Correlation of Rheological and Mechanical Properties for Blends of Recycled HDPE and Virgin Polyolefins

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ABSTRACT: This article investigates the rheological and mechanical properties for blends of recycled high-density polyethylene (HDPE) and virgin polyolefins and attempts to correlate relative shear viscosity and relative stiffness for these blends. These virgin polyolefins comprised a wide variety of flow characteristics, from high-flow injection molding, low-density and linear low-density polyethylene to very low-flow film blowing grade high-density polyethylene. It can be seen that there is a variety of behaviors for the relative viscosity and relative stiffness of the blends studied. Relative viscosity and relative stiffness can largely be described by linear curves. This article categorizes these parameters according to the gradient of these linear curves. The difference between the relative viscosity gradient and relative stiffness gradient is identified as a product of a variety of factors, including branching content, viscosity level, and the nature of any side units. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3505–3512, 2001

Key words: recycled HDPE; polymer blends; modulus ratio; viscosity ratio

INTRODUCTION

This research article is being conducted as part of a larger investigation into the behavior of recycled high-density polyethylene (HDPE)/virgin polyolefin systems. This larger investigation involves a partnership with Visy Plastics, a large recycling company that principally deals with the recycling of plastic bottles, including HDPE milk bottles. The recycling of these HDPE milk bottles produces the HDPE recyclate that is used in this research.

This recycled HDPE is ideal for blow-molding applications, but is less appropriate for use in injection molding and some extrusion applications. To allow more extensive use of the recycled HDPE, its properties must be modified. Here this is done by blending with various virgin polyolefins. For this to be successful, it is important to be able to predict how the properties will vary in the blend. Here the interaction between shear viscosity ratio and tensile modulus ratio is studied.

A significant amount of work was already done on attempts to correlate viscosity and modulus. Nielsen (1994) gave a brief description of equations linking viscosity and shear modulus for particulate filled systems.[1]

The rate of shear in the viscosity equation is replaced by the shear strain in the modulus equation. Thus, for filled systems in which the matrix phase is an elastomer having a Poisson's ratio of 0.5 and the filler phase is rigid, there is a simple

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relationship between relative viscosity and relative shear modulus

$$\frac{\eta}{\eta_1} = \frac{G}{G_1} \tag{1}$$

where G and η are the shear modulus and viscosity, respectively, of filled material and G_1 and η_1 are the shear modulus and the viscosity of unfilled matrix, respectively. So according to the above, calculation of the viscosity of a filled system can also be used to calculate the shear modulus of the same system.

Equation (1), however, is only valid for when the Poisson's ratio of the continuous phase is 0.5, and the rigidity of the filler is very much greater than that of the matrix. Otherwise, the modulus ratio is considerably less than the viscosity ratio, especially at high filler loadings. A more accurate equation, which does take into account the value of the Poisson's ratio,[2] is given as:

$$\frac{\eta}{\eta_1} - 1 = \frac{4 - 5\nu_1}{3 - 3\nu_1}\left(\frac{G}{G_1} - 1\right) \tag{2}$$

In this equation, ν_1 is the Poisson's ratio of the matrix, and it is assumed that the filler particles are approximately spherical in shape.

Other authors have also done work on aspects of relative viscosity or relative modulus. Some[3,4] found that relative viscosity decreases with increasing shear rate and that relative viscosity is a nonlinear function of filler volume fraction.

Faulkner et al.[3] also reported that relative tensile modulus is a linear function of volume fraction and that the slope of the line describing relative tensile modulus is less than half the ϕ coefficient in the Einstein relation. It is suggested that a more even distribution of the filler material caused by the complex flows in the injection molding of the tensile specimens could be responsible for the simple linearity of the relative tensile modulus instead of the less even distribution that was presumably obtained for the simple shear flows during rheological testing.

Einstein[5] also did work on viscosity ratio by deriving an expression for the viscosity of a suspension of rigid spheres,

$$\frac{\eta}{\eta_1} = 1 + k_E\phi_2 \tag{3}$$

where η is the viscosity of the material and η_1 is the viscosity of the matrix, whereas ϕ_2 is the volume fraction of the filler material, and k is a constant known as the Einstein coefficient.

Choi et al.[6] reported that the reinforcing effect of a liquid crystalline polymer is more significant when the liquid crystalline polymer has a viscosity lower than the thermoplastic matrix polymer.

Kim and Do[7] reported that hardness, flexural modulus, yield, and break strength generally increased and elongation at break generally decreased with an increasing viscosity ratio for blends of PP/EPR.

METHODOLOGY

The recycled HDPE used was a Visy Plastics grade called H1 recyclate. The virgin materials were obtained from Qenos, a virgin resin manufacturer in Melbourne, Victoria, Australia, as follows:

injection molding grade HDPE (IM-HDPE)
film blowing grade HDPE (FB-HDPE)
injection molding grade LLDPE (IM-LLDPE)
film blowing grade LLDPE (FB-LLDPE)
injection molding grade LDPE (IM-LDPE)
film blowing grade LDPE (FB-LDPE)
injection molding grade IM-PP (IM-PP)
extrusion grade E-PP (E-PP)

Polymer blending was performed by using an Axon Pacific BX-12 single-screw extrusion blender. Tensile testing was performed at Visy Plastics at room temperature. Rheological testing was performed at Moldflow Pty. Ltd.

RESULTS AND DISCUSSION

Modulus ratio is calculated as:

$$E_r = \frac{\text{Modulus of the blend}}{\text{Modulus of virgin polyolefin}} \tag{4}$$

whereas viscosity ratio is calculated as:

$$\eta_r = \frac{\text{Viscosity of the blend}}{\text{Viscosity of virgin polyolefin}} \tag{5}$$

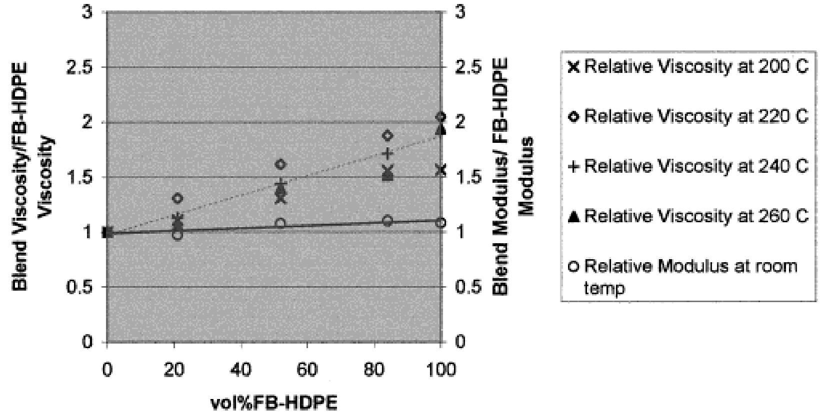

Figure 1 Relative viscosity and modulus for recycled HDPE/FB-HDPE blends at 96 s^{-1} shear rate.

Naturally, a ratio greater than unity means that the inclusion of the virgin polyolefin has created a blend with modulus or viscosity higher than that of the virgin polyolefin.

The viscosity ratios were obtained by performing viscosity testing for a set of temperatures and obtaining a ratio at each temperature.

The data was plotted (Figs. 1–8) as modulus or viscosity ratio versus volume fraction virgin polyolefin. These plots all take the form of a linear curve, $Y = aX + b$, where a is the gradient of the ratio curve and b is approximately 1. This is very similar to the Einstein equation mentioned earlier.

The gradients for the linear fits are shown in Table I. Linear fits to modulus ratio (E_r) data are good, whereas linear fits to viscosity ratio (η_r) data are acceptable.

Table I Gradient of Viscosity Ratio and Modulus Ratio Curves

Virgin Component	η_R Gradient γ 96 s^{-1} ($\times 10^{-3}$)	Standard Deviation ($\times 10^{-3}$)	E_R Gradient ($\times 10^{-3}$)
IM-HDPE	−8.08	0.277	−1.1
FB-HDPE	8.4	1.694	1.2
IM-LLDPE	−7.84	0.182	−6.4
FB-LLDPE	4.5	1.38	−6.8
IM-LDPE	−8.46	0.627	−8.1
FB-LDPE	−2.3	1.036	−7.9
IM-PP	−5.233	0.351	3.6
E-PP	−1.05	0.465	3.1

Because the linear curve constant, b, is approximately equal to one, whether the ratio value is greater or less than one depends on whether the gradient is positive or negative.

The ratio values can be divided into categories depending on their value in comparison to unity. It can be seen that there are four categories:

$$E_r > 1;\ \eta_r > 1$$
$$E_r > 1;\ \eta_r < 1$$
$$E_r < 1;\ \eta_r > 1$$
$$E_r < 1;\ \eta_r < 1$$

There is also a special case of this last option, where $E_r \approx \eta_r$.

Each of these options will be discussed in turn.

$E_r > 1; \eta_r > 1$

The blends that fall into this category are recycled HDPE/FB-HDPE (Fig. 1).

Inclusion of the FB-HDPE into the recycled HDPE results in a reinforcement effect that produces a linear increase in modulus. The FB-HDPE has a modulus ~ 10% greater than the recycled HDPE. The inclusion of the FB-HDPE into recycled HDPE also produces an increase in viscosity.

Understanding why viscosity ratio is significantly larger than unity, although modulus ratio increases by just 10%, can be interpreted in terms of polymer chain flow under the testing conditions. Tensile modulus testing is performed at room temperature, whereas viscosity

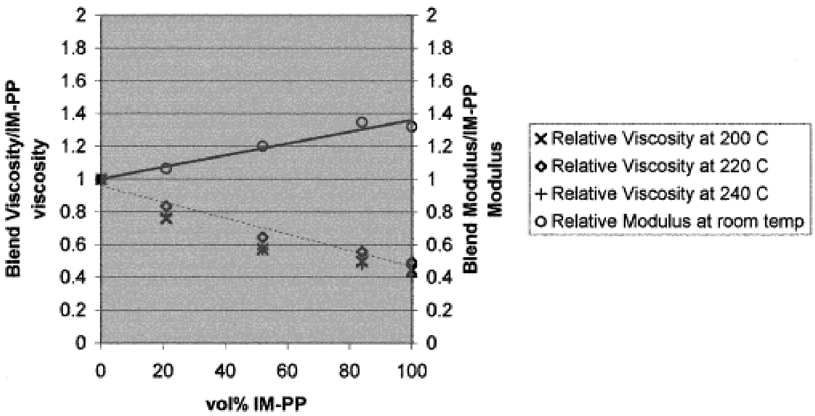

Figure 2 Relative viscosity and modulus for recycled HDPE/IM-PP blends at 96 s^{-1} shear rate.

testing is done at 200°C or higher. This means that although the polymer chains are largely frozen in place during tensile testing, in viscosity testing there is large-scale flow branching interaction between the components. This is perhaps the key difference in explaining the different ratios.

Examination of the viscosity ratios at different temperatures reveals behavior that does not seem to follow a strong consistent pattern; however, it does appear that at lower temperatures, the viscosity ratio is less. This temperature variation is consistent with the idea that at higher temperatures, slightly increased chain mobility will allow branching to more fully participate in influencing the rheology. In modulus testing, this does not happen because the values reflect a preflow condition of the material, and although there are undoubtedly significant chain entanglements during modulus testing, the crucial difference is that at room temperature they do not have sufficient mobility to re-entangle.

Thus, the apparent lack of consistent behavior in the temperature influence on viscosity could reflect a maxima and minima of entanglement efficiency. At 200°C, the viscosity ratio is lowest, whereas at 220°C, the ratio is highest. At even higher temperatures, the ratio is intermediate between these two, suggesting that at these temperatures, 240 and 260°C, the chains have too much mobility and cannot maintain effective chain entanglements.

$E_r > 1$; $\eta_r < 1$

The blends that fall into this category are recycled HDPE/IM-PP and recycled HDPE/E-PP (Figs. 2 and 3).

For both of these blends, the modulus of the PP is greater than the modulus of the recycled HDPE, whereas the viscosity of the PP is less than the viscosity of the recycled HDPE.

However, although the changes in modulus for the two systems are basically identical, the changes in viscosity for the two systems are very different. The E-PP material changes the viscosity of the blend by a decrease of about 15%, whereas the IM-PP material produces a linear decrease with composition, with the IM-PP material having a viscosity of about 50% of the recycled HDPE.

For the modulus ratio, the changes are because the bulky PP side units inhibit deformation, increasing modulus, whereas viscosity changes will likely have more to do with the nature of the branching. The IM grade PP, with its lower branching content, produces a lower viscosity ratio, whereas extrusion grade PP, with its higher branching content, produces a higher viscosity ratio than the IM grade PP.

Again, there appears to be a nonlinear trend in relation to the influence of test temperature on viscosity ratio for the recycled HDPE/E-PP system, similar to what was noted for the recycled HDPE/FB-HDPE system. The viscosity ratio of the recycled HDPE/IM-PP system's lack of sensitivity to temperature can, therefore, be explained by the lower degree of branching.

$E_r < 1$; $\eta_r > 1$

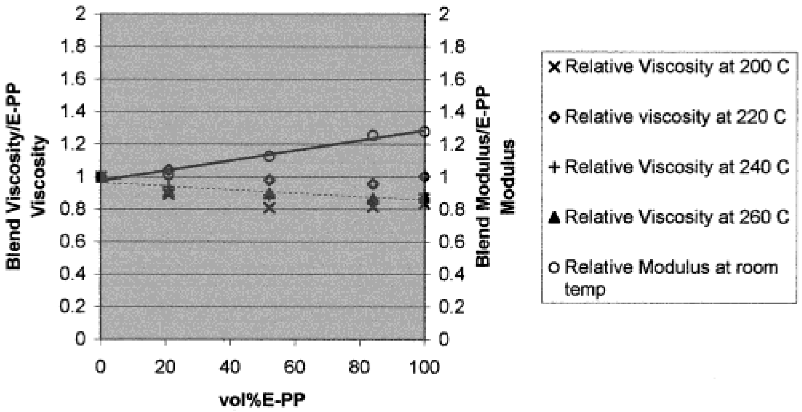

Figure 3 Relative viscosity and modulus for recycled HDPE/E-PP blends at 96 s^{-1} shear rate.

The blends that fall into this category are recycled HDPE/FB-LLDPE (Fig. 4).

Inclusion of the FB-LLDPE into a blend with recycled HDPE produces a rapid linear decrease in modulus, while at the same time producing a rapid linear (reasonably linear) increase in viscosity. The modulus of the FB-LLDPE is about 25% that of the recycled HDPE, whereas the viscosity of the FB-LLDPE ranges between 140 and 180% of the recycled HDPE viscosity.

The decrease in modulus is likely due to the inclusion of the low-modulus FB-LLDPE material. Assuming that the differences between the IM-LLDPE and FB-LLDPE are similar to those of the IM-HDPE and FB-HDPE (the film blowing grade has long-chain branches capable of entanglements), the increase in viscosity ratio is possibly due to the extra branching content of the FB-LLDPE, which creates entanglements and increases the viscosity, much the same way as did the FB-HDPE.

$$E_r < 1;\ \eta_r < 1$$

The blends that fall into this category are recycled HDPE/IM-HDPE (Fig. 5) and recycled HDPE/FB-LDPE (Fig. 6).

The modulus of the recycled HDPE and the IM-HDPE are not greatly different, with IM-HDPE having a modulus about 15% less than the recycled HDPE and a viscosity that is only about 15% that of the recycled HDPE.

Despite being in the same general category as the recycled HDPE/IM-HDPE blend, the recycled HDPE/FB-LDPE blend displays the opposite behavior. Modulus of FB-LDPE totals about 15% of

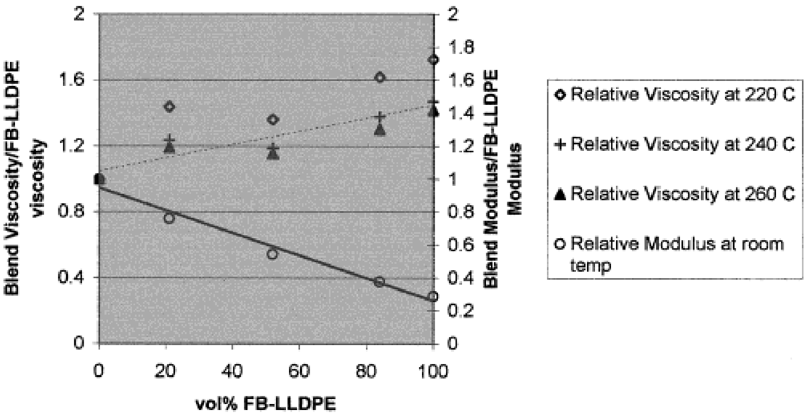

Figure 4 Relative viscosity and modulus for recycled HDPE/FB-LLPE blends at 96 s^{-1} shear rate.

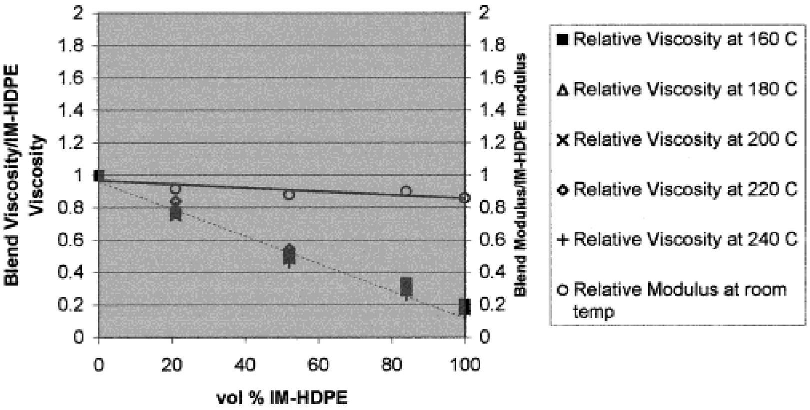

Figure 5 Relative viscosity and modulus for recycled HDPE/IM-HDPE blends at 96 s^{-1} shear rate.

the recycled HDPE value, with a linear rate of change in between. The viscosity of the FB-LDPE is about 15% lower than the recycled HDPE, but depends on temperature. The change in viscosity is still approximately linear, however.

In general, the behavior of the recycled HDPE/IM-HDPE is nearly a mirror image along the ratio = 1 axis. As has already been mentioned, branching content appeared to be a strong factor in the sensitivity of the viscosity ratio to temperature. So, where the recycled HDPE/FB-HDPE system showed viscosity ratio variation with temperature, recycled HDPE/IM-HDPE shows very little, because the IM-HDPE has very little branching content. Because the IM-HDPE is a high flow material, it probably acts as a lubricant around the recycled HDPE. Its very little branching content also produces a decrease in viscosity.

For the recycled HDPE/FB-LDPE system, the inclusion of the LDPE decreases the modulus ratio, as expected, because the FB-LDPE is a much more flexible material. The behavior of the viscosity ratio is also partly expected, in that it is temperature sensitive, and the FB-LDPE has a reasonable branching content.

$$E_r \approx \eta_r$$

The blends that fall into this category are recycled HDPE/IM-LLDPE (Fig. 7) and recycled HDPE/IM-LDPE (Fig. 8).

This category can be considered a special case of the last category, in that both modulus ratio and viscosity ratio are less than one, but also that they are approximately equal to each other.

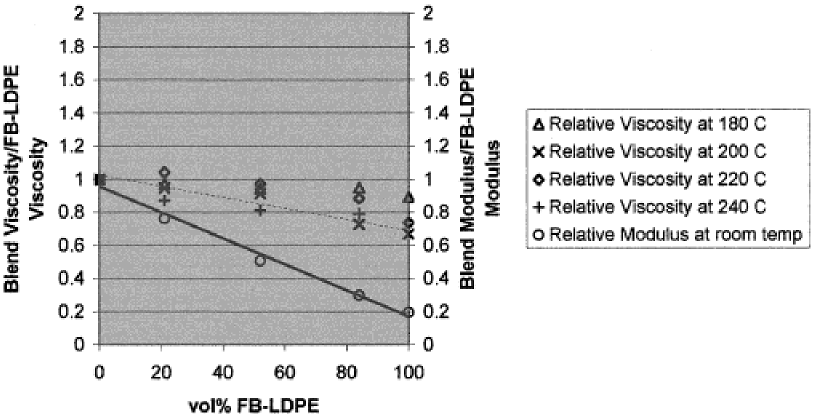

Figure 6 Relative viscosity and modulus for recycled HDPE/FB-LDPE at 96 s^{-1} shear rate.

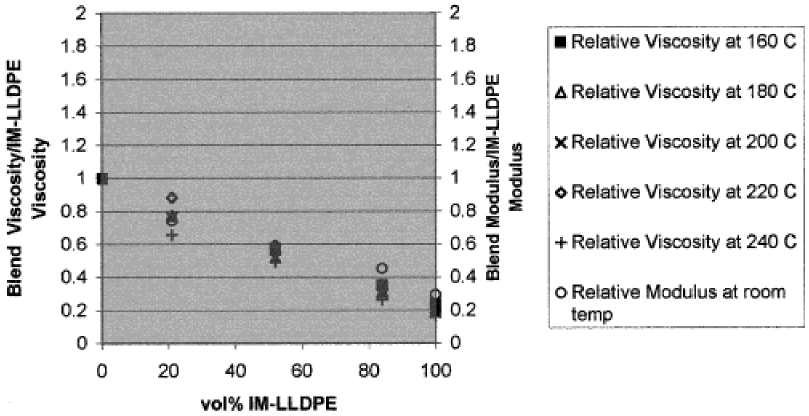

Figure 7 Relative viscosity and modulus for recycled HDPE/IM-LLDPE blends at 96 s^{-1} shear rate.

The linear trend for the recycled HDPE/IM-LDPE data has a slightly steeper gradient than that of the recycled HDPE/IM-LLDPE blend.

Inclusion of IM-LDPE or IM-LLDPE can quite reasonably be expected to lower the viscosity ratio, because both are high flow materials, thereby lubricating the recycled HDPE in much the same way as the IM-HDPE did. It can also be expected to lower the modulus ratio, because both are flexible low-density materials.

What is less easy to explain is why $E_r \approx \eta_r$. On the basis of the evidence collected, it can be proposed that $E_r \approx \eta_r$ for blends involving recycled HDPE with high-flow polyethylenes, a high degree of short-chain branching, and markedly different behavior for viscosity ratio and modulus ratio.

CONCLUSION

Viscosity and modulus ratios were calculated for blends of recycled HDPE with eight different virgin polyolefins. These blends were categorized according to the value of viscosity and modulus ratios in relation to unity.

A number of general conclusions can be made. One is that the branching content and type of branching is important, particularly for the viscosity ratio. Blends with long chains, such as the film blowing grade materials, displayed significant variation in the viscosity ratio compared to those with long chains, such as the injection molding grade materials.

Another conclusion is that the PE/PE blends generally behaved in fundamentally different ways than did the PE/PP blends. The PE/PE blends were

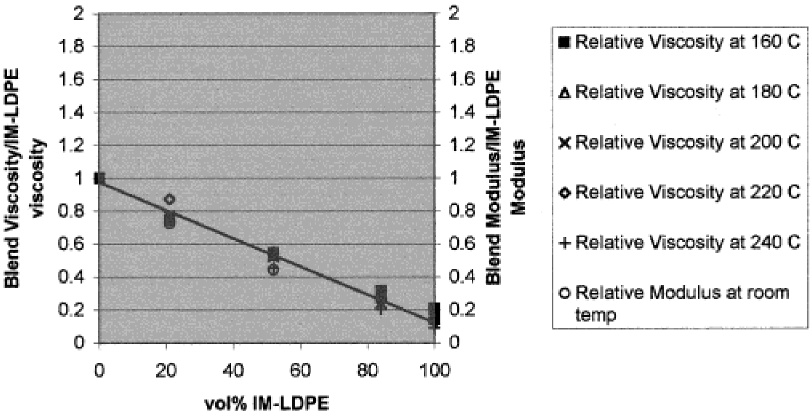

Figure 8 Relative viscosity and modulus for recycled HDPE/IM-LLDPE blends at 96 s^{-1} shear rate.

either stiffened by a higher viscosity material or rendered more flexible by a lower viscosity material. The PE/PP blends, however, were reinforced by the addition of a lower viscosity material.

The only exception to this trend was the recycled HDPE/FB-LLDPE blend, where recycled HDPE was reinforced by the addition of a lower viscosity component.

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