

Tribological Properties of Blends of Melamine-Formaldehyde Resin With Low Density Polyethylene

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Tribological properties of blends of melamine-formaldehyde resin (MFR) with low density polyethylene (LDPE) containing 1, 5, 10, 20, 25 wt% MFR were investigated. We have determined sliding wear by multiple scratching along the same groove using a micro scratch tester. Instantaneous penetration depth is lowered by the MFR addition to LDPE. However, there is less viscoelastic recovery and the residual (healing) depths increase with increasing MFR concentration. Microindentation hardness increases along with the MFR content. Since MFR is only partially miscible with LDPE, MFR-rich islands in the PE matrix offer more interfaces and so increase hardness. Friction determined with a pin-on-disk tribometer using silicon nitride balls as a function of MFR concentration shows a minimum. The result is explained in terms of surface morphology seen in scanning electron microscopy. At the same time, all blend friction values are lower than for neat LDPE. Wear determined in the pin-on-disk tribometer decreases along with the MFR concentration increase. Thus, pin-on-disk wear and friction show different faces of blends tribology. Blending can be used to improve tribological properties of LDPE. POLYM. ENG. SCI., 48:292-296, 2008. © 2007 Society of Plastics Engineers

INTRODUCTION

Polymers have widespread applications in industry, and continue to gain increasing importance as technology advances because of their unique characteristics including low density and advantageous electrical and mechanical properties. However, some adverse effects limit their practical applications. In particular, low scratch and wear resistance and also environmental degradation have hindered many important applications. Thus, there is a need for improved understanding of polymer tribology [1–12].

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On the other hand, polymer blends—subsequently crosslinked or not—have attracted significant scientific and technical interest as they can provide properties unattainable in pure components [13–29].

Since low density polyethylene (LDPE) belongs to the most widely used polymers, we have decided to use blending to improve its properties. To this end we have reported the miscibility behavior and thermal properties of LDPE + melamine-formaldehyde resin (MFR) blends containing 1, 5, 10, 20, 25 wt% MFR [26]. MFRs have been synthesized and blended with a LDPE. Thermal properties have been analyzed by differential scanning calorimetry and thermogravimetric analysis measurements. A detailed study on the miscibility behavior of LDPE + MFR blends has been made by using Fourier-transform infrared spectroscopy, environmental scanning electron microscopy (ESEM), and atomic force microscopy (AFM). The observations were correlated with the properties of the composites. Thermal analysis, AFM, and ESEM support the occurrence of a partial compatibilization.

In this work we have focused on the *tribological* properties of LDPE + MFR blends. A variety of techniques have been used including a Micro Scratch tester (MST), a microhardness, and a Nanovea pin-on-disk tribometer to determine the tribology of the blends as potential design materials for the plastics industry. Effects of composition variation have been evaluated and the results connected to the morphology of the blends.

EXPERIMENTAL PART

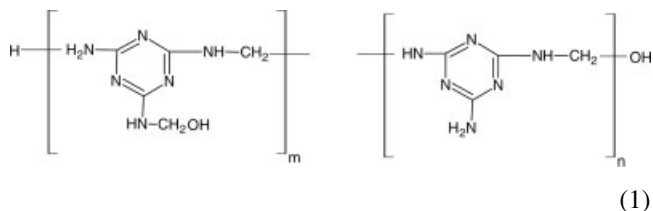
Materials

LDPE was supplied by Aldrich Chemicals. Melamine, $C_3H_6N_6$ (2,4,6-triamino-1,3,5-triazine); formaldehyde CH_2O ; and sodium hydroxide, NaOH used were supplied by Fluka and Sigma Chemicals, respectively.

Synthesize of Melamine-Formaldehyde Resin

MFR was synthesized from melamine by polycondensation reaction with formaldehyde in a basic medium. The

molar ratio melamine/formaldehyde was between 1 and 3. pH of formaldehyde (37.0% by weight in water) was adjusted to 7.5–8.0 by adding 10 wt% NaOH aqueous solution. The resulting solution was placed in a beaker and thoroughly mixed with 20 g melamine; the components were then stirred for 40 min at 120°C. The resulting structure is



The final product was subjected to evaporation. To achieve complete water removal, the evaporation was carried out at 70°C and the residual pressure 13–16 kPa, followed by drying in an oven at 80°C for 24 hr.

Blending and Sample Preparation

Blends of dried PE and MFR were prepared by melt mixing in a C.W. Brabender D - 52 Preparation Station at the rotation speed of 80 rpm and at 160°C. The resulting blends were pelletized and dried. The blends contained in turn 1, 5, 10, 20, and 25 wt% MFR.

Subsequently, the blends were dried for 8 hr at 100°C before compressing them in a Carver compression molding machine at 160°C at the compression pressure 20.7×10^3 kPa.

Sliding Wear Determination

The first tribological test performed for each blend consisted using a Micro-Scratch Tester (MST) from CSEM, Neufchatel, Switzerland, utilizing the CSEM Scratch Software Version 2.3, which applies a constantly increasing force from 0 to 25.0 N to the samples, or else a constant force. Multiple scratching following the same groove provides us with sliding wear determination (SWD) results. For each sample 15 scratches were performed. The parameters used in the tests were the following: load 10.0 N, scratch length 5.0 mm, scratch velocity 5.0 mm/min at room temperature. A conical diamond indenter with 200 μm of diameter and the cone angle of 120° was used. The results consist of the penetration (instantaneous) depth R_p and the healing (recovery) depth R_h determined 5 min later.

Microhardness Measurements

The Vickers microhardness h_{Vickers} of each blend was determined with a dynamic microhardness measurement device, HMV-M Shimadzu Micro Hardness Tester; model M3, from Shimadzu, Kyoto, Japan.

Loads of 100, 200, and 300 g were used to make microindentations. The holding time after completion of

the indentation was 5 s. Five indentations were made for each sample. The mean value of the Vickers microhardness as averaged from five different tests was obtained using the formula

$$h_v = 1854.4 \frac{P}{d^2}, \quad (2)$$

where P is the load in g while d is the mean diagonal of indentation in μm .

Friction and Wear Measurements

Friction tests were conducted on the NanoEvea pin-on-disk tribometer from Micro Photonics. The tribometer provides simulation of friction and wear processes under sliding conditions. It can be operated for solid friction without lubrication and for boundary lubrication with liquid lubricants. Thus, both material properties and lubricant effects can be determined. A stationary test specimen, pin or ball, with a defined normal force is pressed against the surface of another test specimen placed on the rotary disk. The normal force is applied over the pin or ball by means of a set of dead weights between 0 and 60 N. This allows a stable force during the test. The pin, or ball, is mounted on a stiff arm, designed as a frictionless extensometer force transducer.

The friction is determined from the friction force by means of the deflection of the elastic arm. Strain gauges bonded on the elastic body of the arm convert it into a force sensor and allow the direct measurement of the friction force. The rotation of the disk is driven by a servo motor, between 0 rpm and 500 rpm. Thus, except for very small rpm values, we are dealing with *dynamic* friction. Wear/depth measurement can be performed by measuring the changing angle of the arm during the test using an inductive displacement sensor. The geometrical relationship between the arm and support of the sensor provides a measure of wear. Silicon nitride ceramic balls (NBD200) made by Saint-Gobain Ceramics with the diameter 3.2 mm are used. Before each test, the surfaces of the samples were polished with metallographic abrasive paper. Then the ball was cleaned in acetone and thoroughly dried. Each test was performed under the following conditions: temperature (20 ± 2) °C, speed 100 rpm, radius 2.0 mm, weight 5.0 N. The test durations ranged between 20 and 30 min.

SLIDING WEAR RESULTS

The viscoelastic recovery φ has been defined [8] as

$$\varphi = \frac{R_p - R_h}{R_h} \cdot 100\%. \quad (3)$$

The definition is usable in single scratching [8] as well as in SWD tests [27].

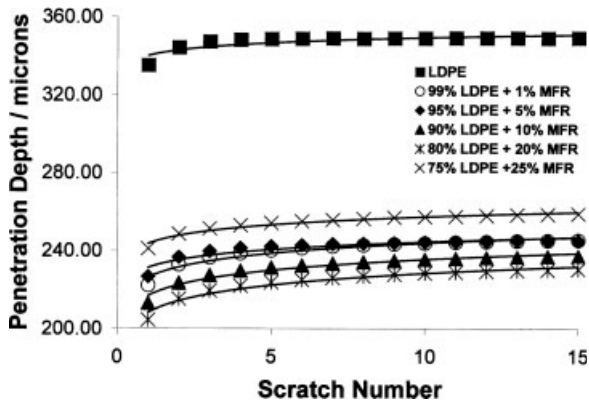


FIG. 1. Penetration depth of LDPE + MFR blends at the constant force of 10.0 N.

In each SWD run made at a constant force we obtain a diagram of the depth as a function of the scratch number. In all runs the full range was 5.0 mm. For detailed analysis we have used the depth at 2.5 mm in the middle of the scratching range.

In Fig. 1 we show the penetration depth R_p curves for constant load as a function of the number of scratch tests performed.

The neat LDPE material was examined as a reference to compare the values with those for the blends. It is clearly seen in Fig. 1 that blends are more resistant to instantaneous deformation by microscratching. At 10.0 N force blends have the original penetration depths R_p ranging from 200 to 250 μm while LDPE has $R_p \approx 350 \mu\text{m}$.

In Fig. 2 we display the residual depth R_h diagrams in the same way.

We see in Fig. 2 that the situation is inverted for the residual depth R_h . All blends have larger residual depth than LDPE. Both Figs. 1 and 2 confirm for LDPE and its blends the phenomenon of strain hardening in sliding wear reported first in Ref. 27. The phenomenon can be explained by in terms of densification of the bottom and sides of the groove [30]. We also recall in this context

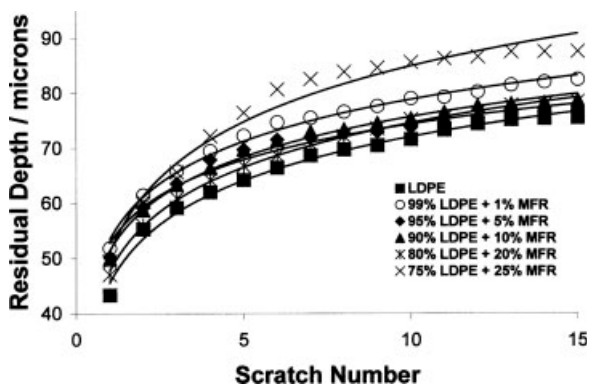


FIG. 2. Residual depth of LDPE + MFR blends at the constant force of 10.0 N.

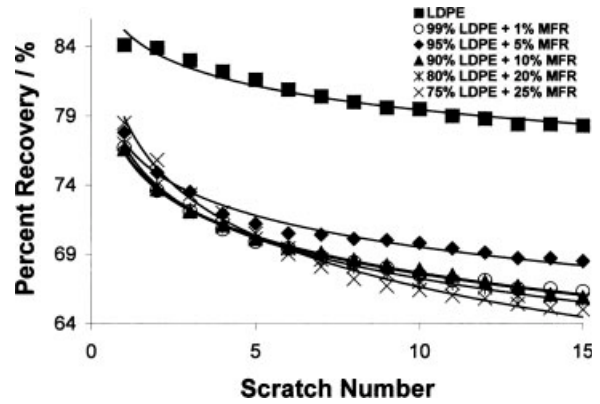


FIG. 3. Viscoelastic recovery of LDPE + MFR blends calculated from Eq. 3 at the constant force of 10.0 N.

a connection between nanoscratching and nanoindentation [31].

In Fig. 3 we can see the values of viscoelastic recovery as defined by Eq. 2, also as a function of the number of tests.

We find that the viscoelastic recovery of blends is in the range between 65 and 80% while that of LDPE is between 80 and 85%. All three series of results can be explained by MFR providing increased crystallinity. Lower penetration depths result, but there is less recovery and thus higher residual depths.

VICKERS MICROHARDNESS

Microhardness values determined as described in Section 2.2 and calculated from Eq. 1 are listed in Table 1. We have covered the range from 100 to 300 g in our experiments. Variations of the microhardness with the load applied are small; neglecting them constitutes a reasonable approximation. For consistency, we list in the Table values for the load of 200 g.

Table 1 tells us that the microhardness values increase with increasing MFR concentration. As concluded in the previous article [26] there is a partial but not complete miscibility of the components. Thus, there exist MFR-rich islands in the predominantly PE matrix. Apparently interfacial boundaries offer more resistance to microindentation than PE alone.

TABLE 1. Vickers microhardness values of the different blends.

Material	Vickers microhardness h_{Vickers}
LDPE	23.9
99% LDPE	24.5
95% LDPE	25.1
90% LDPE	25.8
80% LDPE	26.6
75% LDPE	28.2

PIN-ON-DISK FRICTION

Curves showing the variation of friction with the number of revolutions for LDPE + MFR blends and for pure LDPE are shown in Fig. 4.

We see in Fig. 4 that the friction of pure LDPE is higher than that of the blends. For blends the friction slowly increases in the initial stage of sliding, then in some cases decreases slightly, and eventually reaches a steady stage. For pure LDPE no decreasing period is seen, the friction only increases before reaching a steady stage.

From the Nanovea pin-on-disk tribometer measurements performed for the blends, the average friction and wear was determined over the whole range of cycles, as shown in Fig. 5.

Figure 5 tells us that the friction as a function of composition exhibits a minimum around 10 wt% MFR. One possible explanation can be in terms of “bumps” on predominantly PE-rich surface. The bumps lower the friction as long as they are small. However, upon an increase of MFR concentration above 10 wt%, the bumps apparently increase in their surface areas, thus increasing the friction again. Scanning electron microscopy results reported earlier [26] support this interpretation. However, even for 25 wt% MFR the friction is still lower than for pure LDPE. The behavior of wear is different than that of friction: addition of MFR always results in lowering wear. In this respect wear behaves symbotically with the microindentation hardness, but not with friction. We infer that conclusions on wear cannot be based on friction results only.

CONCLUSIVE REMARKS

As expected the tribological properties of blends are related to their composition. The addition of the MFR to PE causes gradual decreases of both friction and wear, while the scratch resistance increases. As for mechanical properties, the higher the MFR content the higher the hardness of the blend. However, the viscoelastic recovery of blends is only 65–80% while that of LDPE is 80–90%. A possible explanation of this is that higher hardness

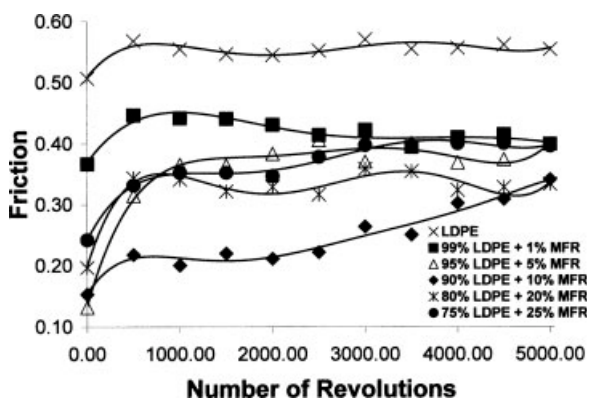
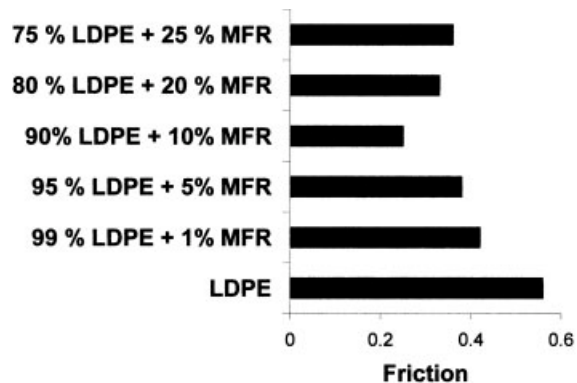
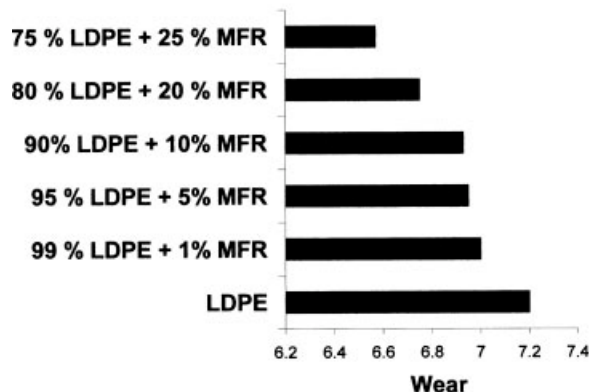


FIG. 4. Friction of LDPE + MFR blends.



(a)



(b)

FIG. 5. (a, b) Average friction and wear of LDPE + MFR blends.

brought about by the MFR component hinders viscoelastic recovery.

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