

Rheological Properties and Morphology of Compatibilized Poly(butylene terephthalate)/Linear Low-Density Polyethylene Alloy

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ABSTRACT: The rheological behavior of PBT/LLDPE and PBT/LLDPE-*g*-AA blends [where PBT is poly(butylene terephthalate), LLDPE is linear low-density polyethylene, and AA is acrylic acid] under a capillary flow was investigated with a capillary rheometer. The Utracki equation was used to describe the viscosity–composition dependence of PBT/LLDPE and PBT/LLDPE-*g*-AA blends at low shear stresses. However, at high shear stresses, this equation was not suitable for these blending systems. There existed a maximum on the curves of the entrance pressure drop versus the blending compositions, and the interlayer slip factor β in the Utracki equation was related not only to the shear

stress but also to the elasticity difference of the two blending components. Morphological observations indicated that at high shear rates, there existed two different morphologies at different positions of the extrudates, and this was the reason that the Utracki equation failed. Near the wall of the capillary, low-viscosity PBT stratified, and this resulted in an additional decrease in the viscosities of the blending systems. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 206–213, 2003

Key words: linear; polyethylene (PE); alloys; compatibilization; rheology; morphology

INTRODUCTION

The rheological behavior of multiphase polymeric materials has received a great deal of attention because of its industrial importance. However, until now, it was not completely understood from a scientific point of view. The rheological properties of polymer blends depend on many variables, such as the properties of the blending components, the compositions, the interactions among components, the processing, and the morphology.

The usual method of studying the rheological behavior of polymer blends is to build a model. Palierne¹ developed an emulsion model and worked out a linear viscoelastic constitutive equation to express the melt viscosity of droplet-matrix emulsions. The effects of the linear viscoelastic behavior of the blending components, the size distribution of the dispersed droplets, and the interfacial tension on the viscosity are considered in this approach. The Palierne model has successfully been applied to describe the rheological

responses of several blending systems.^{2–4} Doi and Ohta⁵ proposed a phenomenological constitutive equation to describe the rheological behavior of a mixture consisting of two immiscible Newtonian liquids. These two models can be used to predict the rheological properties of some immiscible polymer blends.⁶

However, the aforementioned models are only applicable for a small amplitude of oscillatory shear⁷ or below a critical shear rate.⁴ In practical polymer processing, adopted shear rates are as high as 10^2 to 10^5 s^{-1} , and effects that influence the melt viscosity are very complicated and hard to predict. Heitmiller et al.⁸ built an analytical model of laminar flow in a pipe of concentric adjacent fluids. The viscosity at a certain composition can be expressed as follows:

$$\frac{1}{\eta} = \frac{w_A}{\eta_A} + \frac{w_B}{\eta_B} \quad (1)$$

where w_A and w_B are the volume fractions of components *A* and *B*, respectively, and η_A and η_B are the viscosities of components *A* and *B*, respectively. Lin⁹ extended this model by introducing the interlayer slip factor β into this equation.

Utracki¹⁰ classified polymer blends into four groups according to their viscosity–concentration dependence on the basis of the log-additivity rule:

$$\log \eta = \sum_i \phi_i \log \eta_i \quad (2)$$

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TABLE I
Parameters Used for Curve Fitting of Data in Figures 5 and 6

Sample	Shear stress (KPa)	$\lambda = \eta_{PE}/\eta_{PBT}$	Φ_{2I}	η_{max}	β	r^2
LLDPE/PBT	105	6.648	0.284	0	0	0.998
LLDPE/PBT	200	4.288	0.334	0	0.58	0.971
LLDPE/PBT	280	3.283	0.364	0	1.20	0.953
LLDPE-g-AA/PBT	105	3.943	0.343	0	0.04	0.986
LLDPE-g-AA/PBT	200	2.563	0.392	0	0.58	0.927
LLDPE-g-AA/PBT	280	2.020	0.418	0	1.10	0.907

where ϕ_i and η_i denote the volume fraction and viscosity of ingredient i in a blend, respectively. The four groups of polymer blends are additive blends [i.e., η follows eq. (1)], blends with a positive deviation from the log additivity (PDB), blends with a negative deviation (NDB), and blends with both positive and negative deviations (PNDB).

For completely immiscible polymer blends, Utracki¹¹ proposed the following equation:

$$\log \eta = -\log[1 + \beta(\phi_A\phi_B)^{1/2}] - \log\left(\frac{\phi_A}{\eta_A} + \frac{\phi_B}{\eta_B}\right) + \eta_{max}[1 - (\phi_A - \phi_{A-I})^2/(\phi_A\phi_{B-I}^2 + \phi_B\phi_{A-I}^2)] \quad (3)$$

where ϕ_{B-I} is equal to $(1 - \log \lambda/[\eta])/2$, λ is equal to η_A/η_B , η_{max} is a parameter determining the magnitude of the PDB effect, ϕ_{B-I} is the phase-inversion concentration of component B , ϕ_{B-I} is equal to $1 - \phi_{A-I}$, and $[\eta]$ is the intrinsic viscosity.

In this work, the rheological behavior and morphology of PBT/LLDPE and PBT/LLDPE-g-AA blends [where PBT is poly(butylene terephthalate), LLDPE is linear low-density polyethylene, and AA is acrylic acid] under a capillary flow were examined. The dependence of the melt viscosity of the two blending systems on their compositions was investigated with the Utracki model. Their morphology at different shear rates was also examined. The main purpose of this work was to correlate the rheological properties of the two blending systems with the properties of the blending components, the compositions, the interactions among the blending components, the phase behavior, and the morphology.

EXPERIMENTAL

Materials

The PBT used in this work was provided by DSM (Emmen, The Netherlands). Its trade model was Arnite thermoplastic polyester (T04 200). Its $[\eta]$ value (in *m*-cresol) was about 1.85 dL/g, and the content of the carboxylic end groups was about 45 mequiv/kg. LLDPE was supplied by Daqing Petrochemical Co. (China). Its density was 0.918 g/cm³, and the melt-flow rate

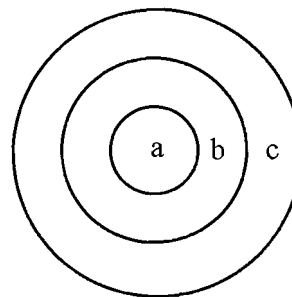
was 2 g/10 min (ASTM D 1238). The LLDPE-g-AA sample was prepared in our laboratory.¹² The grafting degree of AA was 1 wt %.

Preparation of the PBT/LLDPE-g-AA and PBT/LLDPE blends

PBT and LLDPE or LLDPE-g-AA were predried at 120 and 60°C, respectively, for 8 h and then premixed immediately with the compositions shown in Table I. The preparations of both the PBT/LLDPE-g-AA and PBT/LLDPE blends were carried out with an SHJ-30 corotating twin-screw extruder. The diameter of the screws was 30 mm, and the ratio of the length to the diameter (L/D) was 44. L/D was 24 for the reactive zone and 16 for the melting zone. The extrusion temperature was set at 200–260°C from the feeder to the die, and the die temperature was set at 230°C. The twin-screw speed was 150 rpm. The premixed mixtures of PBT and LLDPE or LLDPE-g-AA were added through a feeder. The extrudates were cooled with water and pelletized.

Rheological measurements

The rheological measurements were performed with a capillary rheometer (RH7 series, Rosand Precision, Ltd., United Kingdom). The capillary was configured as follows: 16 mm for the length, 1 mm for the diameter, and 180° for the entrance angle. The entrance pressure drop (P_{ent}) was determined instantaneously by an orifice (zero-length capillary) under the same



Scheme 1 Observed sites in the cross section of an extruding bar of a blend with SEM.

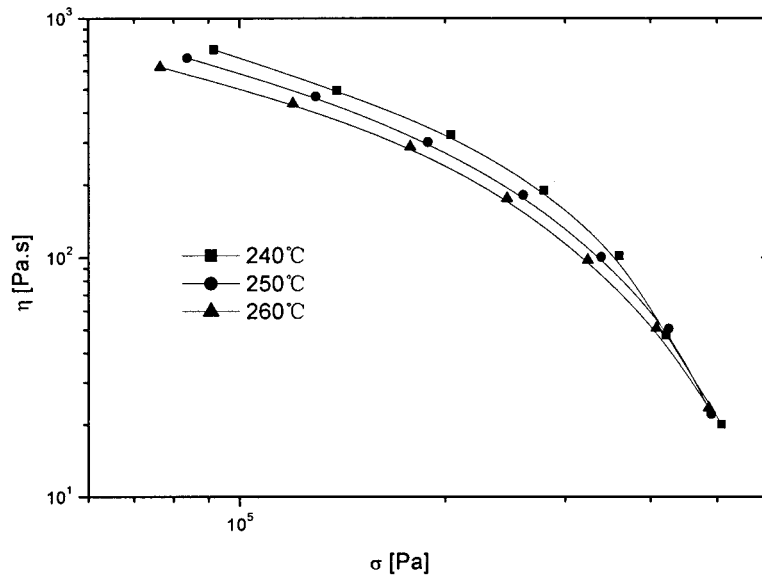


Figure 1 Melt viscosity of LLDPE versus the shear stress.

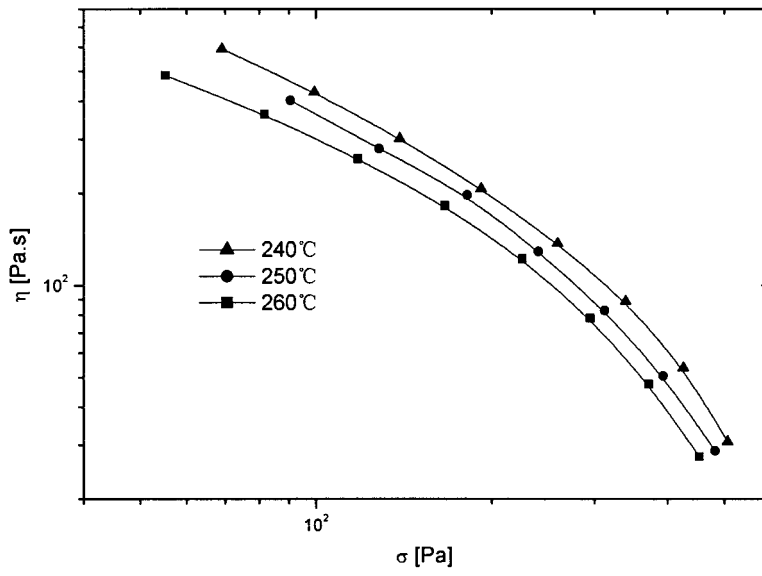


Figure 2 Melt viscosity of LLDPE-g-AA versus the shear stress.

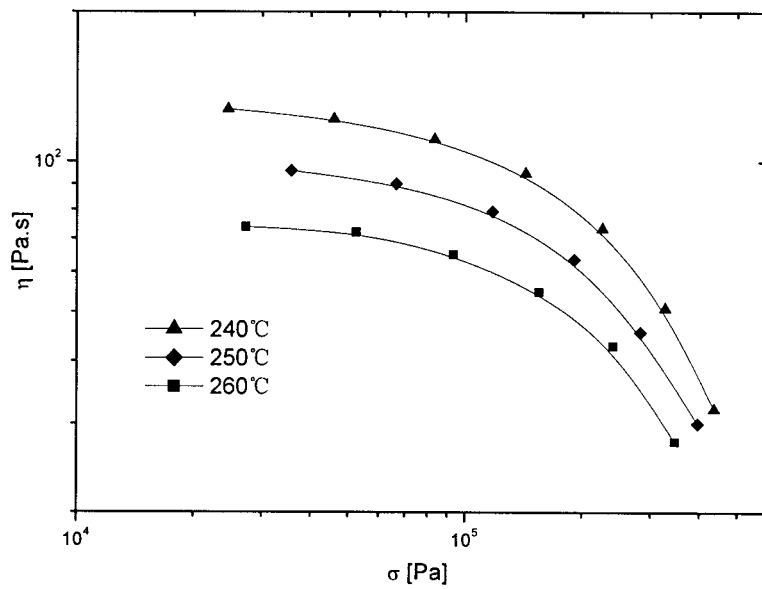


Figure 3 Melt viscosity of PBT versus the shear stress.

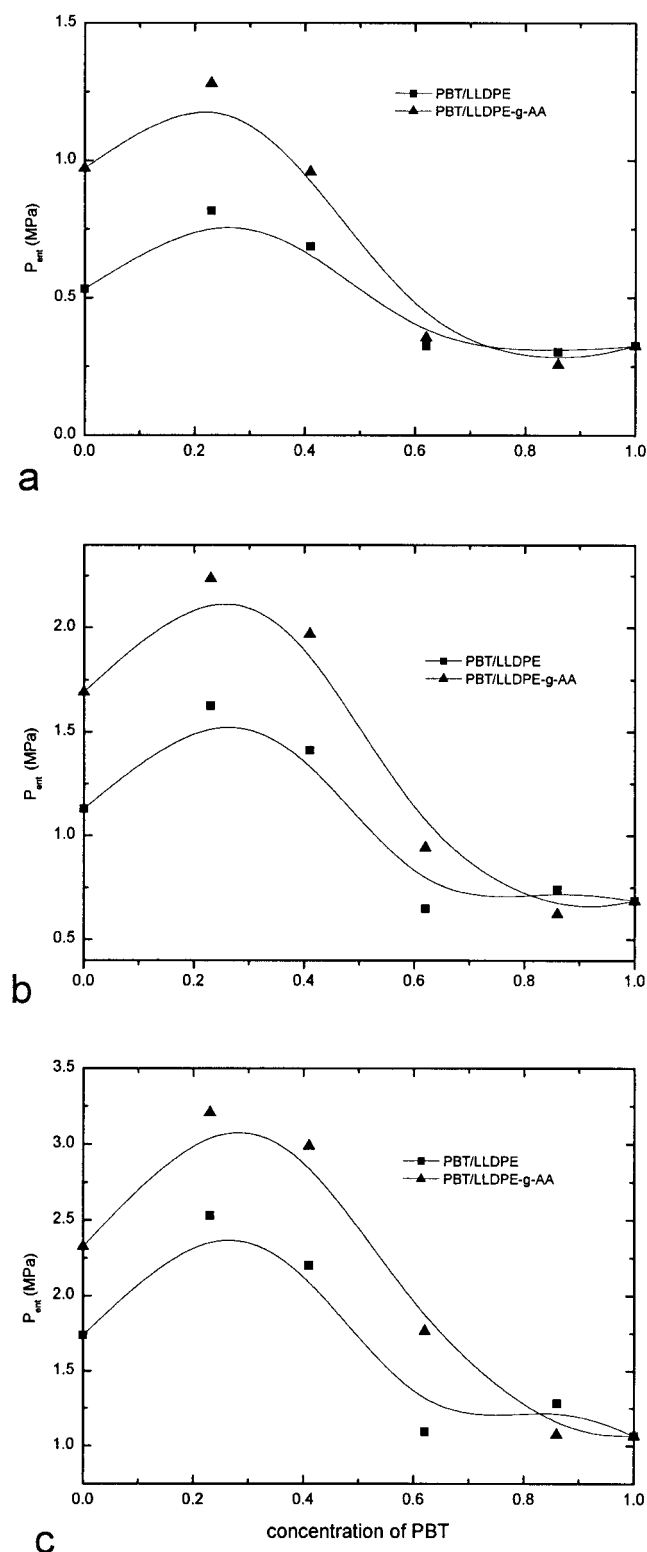


Figure 4 P_{ent} values of PBT/LLDPE and PBT/LLDPE-g-AA blends in a capillary at 240°C: (a) $\sigma = 105$ kPa, (b) $\sigma = 200$ kPa, and (c) $\sigma = 280$ kPa.

conditions. The shear rate and shear stress near the capillary wall were corrected according to the Bagley correction and the Rabinowitsch–Mooney equation,

respectively. The temperature of the barrel was set at 240, 250, and 260°C, respectively, and the shear rate ranged from 10^2 to 104 s $^{-1}$. All the samples were dried at 60°C for 8 h. Before the tests, the samples were preheated for 5 min in two barrels.

Morphology observations

The morphological observation of the extruded samples was carried out with a JEOL JXA-840 scanning electron microscopy (SEM) instrument. The extruded samples were prepared as follows. After extrusion, the samples were immersed immediately in liquid nitrogen and then fractured. Before observation, the samples were etched with a mixture of tetrachloroethane and phenol (1:1 v/v). The etched samples were dried *in vacuo* at room temperature. Before SEM observation, the fracture surfaces of the samples were coated with a thin layer of gold so that electrical charging would be avoided during the examination. Three different positions of a sample were selected for observation. The corresponding positions are shown in Scheme 1.

RESULTS AND DISCUSSION

Curves of the melt viscosity versus the shear stress for PBT, LLDPE, and LLDPE-g-AA are shown in Figures 1–3. Shear-thinning behavior was observed for all three samples. The melt viscosity of LLDPE and LLDPE-g-AA was sensitive to shear stress but not to temperature. In contrast to LLDPE and LLDPE-g-AA, the melt viscosity of PBT was sensitive to temperature but not to shear stress. These features could be tentatively explained as the low-flow activation energy and flexible chain of LLDPE and LLDPE-g-AA. At the same shear stress and temperature, the viscosity of LLDPE-g-AA was much lower than that of LLDPE, and this suggested that grafted AA side chains could act as inner plasticizers. As reported in our previous article,¹³ the AA side chains consisted of AA oligomers with 3–10 AA units.

It is well known that when a viscoelastic polymer melt flows from a large reservoir into a circular tube, it undergoes an exceedingly large pressure drop in the entrance region. P_{ent} can be attributed to the elastic properties of the materials.¹⁴ For two-phase polymer melts, P_{ent} is contributed by two phases: the discrete phase and the continuous phase.¹⁵

Han¹⁵ suggested that a two-phase fluid containing deformable droplets would exhibit a lower apparent viscosity and a more recoverable elastic energy than a single-phase fluid or a two-phase fluid containing nondeformable domains.

As shown in Figure 4, the P_{ent} values of the PBT/LLDPE and PBT/LLDPE-g-AA blends reached a max-

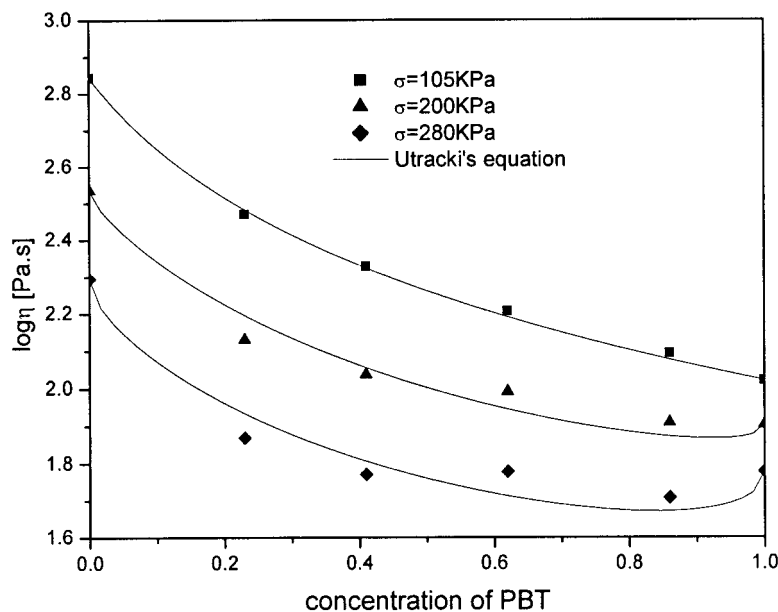


Figure 5 Melt viscosity of PBT/LLDPE blends at 240°C as a function of the blending composition.

imum when the volume fraction of PBT was 23%. The position of maximum P_{ent} did not vary with the shear stress. This meant that the position of maximum P_{ent} was not related to the shear stress. For immiscible polymer blends, the stable morphology is droplet matrix because of their high interfacial tension. When a polymer blend flows from a reservoir into a capillary, the low-viscosity droplet would easily deform into a fiber structure, which would result in high elastic loss and P_{ent} values. For the PBT/LLDPE blend with a 23% volume fraction of PBT, droplets consisted of low-viscosity PBT. Therefore, excess P_{ent} was induced by PBT droplets

It can also be noted from Figure 4 that P_{ent} of LLDPE-g-AA was higher than that of LLDPE. This feature suggested that the melt elasticity of LLDPE-g-AA was higher than that of LLDPE, which originated from the slight crosslinking of LLDPE during melt grafting with AA. Therefore, it could be speculated that the high melt elasticity of LLDPE-g-AA was related to the high molecular weight of LLDPE-g-AA.

The effects of the compositions on the viscosities of both PBT/LLDPE and LLDPE-g-AA blends are shown in Figures 5 and 6. The corresponding parameters of the Utracki equation are listed in Table I. Both blends had a negative deviation from the log-additivity rule.

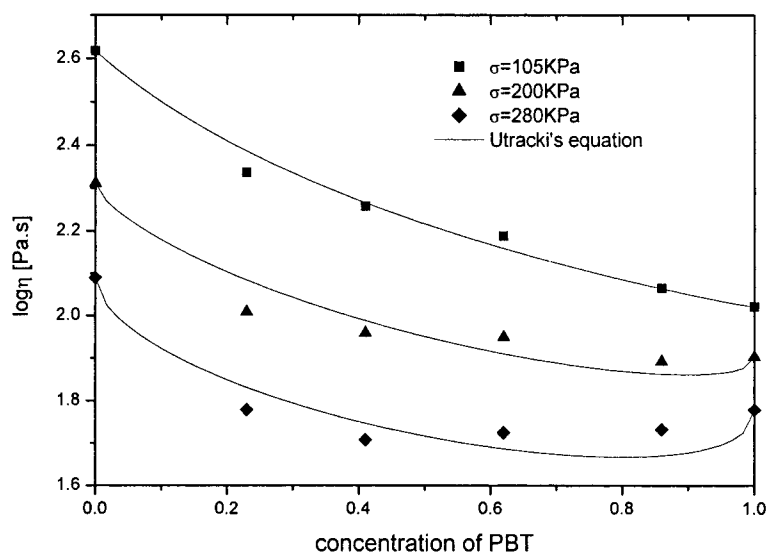


Figure 6 Melt viscosity of PBT/LLDPE-g-AA blends at 240°C as a function of the blending composition.

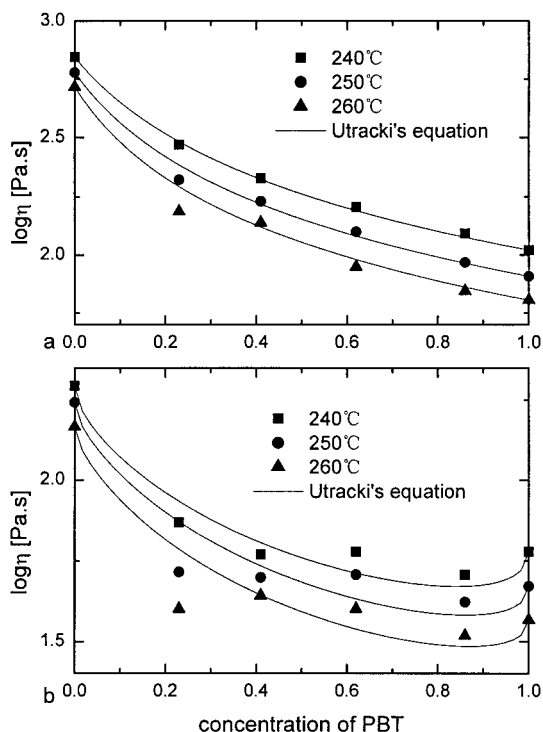


Figure 7 Melt viscosity of PBT/LLDPE blends as a function of the blending composition: (a) $\sigma = 105$ kPa and (b) $\sigma = 280$ kPa.

At low shear stresses, there was a very good fit between the curve obtained with the Utracki equation and the experimental data. The adjustable parameters, β and η_{\max} , were equal to zero. However, with increasing shear stress, the Utracki equation could not describe the viscosity–composition dependence of both blending systems. β was enhanced with increasing shear stress.

With the same blending composition, the β value of the PBT/LLDPE-g-AA blends was not always lower than that of the PBT/LLDPE blends, and this contrasted with the Utracki prediction. According to

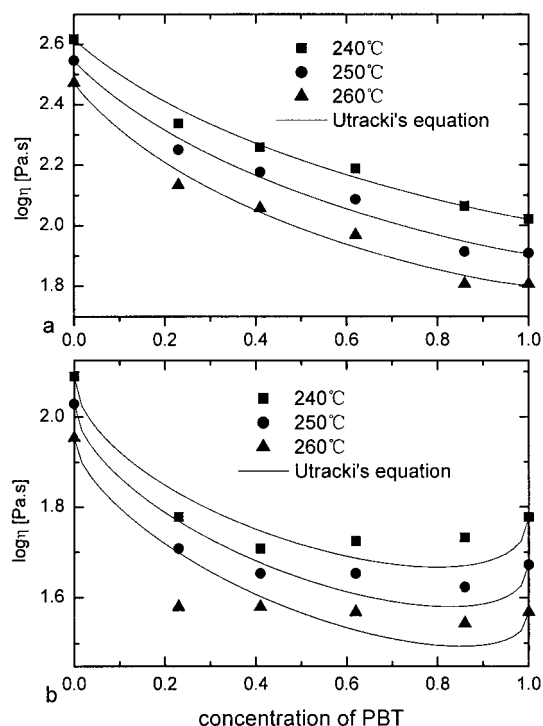


Figure 8 Melt viscosity of PBT/LLDPE-g-AA blends versus the blending composition: (a) $\sigma = 105$ kPa and (b) $\sigma = 280$ kPa.

Utracki's assumption, β was the function of the shear stress and interactions of the blending components. With an improvement in the compatibility of the blending system, β would decrease. Our experimental results verified that β was the function not only of the shear stress and interactions of the blending components but also of the viscoelasticity of the blending components. As the melt elasticity of LLDPE-g-AA was higher than that of LLDPE, elastic recovery for deformed droplets of LLDPE-g-AA would be stronger than that of LLDPE.

TABLE II
Parameters Used for Curve Fitting of Data in Figures 7 and 8

Sample	Temperature (°C)	Shear stress (KPa)	$\lambda = \eta_{PE}/\eta_{PBT}$	Φ_{21}	η_{\max}	β	r^2
LLDPE/PBT	240	105	6.648	0.284	0	0	0.998
LLDPE/PBT	250	105	7.395	0.271	0	0	0.991
LLDPE/PBT	260	105	8.125	0.261	0	0.01	0.985
LLDPE-g-AA/PBT	240	280	3.283	0.364	0	1.20	0.953
LLDPE-g-AA/PBT	250	280	3.723	0.350	0	1.06	0.878
LLDPE-g-AA/PBT	260	280	3.973	0.342	0	1.02	0.865
LLDPE-g-AA/PBT	240	105	3.943	0.343	0	0.04	0.986
LLDPE-g-AA/PBT	250	105	4.346	0.332	0	0.09	0.984
LLDPE-g-AA/PBT	260	105	4.641	0.325	0	0.16	0.985
LLDPE-g-AA/PBT	240	280	2.020	0.418	0	1.10	0.907
LLDPE-g-AA/PBT	250	280	2.277	0.406	0	0.90	0.931
LLDPE-g-AA/PBT	260	280	2.432	0.398	0	0.85	0.851

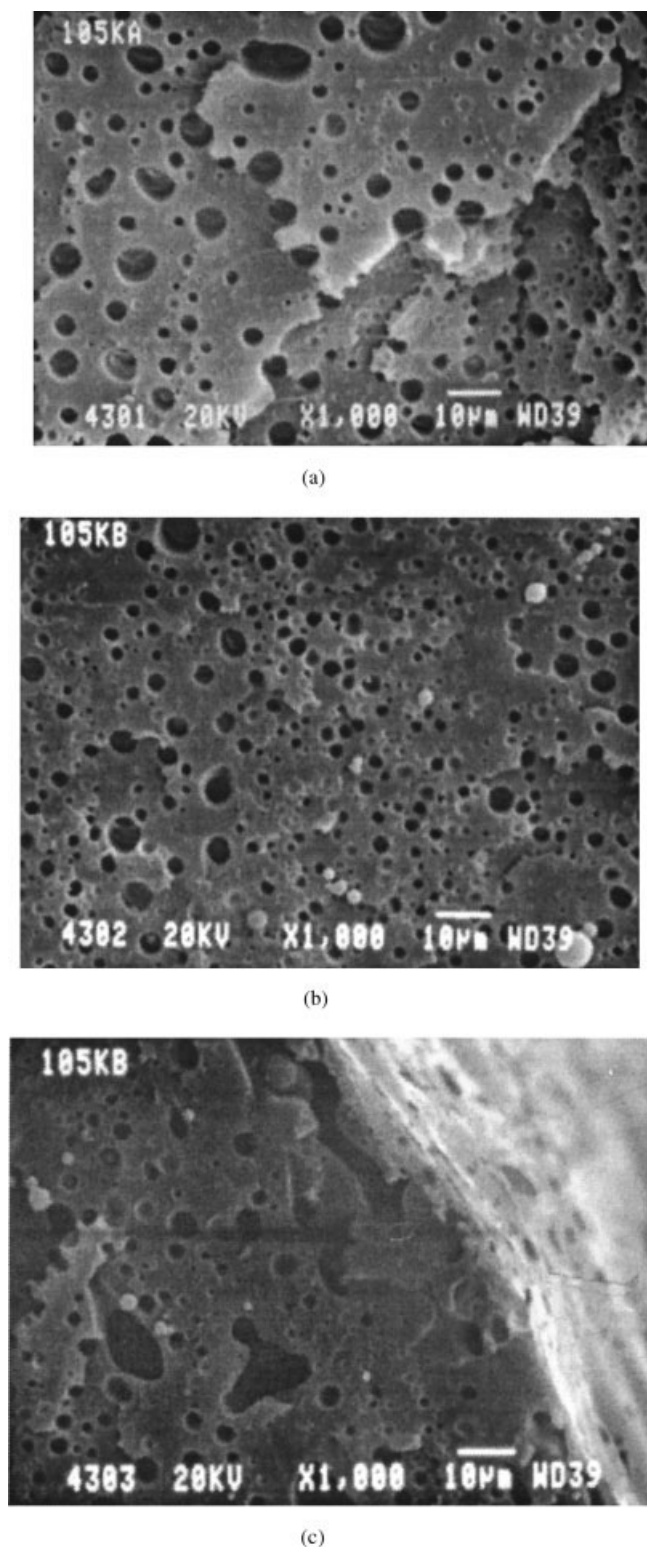


Figure 9 Morphology of sections of an extruding bar of a PBT/LLDPE (20/80) blend at a shear rate of 105 s^{-1} .

The effect of the temperature on the viscosity–composition dependence of the PBT/LLDPE and PBT/LLDPE-g-AA blends is shown in Figures 7 and 8. The

viscosity–composition dependence of these blends was well depicted by the Utracki equation at low shear stresses. However, at higher shear stresses, the Utracki equation could not fit the relationship of the viscosity and composition. This feature indicated that the shear stress played a major role in the applicability of the Utracki equation. The corresponding parame-

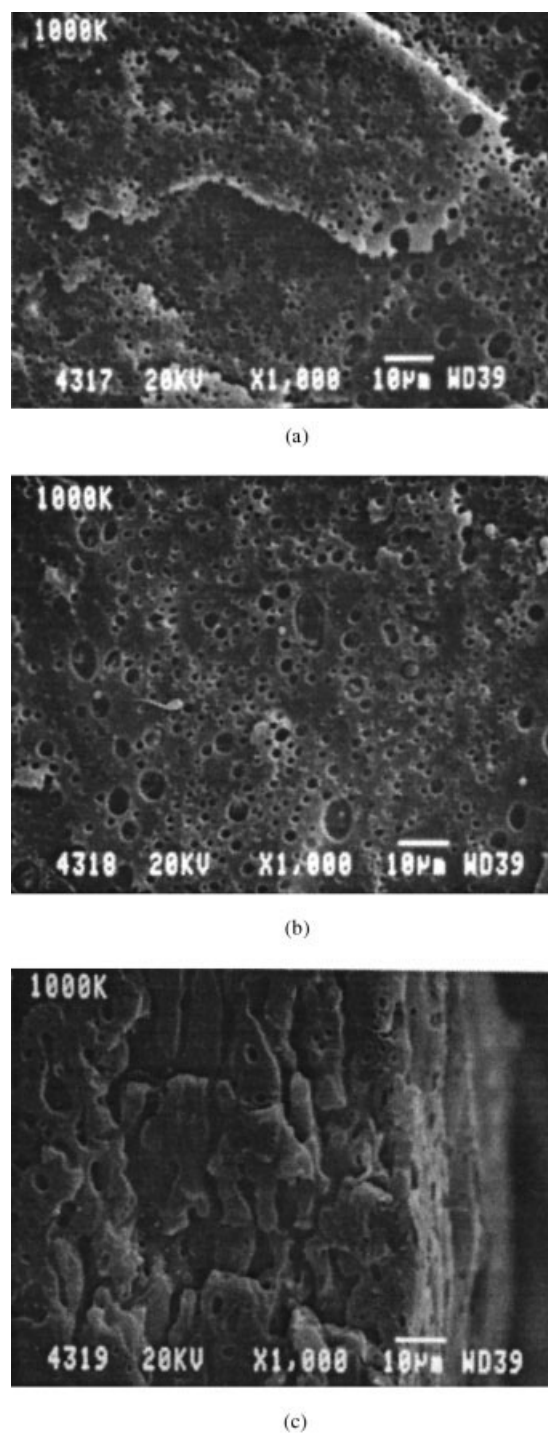


Figure 10 Morphology of sections of an extruding bar of a PBT/LLDPE (20/80) blend at a shear rate of 1000 s^{-1} .

ters in the Utracki equation are listed in Table II. β varied with temperature. Therefore, it could be concluded that β was related not only to the interactions of the blending components and their viscoelastic properties but also to the temperature.

Vanoene¹⁶ developed a theoretical foundation to interpret the mode of dispersion in terms of the droplet size, interfacial tension, and differences in the viscoelastic properties of the two components. According to his theory, a nonelastic fluid (e.g., an incompatible plasticizer or processing aid) stratifies in the viscoelastic phase and will be excluded from the polymer phase. When an additive has a low viscosity, it may migrate to the wall layer during flow, reducing the overall viscosity of the mixture considerably. In other words, the additive may act as a slip agent.

For a circular laminar flow in a capillary, the shear rate was different at different positions. It gradually increased from the center to the wall of a capillary (as shown in Scheme 1). Micrographs of cross sections of an extruding bar with 20/80 PBT/LLDPE are shown in Figures 9 and 10. Because of the high viscosity of the blending system and the short residence time in the capillary, any migration of the dispersed phase toward the wall was not observed. In Figures 9 and 10, it can be seen that at low shear rates, $\dot{\gamma} = 105 \text{ s}^{-1}$, there were droplet-matrix structures at different sites of the sections of the extruding bar. At high shear rates, $\dot{\gamma} = 1000 \text{ s}^{-1}$, a quite different morphology was observed for the same sample. At the center of the sample, a droplet-matrix morphology still could be observed, whereas near the wall of the capillary, a cocontinuous morphology was found. The PBT phase was stratified. This stratification introduced the formation of extrudate envelopes, which provided additional effects for decreasing the viscosity of the blending system.¹⁷ Therefore, the Utracki equation was not applicable for depicting the viscosity–composition dependence of this blending system at high shear rates.

CONCLUSIONS

The Utracki equation successfully depicted the dependence of the viscosity on the composition for PBT/LLDPE and PBT/LLDPE-*g*-AA blends at low shear stresses. The parameter β in the Utracki equation was related not only to the shear stress but also to the

viscoelastic properties of the blending components, the compositions, and the interactions of the blending components.

The P_{ent} values of these two blending systems in a capillary were related to their blending compositions, the interactions of the blending components, and the properties of the components. The maximum pressure drop occurred for 20/80 PBT/LLDPE-*g*-AA. These features were tentatively explained as the deformation of the droplet of the PBT dispersion phase

At low shear rates, a droplet-matrix morphology could be observed at different positions of an extruding bar of 20/80 PBT/LLDPE. At high shear rates, the droplet-matrix morphology still could be observed at the center of the extruding bar, whereas near the wall of the capillary, a cocontinuous morphology was found. A stratified PBT phase was formed. This stratification introduced the formation of extrudate envelopes, which provided additional influence for decreasing the viscosity of the blending system. The variations of the morphology at different positions in the extruding bar caused the Utracki equation to fail to predict the rheological behavior of these two blending systems.

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