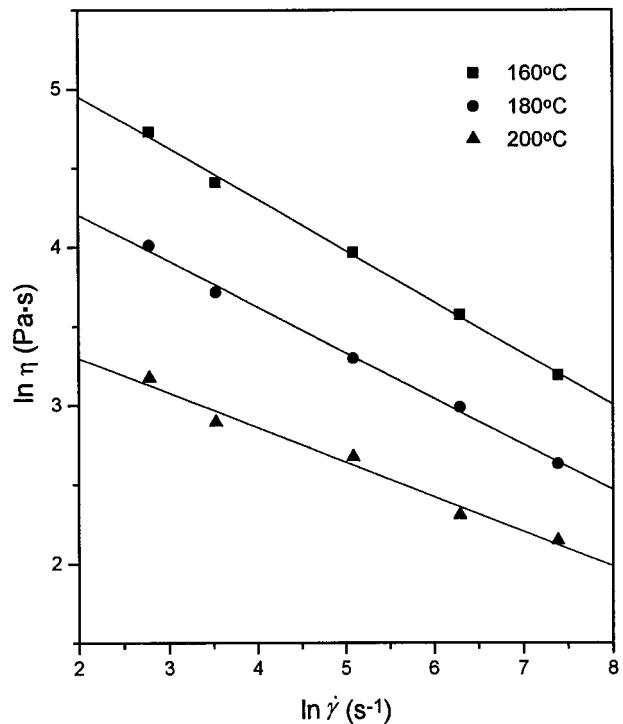


Figure 8 Variation of melt viscosity with shear rate: (■) 160°C ; (●) 180°C ; (▲) 200°C .

α are $9527 \pm 219 \text{ K}$ and 0.90 ± 0.01 , respectively, the value of $\ln \bar{K}$ can be calculated from eq. (1) and the value of $\ln \bar{K}$ is -16.34 ± 0.03 .

From the previous results, eq. (1) can be rewritten as shown below.

$$\ln \eta = -16.34 + \left(0.90 - \frac{535 \text{ K}}{T} \right) \ln \dot{\gamma} + \frac{9527 \text{ K}}{T} \quad (4)$$

To compare measured viscosities with calculated viscosities from eq. (4), measured and calculated viscosities were plotted as functions of shear rate in Figure 10. As shown in Figure 10, steady-state shear viscosities calculated from the proposed rheological equation of state in this study agree very well with measured viscosities.

CONCLUSIONS

Our experimental results lead to the following conclusions: (1) tensile strength of blend decreases with increasing PEA content because of incompatibility between PEA and LDPE, while the modulus increases. Elongation at break decreases with increasing PEA content. (2) This

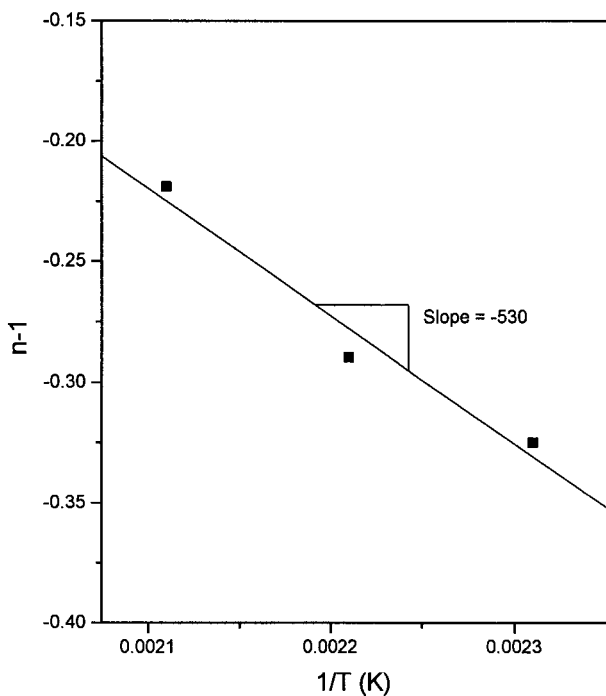


Figure 9 $n - 1$ versus $1/T$.

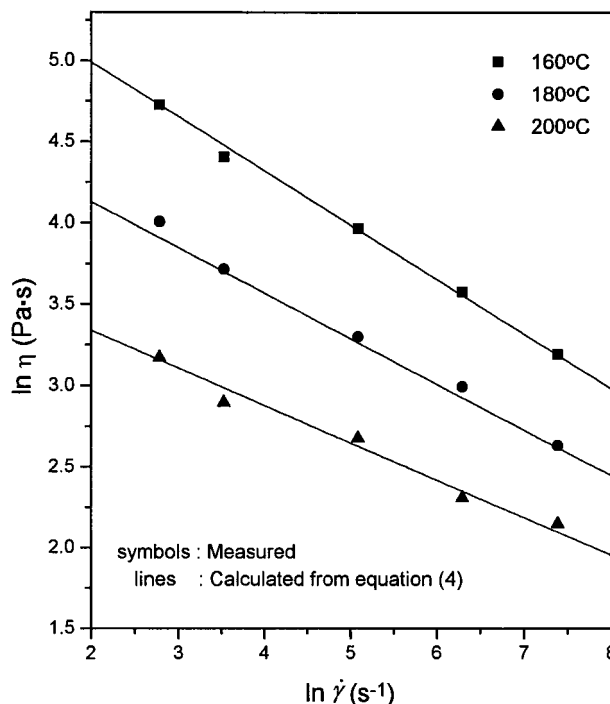


Figure 10 Melt viscosity as functions of shear rate at various temperatures: symbols, measured; lines, calculated using eq. (4).

proposed constitutive rheological equation successfully describes and predicts the effects of temperature and shear rate on the steady-state shear viscosity of PEA/LDPE blend.

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