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Effects of hybrid composition of LCP and glass fibres on abrasive wear of reinforced LLDPE

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Abstract. The hybrid of liquid crystalline polymer (LCP) fibres and glass fibres (GF) provide a combination of modulus and toughness to semi-crystalline linear-low-density-polyethylene (LLDPE). LCP and GF fibres reinforced composites were studied using two-body abrasion tester under different applied loads. Two sets of fibre reinforced LLDPE, 10 and 20 vol%, were investigated. The contents of LCP and glass fibres were varied as 25, 50, 75 and 100 vol% of overall volume of fibres in LLDPE. The effect of replacing glass fibre with LCP fibre on wear is reported. Wear loss increased with the applied loads and glass fibre contents in LLDPE. The replacements of glass fibres with LCP fibres improved abrasive wear resistance of composite. The composite containing 20 vol% of glass fibres in LLDPE showed the specific wear rate nearly double to that of LCP fibre reinforced LLDPE. Incorporation of LCP fibre improved wear resistance of glass fibre reinforced LLDPE. Worn surfaces were studied using SEM. Glass fibres were broken in small debris and removed easily whereas LCP fibres yielded to fibrillation during abrasive action. The overall wear rate was governed by the composition and test conditions.

Keywords. Hybrid composites; abrasive wear; LLDPE; LCP fibre; glass fibre.

1. Introduction

High-toughness, dimensional stability, mouldability, environmental resistance, recyclability, fast production cycle etc are a few advantages of thermoplastic–matrix–composites over the thermosetting ones (Gayle 1998; Ma 1998). The semi-crystalline polyolefins are often used as matrix material for composites due to their high chemical resistance, ease of fabrication, high impact strength and low temperature toughness coupled with low cost, but are also characterized by a low heat deflection temperature (Davies and Cantwell 1994; Thomason and Vlug 1997). To overcome this problem, glass-fibres are used as one of the important reinforcing components in stampable thermoplastic in various forms such as chopped fibre, long fibre and woven mat etc. Addition of short glass fibres to a polymer matrix generally leads to significant improvement in modulus and dimensional stability (Deopura *et al* 1993; Ulrych *et al* 1993; Joshi *et al* 1994; Bijsterbosch and Gaymans 1995; Karger 1995; Kitano *et al* 2000), at the cost of reduction in impact strength of a tough polymer such as LLDPE (Kannan and Misra 1994). The toughness of glass fibre reinforced LLDPE could be improved by reinforcing it with high strength fibres such as Kevlar, LCP etc. A desired combination of high tensile modulus and toughness is possible by using a hybrid of glass fibre and tough organic fibres such as Kevlar, LCP etc in the composites (Hashmi *et al* 2001, 2003). The reinforcement by LCP fibres or their hybrids had shown significant increase in storage modulus (E') of LLDPE (Hashmi *et al* 2001). E' of glass fibre reinforced LLDPE is higher than Kevlar reinforced or LCP fibre reinforced LLDPE. The E' of glass reinforced LLDPE decreases with increased temperature. Once alfa transition of LLDPE is passed, E' of glass fibre reinforced LLDPE diminishes beyond to that of Kevlar fibre reinforced LLDPE. The mechanical, morphological, dynamic mechanical and rheological studies of these hybrid composites have already been reported (Chand *et al* 2001; Hashmi *et al* 2001, 2002a, b, 2003; Kitano *et al* 2001) but nothing is reported on exploration of tribo potential of these composites. On the other hand, extensive data is available on the wear of composites reinforced with short glass fibres, carbon fibres and aramid fibres (Lancaster 1972; Voss and Friedrich 1987; Bahadur and Zheng 1990; Bahadur 1991; Bijwe *et al* 2002). Short glass fibres reinforcement in PEEK deteriorates abrasive wear properties (Voss and Friedrich 1987), whereas aramid fibres exhibit significant improvement (Bijwe *et al* 2002) in abrasive wear performance of poly-etherimide.

Wear behaviour of composites is fairly complex because the individual components have their unique response towards friction and wear. The extension and distribution of individual components and their inter-phase are also

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important in determining the performance of whole system (Santner and Czichos 1989). For reducing wear rate by material engineering instead by improving mechanical design, it is important to evaluate and compare wear of new materials. In the present study, abrasive wear properties of LCP and glass fibre reinforced LLDPE and hybrids of these two fibres reinforced LLDPE have been evaluated under different loading conditions. Effects of change in hybrid composition on wear of fibre reinforced LLDPE have been observed and results are discussed with the help of composition and worn surface studies here.

2. Experimental

LLDPE powder type-A 220 J, of Japan Polyolefins Co. Ltd., Japan, having density, –0·923 g/cc, melt flow index, 20 g/10 min was used as a matrix material. Reinforcing fibres for hybrid composite preparation were: (a) glass fibres from "Nihon glass fibre", Japan, having density, 2·57 g/cc, initial length, 5 mm, diameter, 13 μm and (b) LCP fibres (made of co-polyester based on 2,6-hydroxy naphtholic acid and *p*-hydroxy benzoic acid, Vectra-A950, Kuraray, Japan) having length, 10 mm, diameter, 18 μm.

As mentioned elsewhere (Hashmi *et al* 2001), the composites were prepared by blending LLDPE powder with fibres and then extruded through an elastic melt extruder. The elastic melt extruder works on the Weissenberg principle (Kataoka 1976). The material was fed directly into the shearing zone, which was built by the rotor and stator. The effective rotor diameter was 14 cm. The temperature of extruder was kept constant at 200°C for all compositions. The extruded material was quenched in water at 12°C and was immediately cut by pelletizer to a 5 mm length. The pellets were dried in an air-circulating oven at 75°C for 12 h. The above process was repeated to achieve better mixing. A weighed amount of pellets was placed in the mold. The material was compressed between the hot plates for 3 min under 5 MPa pressure at 200°C. The mould was then cooled immediately under the same pressure by circulating water at 12°C and sheets of 5 mm thickness were prepared. These sheets were cut to rectangular shape for tests.

Two sets of samples of LLDPE reinforced with 10 and 20 vol.% of fibres were prepared. In both the sets, the composition of LCP and glass fibres was varied as 25, 50, 75 and 100 vol.% of total volume of fibres in composite. The samples were designated as per following scheme.

Volume of LLDPE as matrix (vol.% of glass fibre in total volume of fibres/vol.% of LCP fibre in total volume of fibres).

For example, a composite containing 80 vol.% of LLDPE and total 20 vol.% of fibres having within fibre percentage the 25 vol.% of glass fibres and 75 vol.% of LCP fibre would be represented as LL-GF/LCP::80-25/75.

Abrasive wear tests for evaluating abrasion resistance of developed composites were conducted on two-body Suga Abrasion tester model NUS1 (Japan). A rectangular specimen of size $30 \times 40 \times 4$ mm^3 was slid against a rotating wheel on which abrasive paper of 400 grit size was mounted using double sided adhesive tape. The embedded hard silicon carbide particles abraded the composite during the test. Four different loads (1, 3, 5 and 7 N) were applied. Weight losses were measured after each set of 100 cycles. Fresh paper of same grit for each sample at each load was used. Abrasive wear rate (W) was calculated from mass loss measurements by using the following relation

$$W = w/(dr),$$

where r is the density of composite, w the mass loss and d the distance abraded. The specific wear rate (K_0) or normalized wear rate was determined from the following equation:

$$K_0 = W/L,$$

where L is load on the sample.

Worn surfaces were studied using scanning electron microscope (model JSM 5600, JEOL, Japan) after gold coating of samples.

3. Results and discussion

3.1 *Wear behaviour*

Figure 1 shows plots between wear rate and applied load for compositions having 20 vol.% of fibres in LLDPE, including glass fibre reinforced LLDPE, LCP fibre reinforced LLDPE and various hybrids of glass and LCP fibre reinforced LLDPE. Wear rates increased with the increase

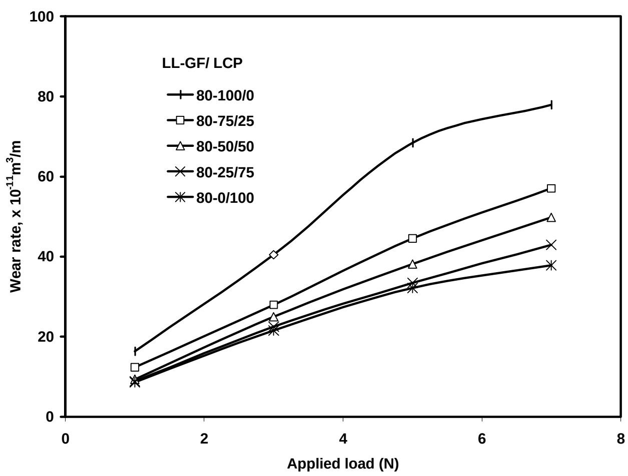

Figure 1. Plots between wear rate and applied load for different composites having 20 vol.% fibres in LLDPE.

in load and volume percent of glass fibres in the composite. Wear rates reduced on replacing glass fibres with LCP fibres in hybrid composite. Maximum wear rate was observed at 7 N load. Slopes of the curves belonging to different compositions varied indicating influence of composition on wear rate. Similarly figure 2 is a plot between wear rate and applied load for compositions having 10 vol.% of fibres in LLDPE. On comparing figures 1 and 2, it was observed that wear rate of samples having 20 vol.% glass fibre in LLDPE was significantly higher as compared to 10 vol.% fibre reinforced LLDPE. Wear rate of all the studied materials increased with applied load that may be an outcome of deeper penetration of abrasive particles in the composite and removal of material therefrom.

A clear separation of various curves from each other was observed in figure 1 contrary to curves shown in figure 2. The curves belonging to 10 vol.% fibres in LLDPE (figure 2) are not clearly separated and different values are overlapping each other. It appears that effects of variation in composition on wear rate were not clearly observed due to low values of wear rates at 10 vol.% fibre-reinforced LLDPE. However, at 20 vol.% fibre-reinforced LLDPE the wear values are sufficiently higher and therefore, effect of variation in composition is distinctly observed and various curves belonging to different composition are separated from each other.

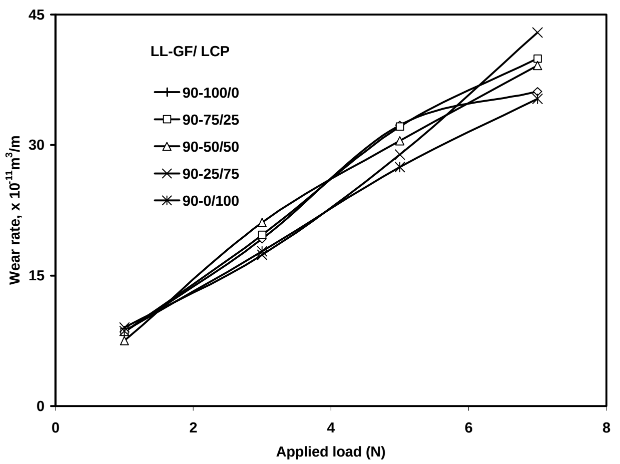

Figure 2. Plots between wear rate and applied load for different composites having 10 vol.% fibres in LLDPE.

Figures 3 and 4 show two sets of data, each one having 10 and 20 vol.% fibre reinforced LLDPE, respectively illustrating the effect of variation of hybrid composition at overall fixed volume percent of fibres in LLDPE at different applied loads. In case of 10 vol.% fibres reinforced LLDPE, no significant change in wear rate with a change in fibre composition was observed as shown in figure 3. Nearly parallel lines were observed in this figure signifying the load effect only. Figure 4 is quite different from figure 3, and the composition effect on wear rate was clearly demonstrated here. It is evident that replacements of glass fibres by LCP fibres decreased the wear rate of hybrid composites. The composition ratio of LCP fibre and glass fibre shows a transition from low to high wear rates as indicated by these curves. The difference in wear rate of glass fibre reinforced LLDPE and LCP fibre reinforced LLDPE is significantly high and can be noticed easily at higher applied load as shown in figure 4.

3.2 *Worn surface*

Figure 5 shows micrographs of worn surfaces of samples after abrading at 7 N load. These micrographs represent 10 vol.% fibre reinforced LLDPE. Fibre composition was varied in these three micrographs. Severe damage on worn surfaces was observed. Deep furrows due to micro plough-

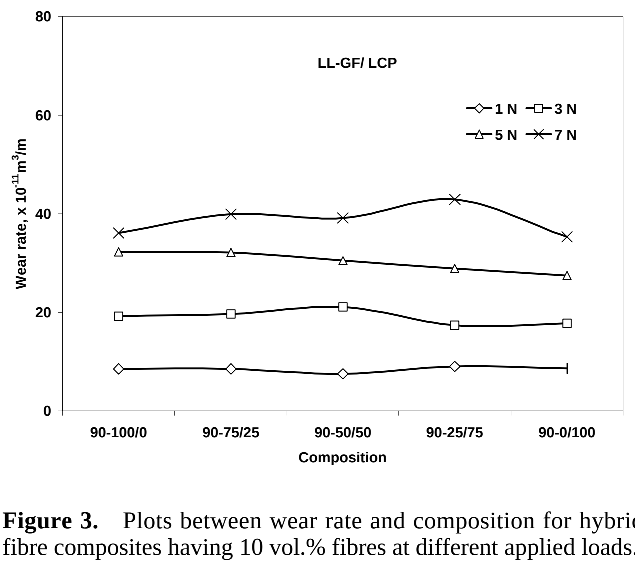

Figure 3. Plots between wear rate and composition for hybrid fibre composites having 10 vol.% fibres at different applied loads.

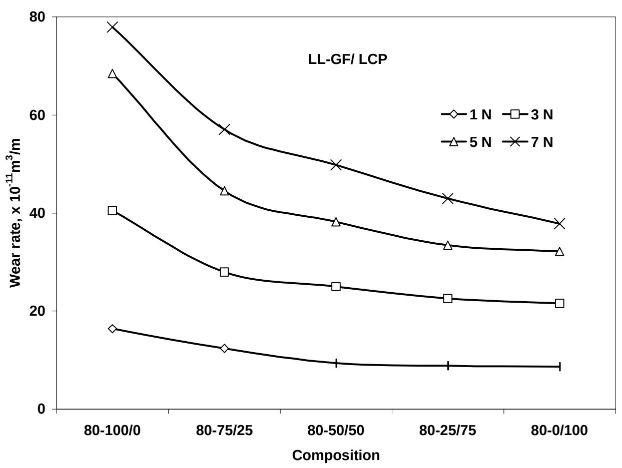

Figure 4. Plots between wear rate and composition for LLDPE and hybrid fibre composites having 20 vol.% fibres at different applied loads.

ing by abrasive grit are evident. Brittle, straight and smooth glass fibres are observed whereas easily deformable LCP fibres are difficult to locate in these micrographs. Elongated and spreading LLDPE matrix is dominating the microstructure. Figure 6 shows micrographs of 20 vol.% fibre reinforced LLDPE worn surface abraded at 7N load. Deep furrows are observed due to abrasive action. Cutting and tearing of matrix is visible. A few glass fibres and LCP fibres are also observed in these micrographs. Glass fibres were broken into small debris on abrasive action whereas LCP fibres show fibrillation with excess abrasion. In both figures 5 and 6, deep furrows due to ploughing action by abrasive grit are evident. LLDPE is a semi-crystalline yet ductile polymer. The failure in matrix occurs after plastic deformation. Cutting action followed by repeated tensile deformation may be the reason of removal of material. Melting point of LLDPE is much lower than that of glass fibre or LCP fibre and there is remote possibility of melting fibres during abrasive action. LLDPE softens and spreads like thin sheet as was observed in the micrographs. Glass and LCP fibre resist the abrasive action and in the process the inter-phase between matrix and fibres are affected. The reinforcement not only offers resistance to abrasive action and thereby increasing temperature but also resists removal of matrix. Glass fibres being brittle are broken easily and get removed in small pieces. LCP fibres are sufficiently long (10 mm) and hence remain with matrix absorbing abrasive stress and yielding fibrillation. Therefore, wear rate does not increase significantly in LCP reinforced LLDPE as compared to all those samples containing glass fibres in any ratio. No evidence was observed related to pulling out or peeling off of LCP fibres from matrix.

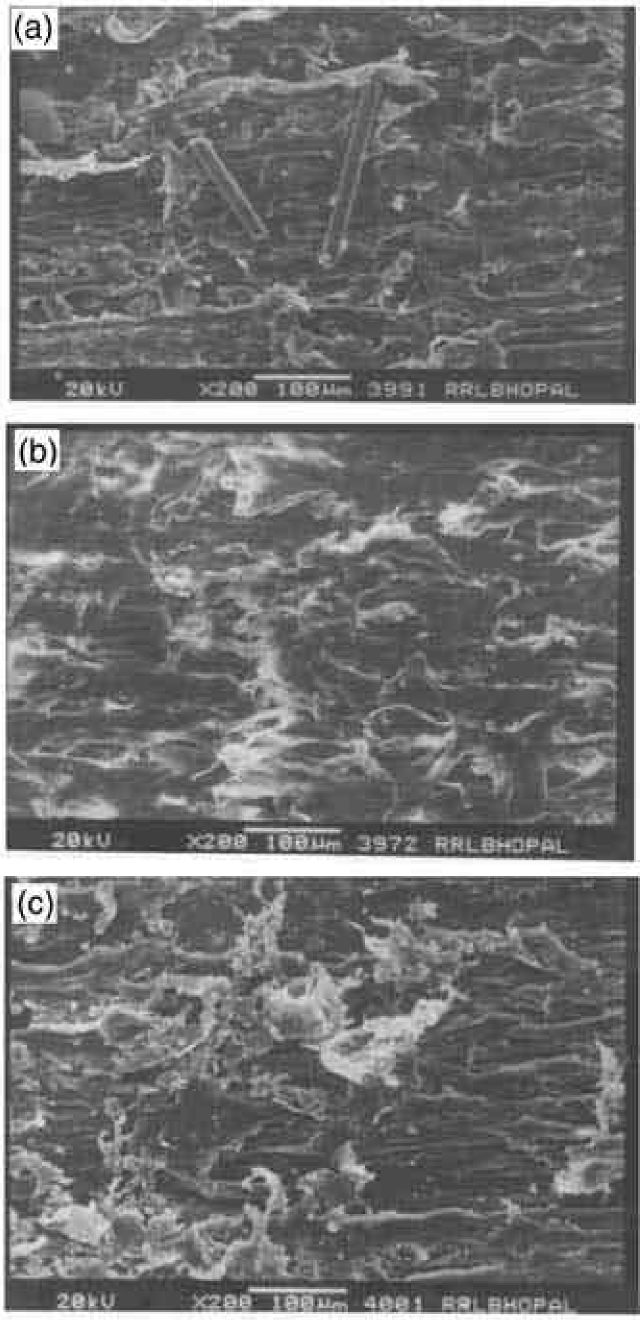

Figure 5. SEM micrographs of worn surfaces of LL-GF/LCP samples: (**a**) 90–75/25, (**b**) 90–50/50 and (**c**) 90–25/75 abraded at 7N load.

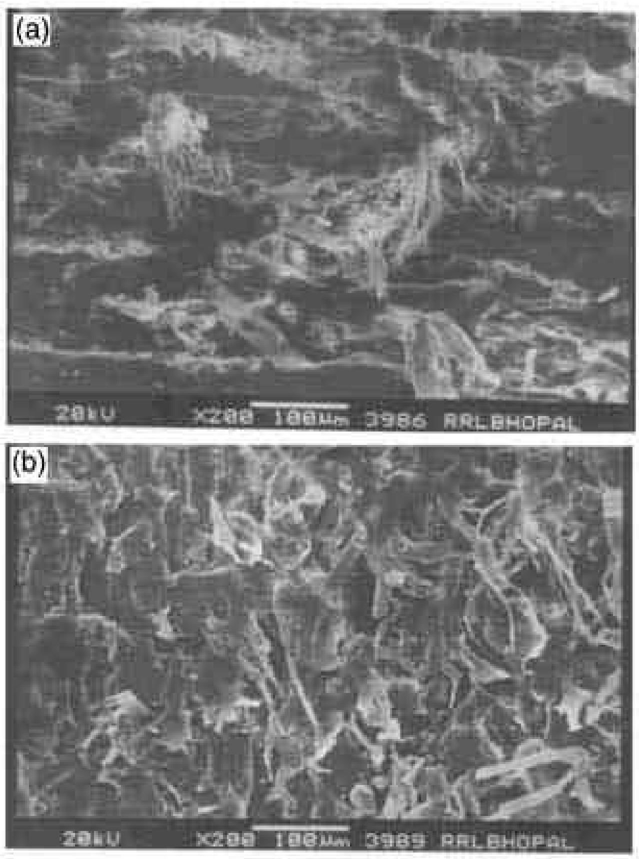

Figure 6. SEM micrographs of worn surfaces of LL-GF/LCP samples: (**a**) 80–50/50 and (**b**) 80–25/75 abraded at 7N load.

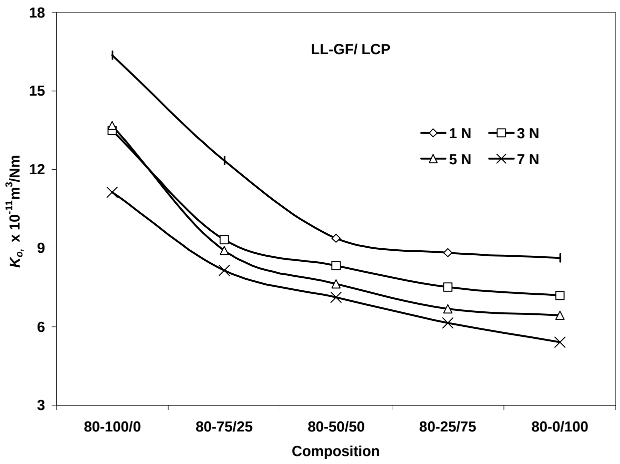

Figure 7. Plots between specific wear rate and composition of fibres in a composite having 20 vol.% fibres.

During abrasion at low loads, the dominant wear mechanisms are micro-ploughing and micro-cutting of matrix. In the present case, fibres are assumed to be randomly distributed, however, due to the process of sample preparation under two hot plates the top and bottom layers of these composites have fibres which are dominantly oriented in a plane (Kitano *et al* 2001; Hashmi *et al* 2003). It may be assumed that a fraction of fibres on composite surface are nearly parallel to abrasive action, another fraction is just about anti-parallel to abrading direction and third fraction is at a certain angle to abrading direction. The fibres in anti-parallel directions to the abrading directions get micro-cracked and micro-cut very easily as compared to parallel fibres (Bijwe *et al* 2002). The stresses developed during shearing of fibre against abrasive grains deteriorate the fibre matrix bonding very effectively and hence pulverized fibre debris is released from composite surface easily. When load is increased the micro cutting and micro cracking process also increase proportionally. It is assumed that abrasive wear volume increases with the real area of contact, sliding distance and the probability of debris particle formation. The probability of debris particle formation is related to ratio between the actual stress and the rupture stress for a given polymer. The wear volume is, therefore, a function of normal load, friction coefficient, sliding distance and rupture stress (Czichos 1983). Glass fibre and LCP fibre reinforcement further complicated the wear mechanism. LCP fibres are inherently very tough and bend without breaking. These fibres also lack notch sensitivity and therefore, offer excellent wear resistance. In contrast, glass fibres are brittle and break easily into small abrasive particles. These particles damage the mating surface as well as matrix material. The overall abrasive wear of composite is, therefore, governed by above mentioned factors and their combination at a certain condition and material composition.

Addition of brittle glass fibre in a tough matrix LLDPE reduced wear resistance of matrix. During abrasion by SiC particles the brittle glass fibres were broken on abrasive action and removed easily from the LLDPE. LCP fibres, on the other hand, were longer and tougher as compared to glass fibres and improved the wear resistance of composite while replacing glass fibres.

3.3 *Specific wear rate*

The performance of material in tribologically sensitive applications may be quantified by evaluating specific wear rate. The specific wear rate is defined as normalized wear rate and can be obtained by dividing wear rate by applied load. In other words, specific wear rate is volume loss per unit length per unit force. Normalized wear rate, K_0, against nominal contact pressure for materials sliding under unlubricated conditions against steel at low contact-pressure range is roughly constant (Ashby 1992), however, it increases rapidly at high contact pressure that reaches to a limiting value beyond which catastrophic failure occurs. Figure 7 shows plots between specific wear rate and composition of hybrid composites having 20 vol.% of fibres in LLDPE at different applied loads. Glass fibre reinforced LLDPE shows higher K_0 values to that of LCP fibre reinforced LLDPE at different loads. All the reinforced LLDPE samples showed a decrease in specific wear rate with increased applied load which indicates that increase in wear rate with applied load is less sensitive to applied load. Had it been highly sensitive to applied load, the K_0 should have shown the increasing trend. The increasing trend of K_0 with load is an indicator of pressure induced materials deterioration/failure. In the present case, within the range of experiments LCP reinforced LLDPE showed nearly double the wear resistance than that of glass fibre reinforced LLDPE. Moreover, the reinforced material exhibited comparatively better performance on normalized applied load basis.

4. Conclusions

Abrasive wear studies for glass fibre, LCP fibre and hybrid fibre reinforced LLDPE concluded as follows:

(I) Abrasive wear rate increased with applied load and glass fibre content in LLDPE. Incorporation of LCP fibre improves wear resistance of glass fibre reinforced LLDPE.
(II) Glass fibres were broken in small debris and removed easily whereas LCP fibres yielded to fibrillation during abrasive action.
(III) LCP fibre reinforced LLDPE showed nearly double the specific wear resistance than that of glass fibre reinforced LLDPE.

(IV) The reinforced LLDPE samples showed a decrease in specific wear rate with increased applied load.

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