Studies on Rheological Behaviour of LDPE/EPDM Blends, Using a Torque Rheometer

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ABSTRACT

In this work, selected grades of LDPE and EPDM have been melt-mixed over the complete range of compositions. The effect of compositions on the rheological behaviour, dynamic elastic properties and flow activation energy was studied by a torque rheometer. The results show that the more LDPE in the blend, the lower melt viscosity and the total work energy but higher flow activation energy and dynamic elastic properties.

Key Words: blend rheological behaviour, dynamic elastic properties, flow activation energy, total work energy, torque rheometer

INTRODUCTION

Polymer alloys and blends represent an important phase of present day research. The purpose of alloying or blending together of two or more polymers or copolymers is to gain synergistic improvement in properties at both micro and macro levels [1].

Blends of polyethylene have long been in use. High density polyethylene (HDPE) has been blended with ethylene vinylacetate copolymer to improve the electrical and aging properties of the former. Nowadays ultra-high molecular weight polyethylene and its blends are gaining importance owing to their excellent mechanical properties, especially abrasion resistance [1].

A considerable amount of work has been reported on the blends of polyolefin and ethylene-propylene-diene terpolymer (EPDM) due to their commercial importance [2-5]. For example, the most useful blends of EPDM and HDPE are prepared by intensive mixing of both polymers and mostly they are used in automotive applications. It has been found that by blending HDPE with EPDM, the low temperature properties, resilience, ozone resistance, aging, chemical resistance and electrical properties are improved. Chlorosulphonated polyethylene and EPDM are also melt-kneaded to give a blend with good processability [1]. Nevertheless, a few papers exist about LDPE/EPDM blends.

In this article, we report on the rheology, dynamic elastic properties and flow activation energy of LDPE and EPDM blends of different ratios by employing a torque rheometer.

EXPERIMENTAL

Materials
The polymer used is a low density polyethylene...
(LDPE) [density 0.9213 g/cm³, melt flow index (MFI) 0.9 g/10 min] obtained from Bandar Imam Petrochemical Co. Ltd., Iran, and commercial EPDM of Royalene 400 [Mooney viscosity, ML (1+8) 125 °C of 38] from Uniroyal Chemical Company Inc., USA. Royalene 400 contains an ethylene/propylene ratio of 68/32, DCPD as a third monomer and 100 phr naphthenic oil.

For thermal stability, 1% Vulkanox HSILG (TMQ) from Bayer Co. Ltd. and 0.5% Irganox 1010 from Ciba-Geigy were added to the blends based on the rubber and plastic weights taken, respectively.

Blend Preparation
The rubber and plastic components were blended in a torque rheometer (Rheomix-750) equipped with a pair of roller blades. The temperature of the mixing chamber was set at 140 °C for the blends preparation, and the dynamic elastic properties of the blends in the melt state which rose to 160–170 °C due to frictional effects, were studied. But, for other experiments the temperature was varied from 140–200 °C at a ramp of 5 °C/min. The rotor rate was set mainly at 60 rpm but for rheological studies, it was changed to 40 and 80 rpm.

The analysis was conducted with a Rheo-cord-90 software copyrighted by Haake Instruments, Inc. This system calculates torque, totalized torque and temperature with respect to mixing time, and plots the parameters in the form of a curve as a function of time.

The torque moment necessary to turn the mixer blades was continuously recorded. The higher rotor speeds led to higher torques, because of the higher shear rate. This can be explained by the power-law behaviour commonly observed for polymer melts [1, 2]:

$$\tau = k \dot{\gamma}^n$$  \hspace{1cm} (1)

where $\tau$ is the shear stress, $\dot{\gamma}$ is the shear rate, and $k$ and $n$ are the power-law parameters.

With a few assumptions, it was observed that there is an equation which is similar to equation (1) [1, 6–9].

$$M = C(n)kN^n$$  \hspace{1cm} (2)

where:
- $M$ = equilibrium torque.
- $n$ = power-law index.
- $C(n)$ = a function which appears to be weakly dependent on $n$.
- $k$ = constant in the power-law shear-stress/shear rate relationship.
- $N$ = rotor speed.

An important parameter to assess and compare the polymers or mix prototypes is the work which is defined as the work energy required to process a unit volume or a unit mass of material. It can be calculated from the totalized torque, which is obtained directly from the rheometer. The totalized torque is defined as the energy required to process a certain material for a certain period of time at given conditions. It is therefore simply the area under the torque-time curve. The totalized torque can be converted to work energy as follows [1, 6, 8]:

$$W_a = \frac{W_t}{V_b} = 61.58 \frac{TTQ}{V_b}$$  \hspace{1cm} (3)

where:
- $W_a$ = total work energy.
- $W_t$ = work energy per charged sample volume.
- $N$ = rotor speed.
- $V_b$ = sample volume.
- $TTQ$ = totalized torque.

Study of Dynamic Elastic Properties of the Polymer Melt
Mixing of LDPE/EPDM blends was carried out by Rheomix-750 at 60 rpm and 140 °C set temperature. After 6 minutes, $(t_a)$ when the torque curve was almost horizontal, the rotors were suddenly stopped and the compound was allowed to rest for 6 minutes, during which the torque value was zero. After further 6 minutes $(t_{a+2})$ the drive was suddenly turned on again and the torque difference.
Flow Activation Energy
The data from a torque rheometer can also be used to calculate the activation energy from the Arrhenius equation [1, 6, 10]:

\[ \eta = Ae^{\Delta E/RT} \]  

where \( \eta \) is the viscosity of the melt, \( T \) is the temperature of the melt in K, \( R \) is Rydberg's constant, \( \Delta E \) is the flow activation energy and \( A \) is the Arrhenius constant which depends on the type of the polymer.

Taking logarithms, the equation (4) changes to:

\[ \ln \eta = \ln A + \frac{\Delta E}{R} \frac{1}{T} \]  

since \( \eta \propto \frac{M}{N} \), the equation (5) can be rewritten as:

\[ \ln \frac{M}{N} = \ln A' + \frac{\Delta E}{R} \frac{1}{T} \]  

where \( A' = \frac{A}{N} \).

This calculation was done by temperature programming in the Rheocord-90 from 140 to 200 °C and carrying out at a ramp of 5 °C/min at 60 rpm. The M/N values at four selected temperatures (140, 160, 180 and 200 °C) were calculated and \( \ln \frac{M}{N} \) versus \( T^{-1} \) (K) was plotted. From the slope of the straight line (\( \Delta E/R \)), the activation energy can be calculated.

RESULTS AND DISCUSSION

Figure 1 shows the torque values as a function of the blend compositions at 160 °C which is the melt temperature for different rpms of the rotors. These torque values may be taken as proportional to the viscosity of the system at the melt temperature and the shear rate involved. In all cases the viscosity of the melt is found to decrease with increase of LDPE content. This is obviously an evidence for improvement in the processability with increase in LDPE content, where the lower values of effective viscosity make it possible to reduce the processing temperatures leading to reduction in the energy required for production. Table 1 shows that the higher the LDPE content, the lower would be the energy consumed for mixing of the blends of different ratios after 6 minutes mixing. Meanwhile, with increase of the LDPE content, the values of the viscosity at various rotor speeds converge together.
Figure 2 shows the variation of the torque with the blend compositions at various melt temperatures at a fixed shear rate (60 rpm). As expected, the viscosity decreases with increase of the temperature in all cases. As it can be seen from Figure 2, same as in Figure 1, the flow curves approach one another at various temperatures with increase of the LDPE content.

Figure 3 shows the difference between the shock torque ($M_{12}$) and the last recorded torque ($M_{6}$) which is different for the blends of various ratios. The ratio of these torques ($M_{12}/M_{6}$) as a function of EPDM content is shown in Figure 4. It can be seen that with higher amount of LDPE content the difference is higher and when the amount of rubber exceeds 50% by weight, the $M_{12}/M_{6}$ ratio approaches to about 1. It seems that the recovery of conformational changes (due to shear forces of the rotors) to the original state during the rest period for the blends with higher amounts of rubber are not time-dependent and these blends dissipate all of the applied forces. But, polymer chains of LDPE in the melt state orient along the applied force and recover to the original state during the rest time. Therefore, when the drive turns on, LDPE shows both storage and loss behaviour.

Variation of torque values as a function of the melt temperature for the blends of different ratios is depicted in Figure 5. From this figure the suitable data for calculating the flow activation energy for a range of temperatures are obtained. Figure 6 shows the ln $M/N$ versus $1/T$ of the Arrhenius equation for the various blend compositions. The linear plots confirm the
Arrhenius type behaviour. It can be observed from the lines that more or less the flow activation energy increases with increase of the LDPE content due to the progressive increase in the slope of the lines. It means that the viscosity of the blends with higher amounts of LDPE is more sensitive to variation of temperature than the blends containing higher amount of EPDM rubber.

The values of the flow activation energies as a function of blend compositions is shown in Figure 7.

CONCLUSION

Studies on rheological behaviour of LDPE/EPDM blends using a torque rheometer showed that the viscosity of the blends decreases with increase of the LDPE content at various melt temperatures and rotors speed. Moreover, with increase of the LDPE content, the flow curves at various melt temperatures and rotors speed approach each other.

By dynamic property measurements, using Rheocord-90, it was found that with higher amounts of rubber, the lower would be the elastic response.

Flow activation energy was calculated by temperature programming in the Rheocord-90. From calculations involving an Arrhenius type equation it was found that the more the LDPE content, the higher would be the flow activation energy. Hence, the viscosity is sensitive to the variation of temperature.

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