

# Mechanical and tribological properties of polyamide 6 and high density polyethylene polyblends with and without compatibilizer

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## Abstract

The structure and the mechanical and tribological properties of polyamide 6 (PA6) and high density polyethylene (HDPE) polyblends with and without the compatibilizing agent maleic anhydride propylene were studied. Polyblending was carried out in a modular intermeshing co-rotating twin-screw extruder. The blended materials were injection molded to provide the test samples. Polyblends with 20, 40, 60, and 80% polyamide 6 in high density polyethylene were obtained. The mechanical properties were studied in terms of the tensile strength, hardness and elongation-to-break. Friction and wear experiments were run under ambient condition in a pin-on-disk machine with the composite pin riding on the flat surface of a steel disk at a sliding speed of 1 m/s and under a normal load 19.6 N. It was found that the tensile strength of polyblends increased when polyamide proportion was more than 20 wt.% and hardness increased with any polyamide proportion. The coefficients of friction of all polyblends were lower than those of the polymers. The best polyblends for low coefficient of friction and high wear resistance were 60 wt.% PA6–40 wt.% HDPE and 80 wt.% PA6–20 wt.% HDPE. The wear behavior is explained in terms of the ability of the polyblends to form transfer film on the steel counterfaces. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Tribology; Polyamide; High density polyethylene; Polyblends; Transfer film; Wear; Friction

## 1. Introduction

The use of polymers and polymer-based composites in situations, which require a combination of good mechanical and tribological properties, is very common. It is often found that such properties are not attainable with a homopolymer. This has led to the development of copolymers and fiber-reinforced polymers. Another technique, which has mostly been used with respect to the mechanical properties, is polyblending which is fascinating because it unfolds unlimited possibilities of producing materials with variable properties. Such materials are prepared by blending two or more polymers and are known as polyblends. There are numerous studies on the tribological properties of polyblends with some of the recent ones reported in Refs. [1–4].

Polyamide 6 (PA6) and high density polyethylene (HDPE) are large-volume commercial polymers that have many complementary attributes. The properties that account for the popularity of PA6 are high crystalline melting point, good resistance to hydrocarbons, high strength, and the ease of fabrication and processing. As for HDPE, it has excellent low temperature flexibility, low cost and good resistance to

moisture permeation. It is thus conceivable that the blends of PA6 and HDPE can be prepared with a reasonable mix of properties of both the polymers. In fact some limited studies on the blends of these polymers have been made in terms of melt-flow stability, homogeneity of structure, and mechanical properties such as impact strength and percentage of elongation, but not for tribological properties.

The tribological behavior of polyamide, high-density polyethylene, and their composites has been reported in earlier papers [5–7]. Polyamide has been reported to have a superior wear resistance sliding against a steel counterface relative to other polymers. The coefficient of friction of polyamide is affected greatly by normal load, sliding speed, and temperature and the coefficient of friction values as high as 1.0–2.0 have been reported under certain rubbing conditions [5]. HDPE exhibits low friction and low wear and forms a thin highly oriented film on the metal counterface, when sliding against a metal surface under mild conditions [7]. It should thus be possible to produce polyblends of PA6 and HDPE with a very desirable array of tribological properties.

Polymer blends are mixtures of at least two macromolecular species, polymers and/or copolymers. Mixing two polymers usually leads to immiscible blends, characterized by a coarse, metastable morphology, and poor adhesion between

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the phases. The properties most affected because of this phase-separated morphology are elongation-at-break, toughness, and tensile strength. For improved performance the immiscible blends usually need compatibilization.

The latter is the process of modification of the interfacial properties of an immiscible polymer blend, leading to the creation of a polymer alloy. The process is used to reduce interfacial tension, which facilitates a finer dispersion during mixing, and enhances adhesion between the phases in the solid state. There are many types of compatibilization. One of them is the reactive compatibilization which consists of creating conditions for chemical reactions between two components in the molten state, often by introduction of either a reactive third component with appropriate functional groups or a catalyst. The process may simply be defined as a reaction between two or more polymers to form a copolymer. The other methods for compatibilization are via the addition of block and graft copolymers, or functional/reactive polymers, and in situ grafting or polymerization (reactive blending) [8,9]. The interfacial tension, phase morphology and phase growth have been studied for polyamide 6/polyethylene polyblends by White and co-workers [10–12]. They reported that the addition of various potential compatibilizing agents to blend systems results in lowered interfacial tension, and finer and stabilized phase morphologies. The rheological properties of polyamide 6/high density polyethylene have been reported by many workers [13–15].

This study attempts to understand the tribological behavior of polyamide 6 and high density polyethylene polyblends with and without compatibilization in light of the structure and mechanical properties.

## 2. Experimental details

Polyblends of polyamide 6 and high density polyethylene were prepared for this study both with and without a compatibilizer. The latter was maleic anhydride polypropylene (MAgPP). The sources and characteristics of these materials are listed in Table 1. The blends were produced in different proportions of 20, 40, 60, and 80% by weight. In the case of blends made with compatibilizer, the amount of compatibilizer added was 5 wt.% based on the recommendations of White et al. [11] who reported that this compatibilizer

proportion was high enough for interaction with PA6 and HDPE interface.

The polymer blends were produced using an American Leistritz 18 modular intermeshing co-rotating twin screw extruder. All the materials were dried at 85°C for 48 h before compounding to avoid plasticization and hydrolyzing effects from humidity. The temperatures maintained in five zones of the extruder barrel were 180, 235, 240, 245 and 240°C and the temperature at the die was 235°C. The screw speed was set at 80 rpm which yielded a feed rate of 6 kg/h. The extrudate was obtained in the form of a cylindrical rod which was quenched in cold water and then pelletized. The initial 1 kg of the extrudate was discarded in order to ensure steady-state operation and to flush impurities out of the system before getting the polyblends samples. The processing of blends with the compatibilizer was good as the extruded material flowed out of the die smoothly. In case of processing without the compatibilizer, the flow of extruded material was erratic, and it was accompanied by swelling and thinning resulting in rupture of the extrudate from time to time.

The test specimens for tensile tests (ASTM D638, Type 1) and tribological tests were injection molded from the pelletized polyblends material using a BOY 30M reciprocating screw injection molding machine. The temperatures maintained in the three zones of the barrel were 215, 220 and 240°C, in the nozzle 230°C and in the mold 90°C. The screw speed was set at 10 rpm and the injection pressure at 800 bar. The times for injection, cooling, and ejection were 8, 30 and 1.5 s, respectively. The molded specimens were visually inspected for air bubbles and those with defects were discarded.

Friction and wear tests were performed in a pin-on-disk machine in which the stationary polymer pin was in contact with a rotating steel disk. The size of polymer pin was 6 mm diameter and 18 mm long. Before testing, the pins were abraded against a 600-grade SiC paper to ensure good contact between the sliding pin surface and the counterface during a sliding experiment. The counterface was made of quench-hardened AISI 02 tool steel (0.90% C, 1.6% Mn). The size of the rotating disk was 75 mm diameter and 5 mm thick. It was hardened to HRC 58 and finished by grinding followed by polishing with 320-grade SiC paper to give a surface roughness of 0.10–0.11  $\mu\text{m}$   $R_a$ . Dry sliding at ambient condition (with 35–40% relative

Table 1  
Data on the polymers and compatibilizing agent

Polymer	Designation	Source	Density (kg/m <sup>3</sup> )	Melting point (°C)
Polyamide 6	PA6	Allied Signal Plastics Capron 8200	1130	213
High density polyethylene	HDPE	Dow Chemical DOW HDPE 30360M	960	137
Maleic anhydride propylene	MAgPP	Allied Signal Plastics A-C 597p	940	133

humidity) with a normal load 19.6 N (0.64 MPa nominal pressure) and a sliding speed of 1 m/s was performed in a track of 65 mm diameter. Before testing, the pin and the disk surfaces were cleaned with acetone and thoroughly dried.

The amount of wear was measured by interrupting the sliding test at suitable intervals for weighting the pin to an accuracy of 0.0001 g in a precision balance. The friction force was measured from the output of a pair of strain gauges mounted on the vertical arm that carried the pin. For each condition, at least three tests were performed and the plotted values are the means calculated from the data of these tests. The variation in the coefficient of friction was about  $\pm 10\%$  and in wear  $\pm 20\%$  from test to test. The transfer behavior of

polymeric materials under different rubbing conditions was studied by optical microscopy.

The phase morphologies were characterized using a scanning electron microscope (SEM). For this purpose, samples from the injection-molded parts were fractured in liquid nitrogen and were coated with a gold–palladium alloy.

### 3. Results and discussion

#### 3.1. Structure

Blending PA6 with HDPE leads to a thermodynamically immiscible two-phase system. Maleic anhydride grafted

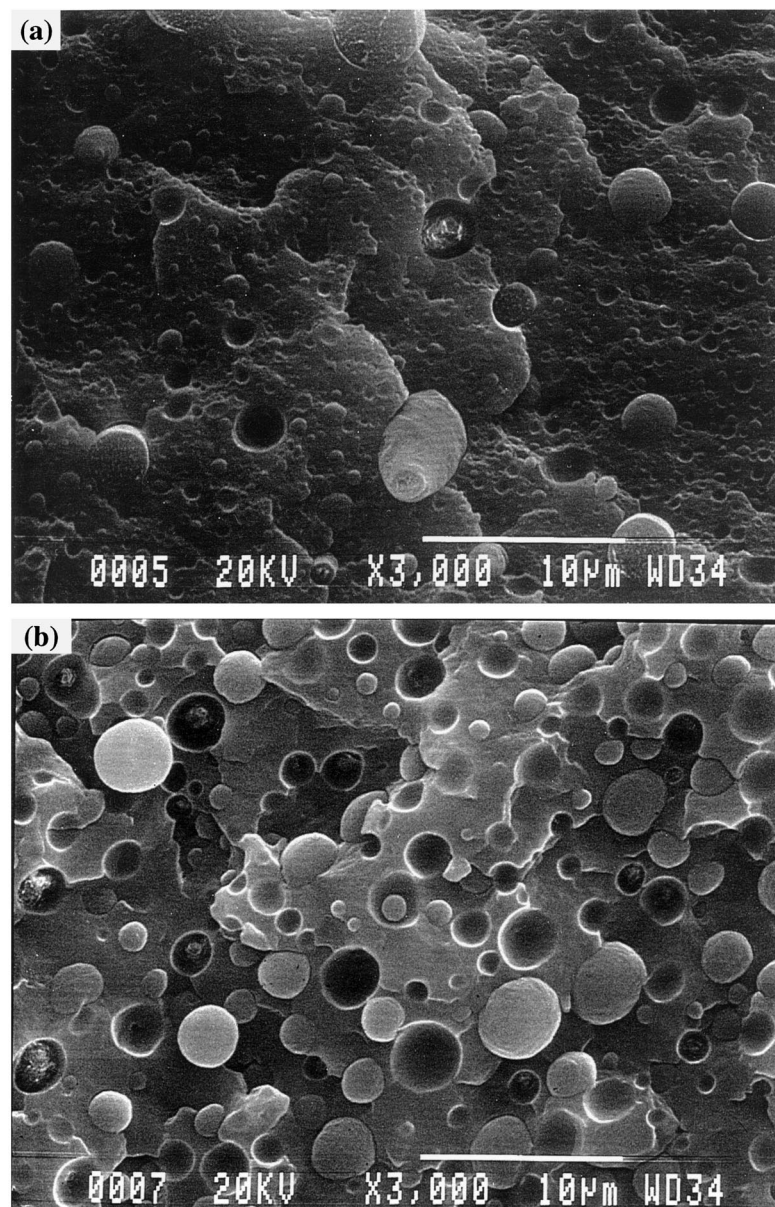


Fig. 1. SEM photomicrographs of 80% PA6–20% HDPE with and without the MAGPP compatibilizer.

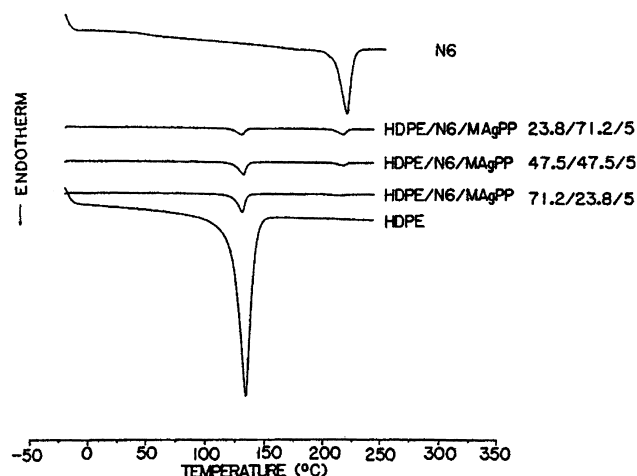


Fig. 2. DSC traces of PA6, HDPE, MAgPP, and two polyblend proportions [10].

polyolefin (MAgPP) serves as a precursor for reactive compatibilization. The polyolefin-grafted anhydride groups are expected to react readily with the amine end group(s) of the polyamide, and polypropylene blends in high density polyethylene because the two are miscible. The addition of compatibilizing agent such as maleic anhydride grafted polyolefin to polyamide–polyethylene blends stabilizes the phase dimensions. Fig. 1 shows the SEM photomicrographs of 80% PA6–20% HDPE with and without the compatibilizer. The addition of 5 wt.% MAgPP compatibilizing agent has a strong effect on the morphology. Because of large differences in chemical structure of the monomers, clean phase separations of spherical particles-in-matrix are observed in the absence of compatibilizer. The size of the spherical structure varies from 2 to 5  $\mu\text{m}$ , as seen in Fig. 1(b). When the compatibilizer is used, it reduces interfacial tension which promotes fusion of different phases. This is seen in Fig. 1(a) where regions with both the blended and discrete morphology are seen. It is also possible to think that MAgPP locates itself at the interface between PA6 and HDPE and thereby provides adhesion between them.

From the differential scanning calorimeter traces in Fig. 2, it is seen that the blended specimens exhibit endothermic peaks corresponding to the melting points of each polymer. This indicates that blending never occurs to the extent that individual polymers lose their identities. In other words, the blends have distributed phase structures.

### 3.2. Mechanical properties

Fig. 3 shows the tensile strengths of PA6–HDPE polyblends as a function of PA6 proportion in HDPE, both with and without the compatibilizer MAgPP. It should be noted that the tensile strength of PA6 is 65.4  $\text{N/mm}^2$  while that of HDPE is 17.4  $\text{N/mm}^2$ , which is much lower. Thus, the polyblend may be considered as an alloy comprised of a hard

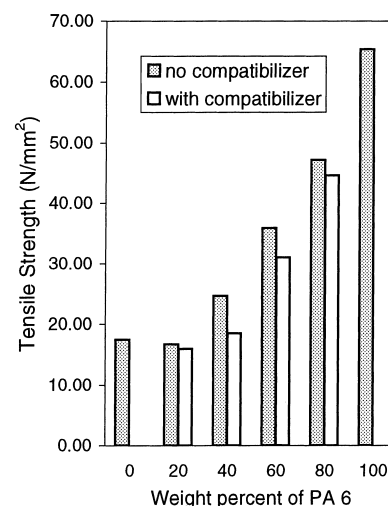


Fig. 3. Tensile strengths of various compositions of PA6–HDPE polyblends with and without compatibilizer.

phase and a soft phase. When the proportion of the hard phase is small, there may not be any effect on the strength of the alloy. In other words, there is a critical proportion of the hard phase to have any significant effect on strength and this critical value will vary from system to system. From Fig. 3 it is noted that this critical value for the PA6–HDPE polyblends system is higher than 20% PA6 because there is no difference between the tensile strengths of 20% PA6–80% HDPE polyblend and HDPE. Above this value, the tensile strengths of the polyblends increase with increasing PA6 proportion. Since these values are slightly lower than those obtained by the law of proportions, it appears that the two phases do not have a near-perfect bond.

The tensile strength values of polyblends with the compatibilizer are slightly lower than those without the compatibilizer for any PA6 proportion. This indicates that although the compatibilizer produces adhesion between the two polymer phases, it also introduces a weak boundary phase. This is to be expected because the compatibilizer is a low molecular weight material. It further indicates that there is a reasonably good bond between the phases in the solidified state even in the absence of the compatibilizer. This was not the case in the molten condition out of the extruder as indicated by the swelling and thinning of the extrudate.

The hardness of polyblends also varies similar to the tensile strength, as seen in Fig. 4. The higher is the proportion of PA6, the greater is the hardness of the polymer blend. In the mode of indentation which involves compression, the hardness increases even for 20% PA6–80% HDPE. The compatibilizer again lowers the hardness for any polyblend composition.

As for the elongation-to-break, it decreases with polyblending reaching a minimum for 40% PA6–60% HDPE, as seen in Fig. 5. Unless there is perfect bonding between the phases, this is what would be expected. There is no significant effect of the compatibilizer on elongation-to-break either.

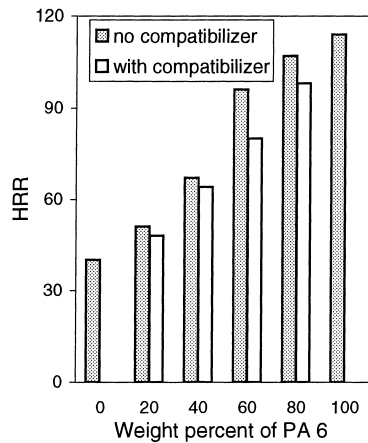


Fig. 4. Rockwell hardness (*R*) of the various compositions of polyblends with and without compatibilizer.

### 3.3. Wear and friction

Fig. 6 shows the variation of wear volume loss with sliding distance for PA6, HDPE and their blends with varying polymer proportions without the compatibilizing agent. It should be noted that the wear resistance of polyblends with the exception of 20% PA6–80% HDPE is very high compared to that of the polymers. This behavior is in agreement with that of the tensile strength. It also shows that a certain critical proportion of the hard phase (polyamide here) in the material is needed to produce an improvement in the wear resistance. The steady state wear rate of other polyblend compositions is an order of magnitude lower than that of HDPE and is also considerably lower than that of PA6 (see Table 2).

From Fig. 7 it is seen that the coefficient of friction of the polyblends is lower than that of the polymers. It varies from 0.23 to 0.26 which is a fairly low value for dry sliding at a speed of 1 m/s. The steady state coefficient of friction of PA6 was very high (0.82). The coefficient of friction of this

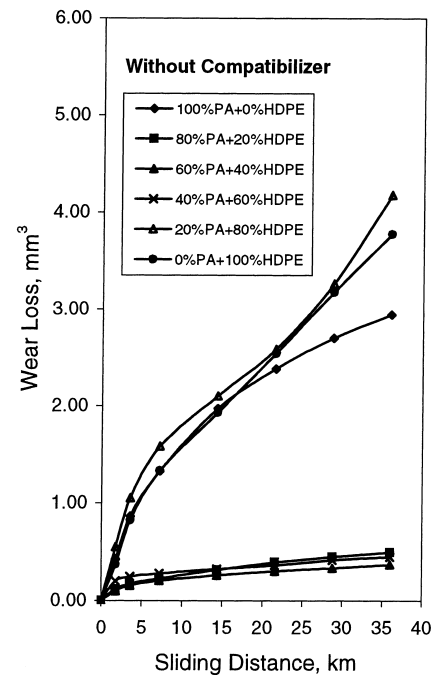


Fig. 6. Variation in wear volume loss with sliding distance for PA6, HDPE and their polyblends without the compatibilizing agent. Test conditions: 19.6 N load (0.64 MPa normal pressure), 1.0 m/s sliding speed.

material kept increasing after the commencement of sliding and the steady state condition started after the sliding distance of 14 km. The frictional sliding of PA6 was accompanied with an audible noise which would make the use of this material unacceptable for practical sliding applications. The sliding for polyblends was smooth and virtually free from audible noises. Thus, polyblends are excellent materials for sliding applications with high wear resistance and low coefficient of friction.

Fig. 8 shows the variation of wear volume loss with sliding distance for the polymers and their polyblends prepared using the compatibilizing agent. In this case, the

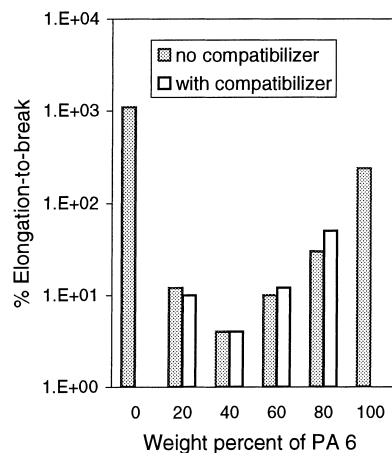


Fig. 5. Elongation-to-break of polyblends with and without compatibilizer.

Table 2

Coefficients of friction and wear rates for polymers and their polyblends

Material	Coefficient of friction	Wear rate $\times 10E - 6 \text{ mm}^3/\text{N/m}$
HDPE	0.31	4.33
PA6	0.82	2.80
(a) Polyblends without compatibilizer		
20% PA6 + 80% HDPE	0.23	4.49
40% PA6 + 60% HDPE	0.26	0.31
60% PA6 + 40% HDPE	0.24	0.29
80% PA6 + 20% HDPE	0.24	0.47
(b) Polyblends with compatibilizer		
20% PA6 + 80% HDPE	0.18	26.34
40% PA6 + 60% HDPE	0.18	5.04
60% PA6 + 40% HDPE	0.19	0.18
80% PA6 + 20% HDPE	0.25	0.22

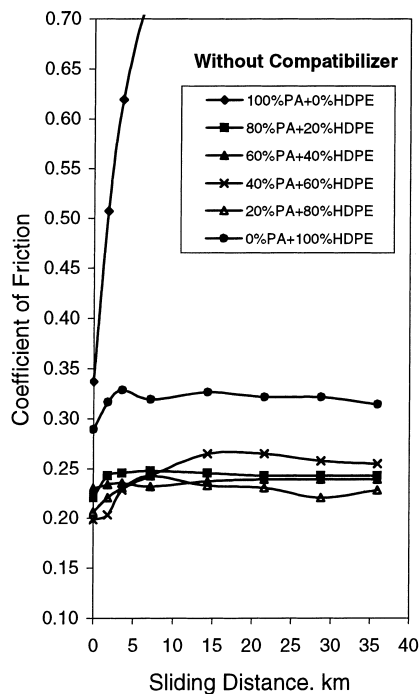


Fig. 7. Coefficient of friction vs. sliding distance for polymers and their polyblends without the compatibilizer. Sliding conditions same as in Fig. 6.

steady state wear rates of 60% PA6–40% HDPE and 80% PA6–20% HDPE are even lower than those of the corresponding polyblends made without the compatibilizing agent (see Table 2). The presence of the compatibilizer

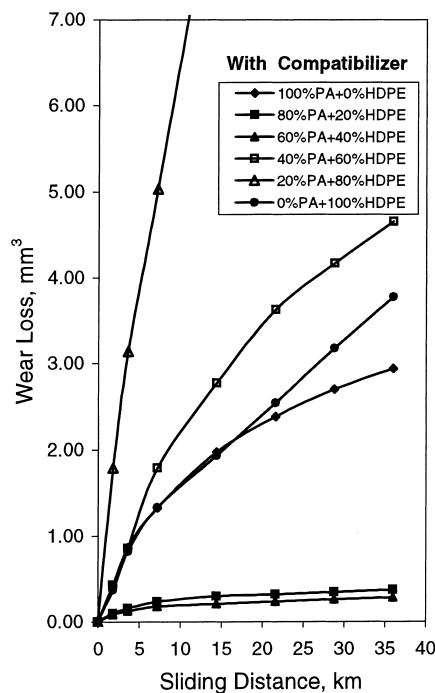


Fig. 8. Variation in wear volume loss with sliding distance for PA6, HDPE and their polyblends with the compatibilizing agent. Test conditions: 19.6 N load (0.64 MPa normal pressure), 1.0 m/s sliding speed.

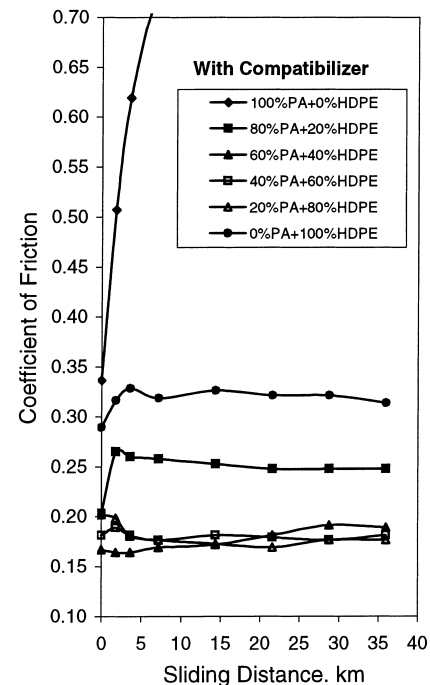


Fig. 9. Coefficient of friction vs. sliding distance for polymers and their polyblends with the compatibilizer. Sliding conditions same as in Fig. 6.

may be expected to change the transfer film characteristics which is discussed in Section 3.4. The surprising feature was that the wear rates of 20% PA6–80% HDPE and 40% PA6–60% HDPE increased considerably with the use of the compatibilizer. The data for these cases was verified further by additional tests. As stated earlier, the compatibilizer being a low molecular weight material provides weak phase boundaries so that unless there is enough localized

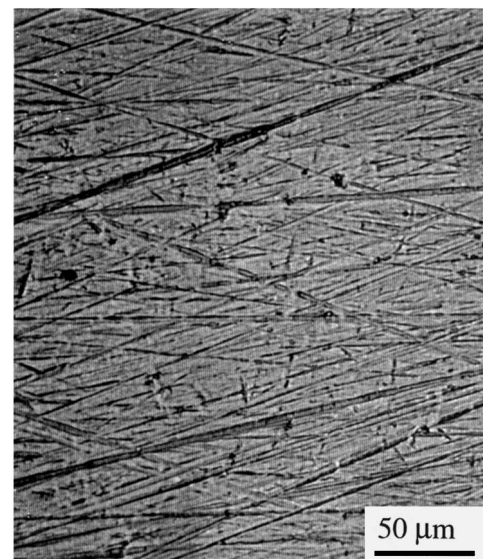


Fig. 10. Optical micrograph of an unrubbed hardened tool steel counterface ( $R_a = 0.10 \mu\text{m}$ ).

strengthening because of the hard phase, the wear resistance may be expected to be affected adversely. The coefficient of friction values for the polyblends with compatibilizer were lower than those of the polymers (Fig. 9), as observed earlier for the polyblends made without the compatibilizer as well.

### 3.4. Transfer films

As is well known, the wear behavior of a polymer in dry sliding against a metal counterface is strongly influenced by its ability to form a transfer film on the counterface. Once a transfer film is formed, subsequent interaction

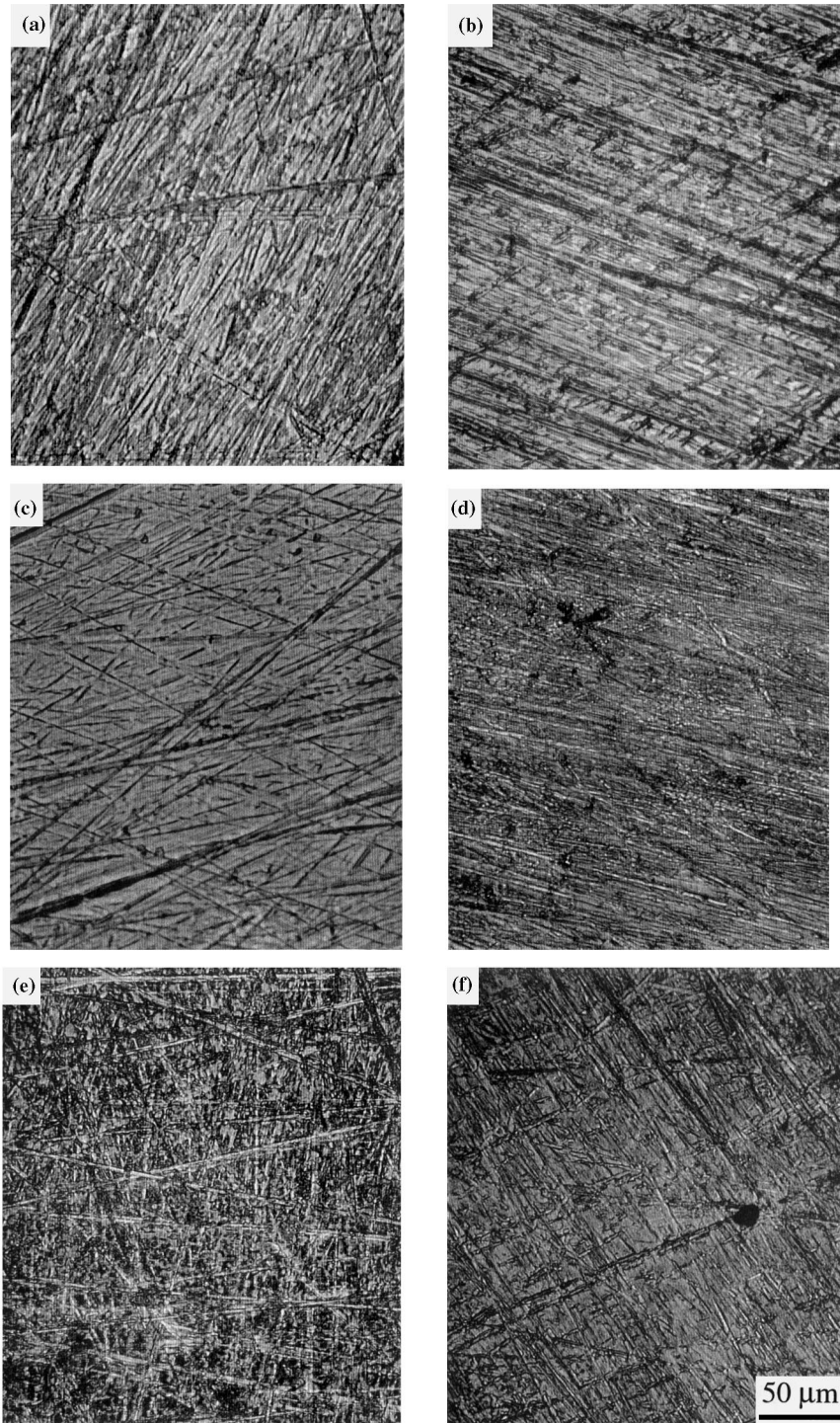


Fig. 11. Optical micrographs of steady-state transfer films formed by (a) 100% HDPE; (b) 100% PA6; (c) 20% PA6–80% HDPE; (d) 40% PA6–60% HDPE; (e) 60% PA6–40% HDPE; and (f) 80% PA6–20% HDPE polyblends with no compatibilizer, sliding against a tool steel counterface. Arrow indicates sliding direction.



occurs between the polymer and a layer of similar material, irrespective of the composition of the substrate. Fig. 10 shows the typical features of the unrubbed steel disk surface with a roughness of  $0.10\text{ }\mu\text{m Ra}$ , as prepared for the wear test. It exhibits the abrasion marks left by finishing operation. It should be noted that, apart from providing a finer surface finish, sequential polishing with abrasive papers changed the unidirectional grooving pattern of the ground surface. This was necessary because a ground surface has been observed to produce abrasion and thereby contribute to excessive wear [7].

The transfer films formed on steel counterfaces by HDPE, PA6, and PA6–HDPE polyblends prepared without the compatibilizing agent are shown in Fig. 11. Fig. 11(a) and (b) shows transfer films for the cases of HDPE and PA6, respectively. Except for very few minute patches, there is no transfer film on the surface because the sharp abrasion marks left over from finishing operation are clearly seen. Thus, there was practically no protection offered to the sliding pin surface from the transfer film. Fig. 11(c) shows the wear track on the counterface for 20% PA6–80% HDPE

polyblend. There is no transfer film on this surface either and so the wear rate of this polyblend was not much different from that of the polymers. The examination of counterfaces for the polyblends with 40, 60, and 80% PA6 showed that most of the abrasion marks produced during polishing were obscured by the presence of transfer film on the surface. Thus, the pin was not subjected to the aggressive damage by hard metal asperities. There was also a quick change over observed from transient state to steady state wear. For these reasons, the steady state wear rates for these polyblends were very low. The wear debris generated in these low wear polyblends was in the form of small particles which were generated by the mechanism of fatigue. The wear debris in high wear cases was in the form of large agglomerates.

The transfer films formed on steel counterfaces by the polyblends made with the compatibilizing agent are shown Fig. 12. Fig. 12(a) and (b) shows that there were no transfer films formed in cases of the polyblends with 20 and 40% PA6. The steady state wear rates for these polyblends were thus very high. On the other hand, the wear tracks for polyblends with 60 and 80% PA6 were

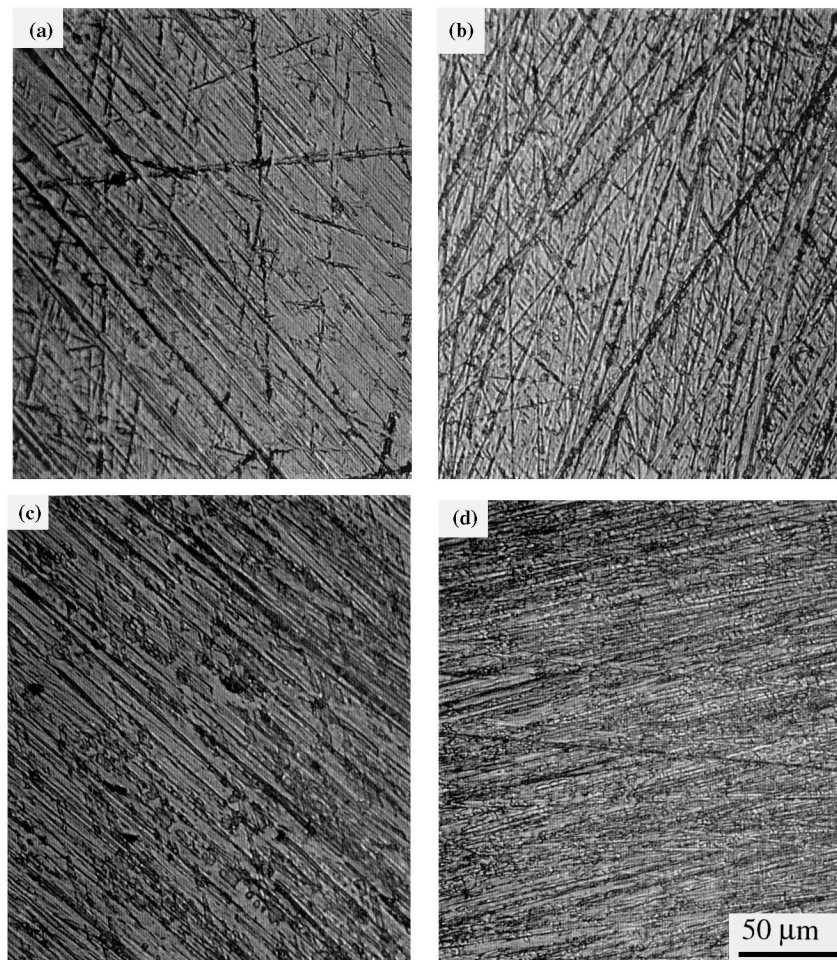


Fig. 12. Optical micrographs of steady-state transfer films formed by (a) 20% PA6–80% HDPE; (b) 40% PA6–60% HDPE; (c) 60% PA6–40% HDPE; and (d) 80% PA6–20% HDPE polyblends with compatibilizer, sliding against a tool steel counterface. Arrow indicates sliding direction.



covered with transfer films as the abrasion marks from finishing operation on the counterface can barely be seen. Due to the protection offered by this transfer film to the pin surface, the wear rates for these cases were very low and the wear debris generated was in the form of minute particles.

### 3.5. Discussion

Polyblending which was done in an extruder revealed that the use of compatibilizer was necessary in practical processing. The erratic expansion and shrinkage of the extrudate diametrically in case of polyblends made without the compatibilizer resulted in intermittent breaking of the extrudate. This was caused by the lack of bonding between the two polymers because the polyblends of PA and HDPE are inherently immiscible. Whereas the two polymers mixed well in the molten condition under pressure, the polymers tended to segregate on relief of pressure during which like molecules were pulled together. The use of compatibilizer led to bonding between the phases thereby restoring homogeneity in the material.

By tailoring polymer proportions, polyblends with any tensile strength between the tensile strengths of polymers as the extremes can be produced. The same thing applies to hardness. This is typical of distributed phase materials and it provides a great flexibility because the proportions may be adjusted to obtain the desirable mix of properties. The reduction in elongation-to-break with polyblending is not objectionable in view of the practical usage because the polyblends did not become brittle. With the use of MAGPP as the compatibilizer, the tensile strength and hardness values were slightly lower than those without the compatibilizer for any polyblend composition. It is possible that other compatibilizers may reduce or eliminate this penalty.

The results from tribological studies were dramatic because polyblending produced many compositions which had much lower wear rates and the coefficients of friction than those of the polymers. The polyblend with composition 60% PA6–40% HDPE had an exceptionally low coefficient of friction of 0.19 and also a real low steady state wear rate of  $0.18 \times 10^{-6} \text{ mm}^3/\text{N.m}$ . In view of high tensile strength, hardness, and ductility and such good tribological properties, this polyblend composition compares favorably with other materials for practical applications.

It was found that wear was governed by the ability of material to form transfer film. In cases where a good transfer film was formed, wear rate was very low and vice versa. It is not understood why some polyblends formed a good transfer film while others did not. The reduction in the coefficient of friction for all polyblends occurred presumably because of the two phase structure of the material in both the pin and transfer film so that sliding encountered contacts between the like (compatible) and unlike (incompatible) phases intermittently.

## 4. Conclusions

From the studies on PA6–HDPE polyblends with and without the MAGPP compatibilizer, the following conclusions were drawn.

1. The extrusion of polyblends in the absence of the compatibilizer was erratic because the extrudate swelled and thinned rendering extrusion discontinuous. When compatibilizer was used, the extrusion was smooth and uniform.
2. In the presence of compatibilizer, the polymer phases blended better than when the compatibilizer was not used.
3. With the exception of 20% PA6–80% HDPE, the tensile strength and hardness of the polyblends increased with increasing proportion of PA6 in HDPE. When polyblends were prepared with the compatibilizer, the tensile strength and hardness values were slightly lower than those without the compatibilizer.
4. The elongation-to-break values for polyblends were lower than those of the polymers.
5. The coefficients of friction of polyblends were always lower than those of the polymers. There was no audible noise, as observed in the dry sliding of polyamide, when polyblends were involved in sliding.
6. The wear rates of 60% PA6–40% HDPE and 80% PA6–20% HDPE with compatibilizer were the lowest along with very low values of the coefficient of friction.
7. With 20% PA6 in the polyblend with and without the compatibilizer, there was no reduction in wear. There was no reduction in wear also with 40% PA6 when the polyblend was prepared with the compatibilizer.
8. For reduction of wear, the development of transfer film on the counterface was a necessary condition.

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