

Effect of water absorption on erosive wear behaviour of polyamides

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Two polyamides (PAs) viz. PA 6 and PA 12 were selected for investigating the influence of water absorption on some physical, mechanical and tribological properties. Erosive wear studies on water treated and untreated samples were carried out at two impact angles viz. 30° and 90°. Tests on tensile strength of untreated and treated polyamides revealed that the water treatment resulted in enhancement for PA12 and reduction for PA 6. Exactly similar trends were reflected in their erosive wear performance also. The water absorption deteriorated the wear performance of PA 6 at both the angles, whereas the erosion wear behaviour of PA 12 improved at both the angles due to water absorption. The improvement was more significant at the angle of 30° rather than 90°. Scanning electron microscopic (SEM) investigations were done to study the topography of worn surfaces and to understand the wear mechanisms. © 2002 Kluwer Academic Publishers

1. Introduction

Polymers and composites are extensively used in tribo-applications in various wear situations such as adhesive, abrasive, erosive, reciprocating etc. because of their special features such as high specific strength, resistance to wear, corrosion, impact, radiation and chemicals, quiet operation due to vibration absorption etc [1]. In particular, these are used in applications such as helicopter rotors, radomes etc. where the components continuously undergo impact of particles like dust, sand, splinters of materials, slurry of solid particles etc [2]. Though the resistance to erosion is a key factor for the material selection, little is reported on the various influencing factors on erosive wear behaviour of the polymers and composites especially in the background of a vast literature reported on adhesive and abrasive wear behaviour [3]. In particular, though polyamides (PAs) and composites are known as very good tribomaterials because of quite a good combination of mechanical, tribological and thermal properties along with a moderate cost, less efforts have been focussed on investigating erosion wear resistance of PAs [2–6]. In fact, PAs form a class of polymers with two types viz. condensation and addition. By varying the methylene to amide ratio (CH₂/CONH), a series of PAs has been synthesised. This ratio along with other properties such as molecular weight, glass transition temperature, density,

crystallinity etc. controls the various properties of PAs [7]. In fact, the effect of this ratio on abrasive wear behaviour has been recently studied in the authors' laboratory [8] in the case of ten PAs. Erosive wear behaviour of seven such PAs has also been studied and shown interesting correlation between erosive wear rate and the brittleness index [9].

The sensitivity of PAs towards moisture/water has always been the matter of concern for the polymer scientists. The problems associated with not only the changes in mechanical properties but the dimensional clearances as a result of swelling also emerge because of water absorption. The presence of amide groups (—NHCO—) in the PA backbone favours the water absorption by forming the hydrogen bonding with water molecules owing to its higher polarity [10]. This water uptake depends on the amide group concentration in the molecular chain. Since the mechanical properties are directly related to the tribological properties, it is expected that the water absorption should affect the tribological properties also. Interestingly, very few efforts have been focussed to study this effect in the case of various polyamides. Furukawa *et al.* [11] for example, reported that the static and kinetic friction coefficients and the sliding wear rate of PA 6 decreased with the increasing contents of absorbed water. Stuart and Briscoe [12] observed the increase in friction coefficient of PA 66 at various

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TABLE I Details of the materials selected and their mechanical properties

Property	PA 6 -[CO(CH ₂) ₅ -NH]-		PA 12 -[CO(CH ₂) ₁₁ -NH]-	
	Untreated	Treated	Untreated	Treated
Density (kg/m ³)	1120	1130	1000	1000
Tensile strength (MPa)	55.4	47.9	47.0	51.0
Tensile elongation (%)	385	341	446	485
Hardness (Shore D value)	74	72	76	78
Izod impact strength (kg-m/mm)	4.9	74.8	10.8	11.8

loads due to water absorption. This enhancement in friction was thought to be due to increase in the real area of contact because of the extensive plasticisation of the polyamide surface and which was confirmed by the reduction in hardness. Clarke and Allen [13] found that the extensive water absorption by MoS₂ filled PA 6 composite resulted in the swelling of the composite, which in turn affected the mechanical properties and hence, led to higher wear rate. Interestingly, no literature reporting on such behaviour on erosive wear performance of PAs could be available. Hence it was proposed to carry out such investigations on PAs in erosive wear mode. The results of the studies on two PAs viz. PA 6 and PA 12 are reported in this paper.

2. Experimental

2.1. Materials selected

Details of the selected polyamides along with their structures and properties are shown in Table I. These were procured in the form of granules, which were then dried in a vacuum oven at 80°C for 12 hours prior to compression moulding. Sheets (200 mm × 200 mm × 6 mm) of these PA 6 and PA 12 were compression moulded by heating the granular materials placed in the mould at 270 and 215°C respectively for an hour. The pressure (5 MPa) was then applied for one hour with intermittent bumpings to release the trapped moisture, if any. The mould was cooled to ambient temperature under pressure. Test samples (30 mm × 30 mm × 6 mm) were cut from these sheets for erosive wear studies. Samples for studying mechanical properties as per ASTM standards were prepared by injection moulding.

2.2. Water treatment

Both the injection moulded and compression moulded samples were weighed prior to water treatment and then immersed in water for various times. Prior to weighing, they were blotted with tissue paper to remove water on the surface. The samples were reweighed after regular intervals of 2 hours to find out the amount of water absorption as a function of time. Specific gravity of the samples was measured on a weighing balance (with a precision of 0.0001 g) attached with specific gravity kit.

2.3. Erosive wear studies

The solid particle erosion experiments were carried out on the erosion test rig discussed elsewhere [9] using silica sand (90–180 μm size) as the impinging particles. The test rig consisted of an air compressor, air drying unit, a conveyor belt-type particle feeder and air particle mixing and accelerating chamber. The dried and

compressed air was allowed to mix with the silica sand, which had been fed constantly by the conveyor-belt type feeder in the mixing chamber. These fluidized silica sand particles were accelerated by passing through a tungsten carbide converging nozzle of 6 mm diameter to bombard the polymer target (25 mm × 25 mm × 6 mm) held at a specific angle with respect to the flow of the impinging particles. The distance between the target material and the nozzle was approximately 10 mm. The following were the operating parameters.

Dose of erodent	80 g
Flux rate	4 g/min
Duration of erosion	20 min
Impact angles	30 and 90°
Impinging velocity of particles	80 m/s

The impact velocity of the erodent particles was determined experimentally using the rotating disc method [14]. Erosive wear studies were done at selected impinging angles (30 and 90°). Scanning electron microscopic (SEM) studies on eroded surfaces (after silver sputtering) were carried out on Jeol JSM-840 scanning electron microscope to investigate the erosion mechanism.

3. Results and discussion

3.1. Erosive wear studies

Results of water absorption by PAs for various times is shown in Fig. 1. Though the curve showed saturation effect after twelve hours, the time for immersion was taken as 24 hours [12]. Influence of water treatment on various physical and mechanical properties of selected PAs is shown in Table I. Erosive wear of untreated and water treated polyamides as a function of the number of 80 g doses of impinged erodent particles with the feed

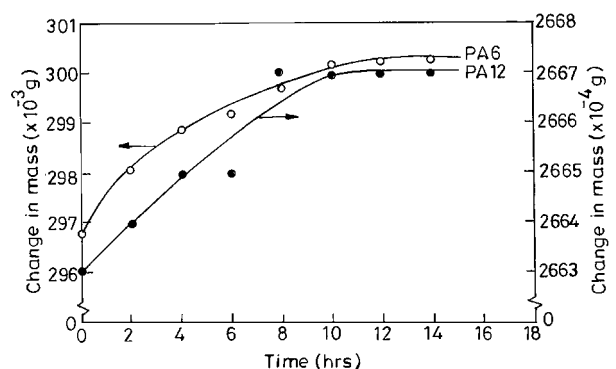


Figure 1 Water absorption as a function of time for PA 6 and PA 12.

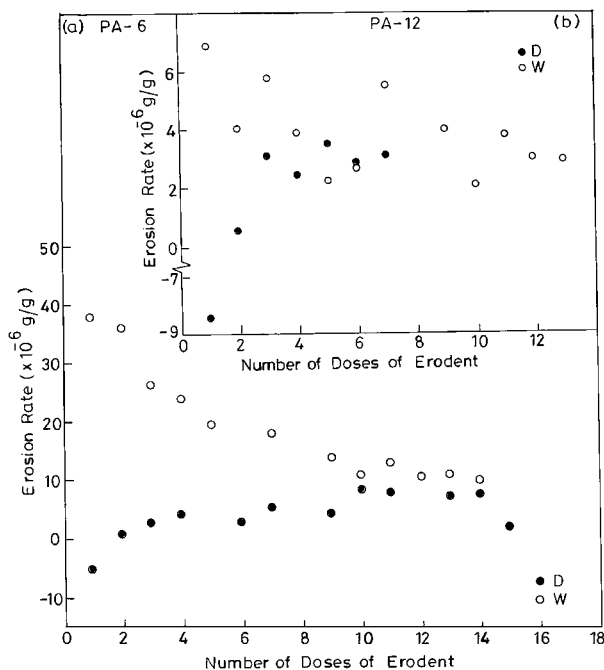


Figure 2 Erosion rate as a function of the number of 80 g doses of erodent at an impact angle 90° , (W = water treated and D = untreated) (a) for PA 6 and (b) for PA 12.

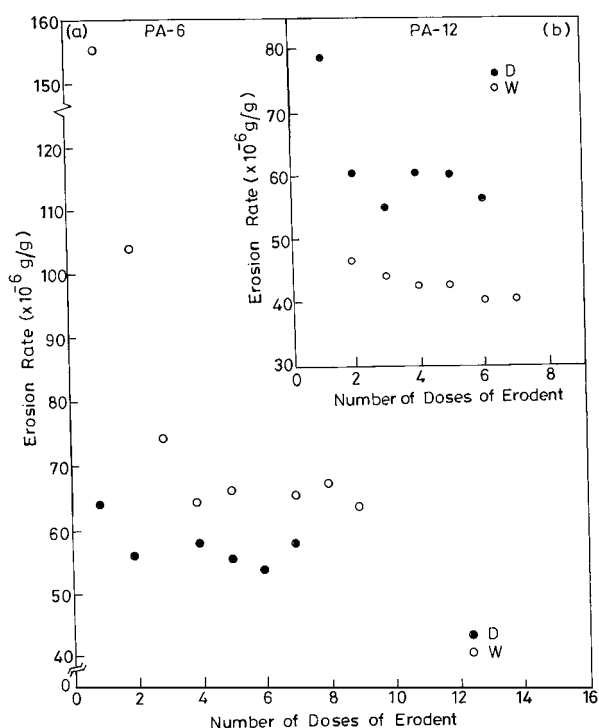


Figure 3 Erosion rate as a function of the number of 80 g dose of erodent at an impact angle 30° , (W = water treated and D = untreated) (a) for PA 6 and (b) for PA 12.

rate of 4 g/min at two impinging angles viz. 90° and 30° is shown in Figs 2 and 3 respectively. The possible form of the associated water in PA 6 is shown in Fig. 4 while SEM studies are collected in the form of micrographs in Figs 5 and 6.

Following are the salient observations emerged from the work.

- Water absorption capacity of PA 6 was significantly higher than that of PA 12. (PA 6 absorbed 1.13% while PA 12 absorbed 0.15%)

- Water absorption enhanced the tensile strength of PA 12 whereas it caused a decrease in the case of PA 6. Elongation to break on the other hand, decreased for PA 6 and increased for PA 12.
- Water treatment decreased the hardness of PA 6 while in the case of PA 12 the reverse trend was observed.
- Significant improvement in the Izod impact strength was observed for PA 6, but not for PA 12.
- During normal impact, the central part of the crater turned black, the intensity being maximum in the centre. Such blackening of the surface is reported due to thermal degradation of polymer [15].
- At normal impact initially weight gain was observed for both the untreated polyamides due to initial embedment of sand particles.
- In the case of untreated samples, erosive wear (steady state) behaviour of PA 12 was little better than that of PA 6 at both the impact angles.
- Wear loss was significantly higher (for PA 6, approximately 6 times and for PA 12 approximately 18 times) at 30° impact angle as compared to 90° .
- Water treatment deteriorated the steady state wear behaviour of PA 6 at both the impact angles, while for PA 12 beneficial effect was seen at both the impact angles, though it was less significant at 90° .
- For both the types of PAs the difference between the steady state erosion rates of untreated and water treated samples was minimum at normal impact whereas at an oblique impact the difference was much higher.

It was clear from the study that water absorption had pronounced effect on physical, mechanical and tribological properties of the selected PAs. A lot is reported in the literature on the influence of such treatment on various physical and mechanical properties of polymers and composites [16–25]. This is mainly about disrupting the existing inter chain hydrogen bonding [16, 17], structural changes in the crystalline domains [18], induced secondary crystallisation [19] due to replacing original hydrogen bonding by the new one with water [6, 7, 10], plasticisation [20] increasing the order of monoclinic lattice and changes in the sign of residual stresses [21–23]. Absorption of water resulted in changes in various properties such as, reduction in tensile strength, stiffness, resistance to creep, insulation and dimensional stability for PA6 [18], hardness for PA 6 [16], reduction in yield stress and increase in toughness and impact strength for PA6 [7], decrease in tensile stress, modulus, flexural strength and modulus but increase in tensile elongation for EPDM rubber modified PA66 [25].

The exact nature of association of water with the PAs and the mechanisms controlling the properties of PAs, however, are not yet clear. While discussing the effect of water uptake on various properties of polyamides, PA 6 in particular, Song and Ehrenstein [10] reported that the uptake is caused by the polar amide groups having affinity for water. While discussing two possibilities i.e. hydrogen bonding and self-association (Fig. 4), the authors claimed that while diffusing into the PA

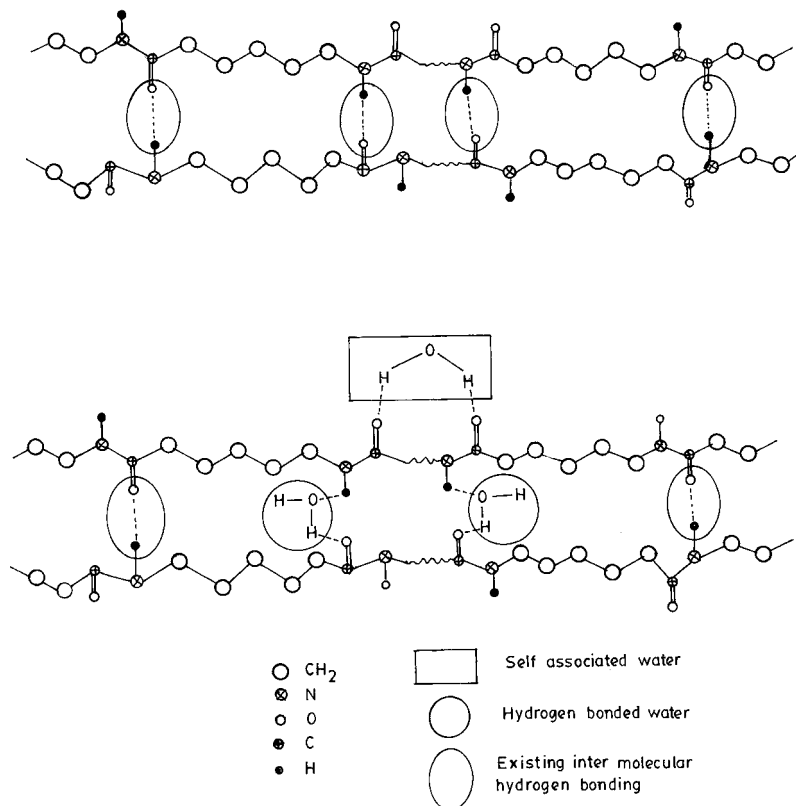


Figure 4 Probable association of water molecules with PA 6 [10].

surface, water molecule loosen the existing hydrogen bonds and form its own hydrogen bonds with amide groups. This weakens the intermolecular forces in the PA and in particular, mobilises those molecular segments, which are not fixed in crystallites. This increased flexibility of molecular segments reduces the flow temperature for the amorphous region. Thus this softening effect emerges more prominently in those polyamides which have high density of amide group and higher extent of amorphous region. This is why PA 6 absorbs more water than PA 12. The processing conditions affect the crystallisation and hence, water absorption. The present observations are similar. As seen from Table I, all properties except impact strength deteriorated due to water absorption.

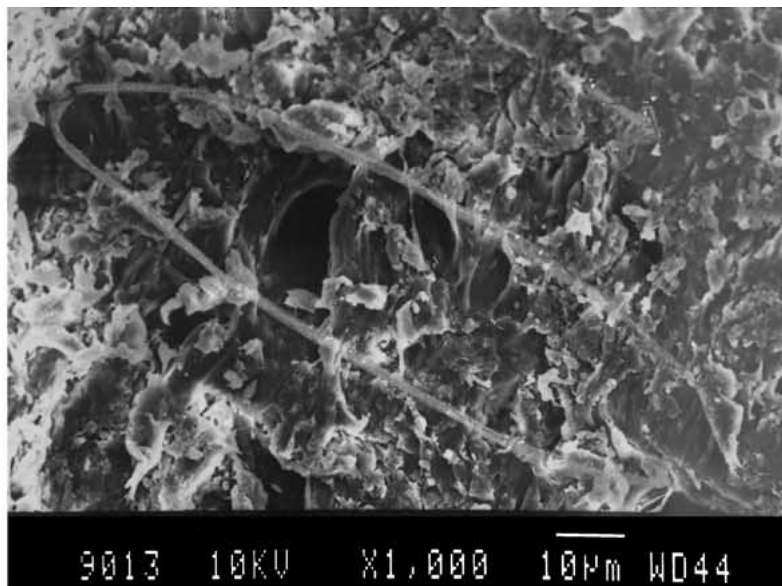
Thus the literature highlights clearly the role of water absorption in the case of PA 6. The detailed mechanism of water absorption on PA 12 could not be available in the literature. As per available information [10] PA 12 cannot have loosely bound water, which acts as plasticiser and which is responsible for the increase in impact properties and decrease in other mechanical properties. In the present investigations, water absorption led to increase in almost all the mechanical properties of PA 12. The erosive wear behaviour of water treated PA 12 showed significant improvement at an oblique angle of 30° and PA 6 showed significant deterioration in the identical conditions, which could be analysed from the changes in the mechanical properties.

3.2. Studies on worn surfaces with scanning electron microscopy

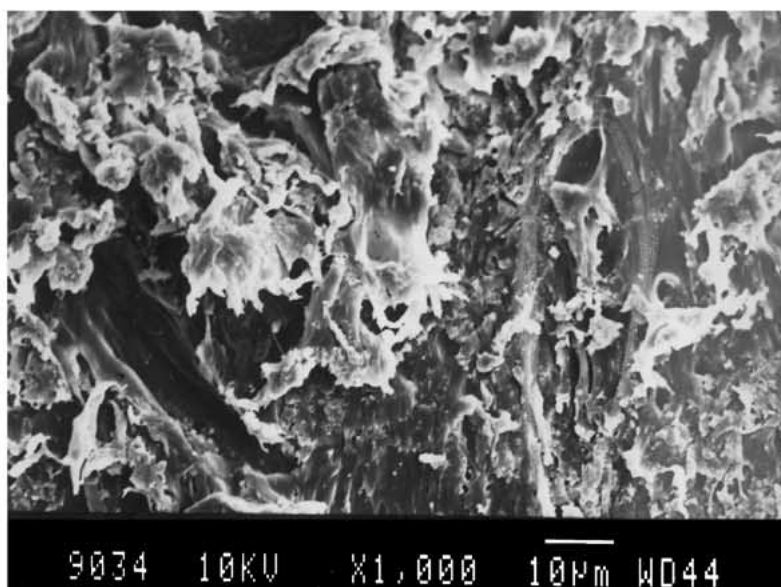
PA 12 has shown significantly better tribological and mechanical strength behaviour due to water treatment and this reflected in the appearance of worn surfaces

also. Micrographs 5a and b are for eroded surfaces of PA 12 (steady state behaviour at 30° impact angle) without and with water treatment respectively. The most prominent feature from the micrograph 5b is the fibrillation of PA 12 due to water absorption (water treatment has increased the elongation to break). This tendency was observed only at 30° impact angle. Micrographs 5a and c compare the difference between the topography of the eroded surfaces (untreated) at 30° and 90° impact angles respectively. At 90°, the surface is full with a network of fine microcracks intersecting at various points and confirming brittle fracture of the material. Such intersections of cracks are responsible for generating wear debris. While in the case of 30° erosion (micrograph 5a, marked portion along the travel direction of the sand particles after impacting), the sand particles appear to show an additional type of wear mechanism. Depending on the resilience of the material and the angle of impact, the sand particles tend to rebound from the central portion of impact [26]. The extent of this re-bounce is a function of the material itself, the angle of impact and the energy carried during the impact. They make secondary impacts on the surface with significantly low energy. During this process of ductile erosion, they form ripples or ridges as marked in the micrograph 5a. For normal impact, such behaviour was not observed.

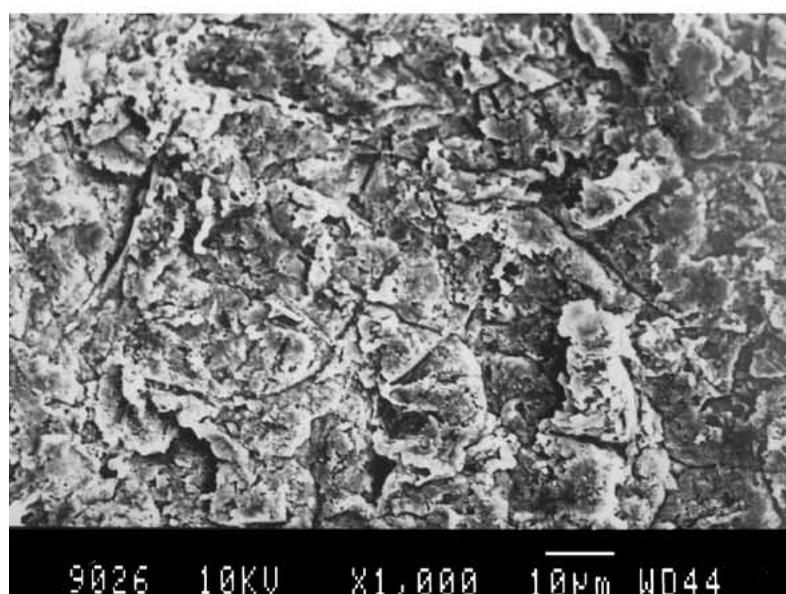
Fig. 6 is for the micrographs showing eroded surfaces of PA 6 at two impact angles. Micrographs 6a and b are for eroded surfaces at normal impact. Micrograph 6a is for an untreated sample while micrograph 6b is for a water treated sample. The severe surface damage for the water treated sample can be clearly seen in the form of large and deep crater, deeper cracks and rougher topography. Micrographs 6a and c are for comparing



(a)

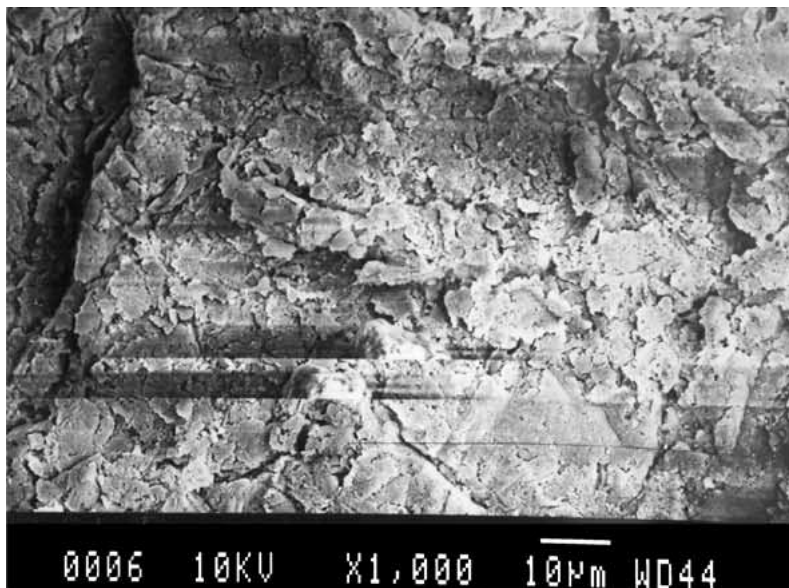


(b)

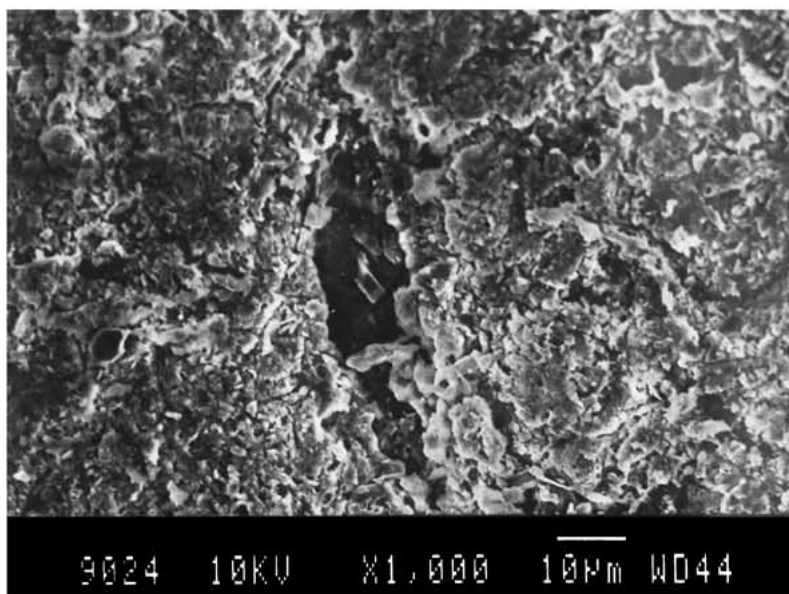


(c)

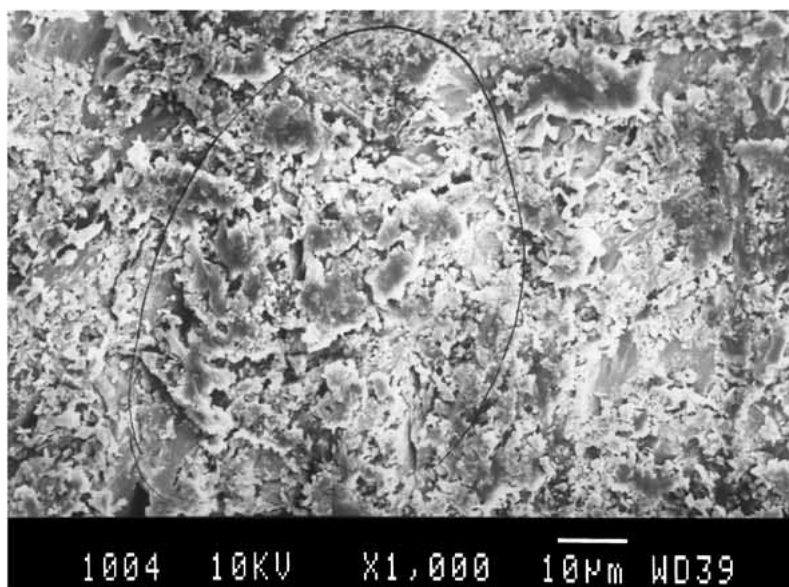
Figure 5 SEM micrographs of eroded surfaces of PA 12. (a) Untreated—eroded at 30° angle surface showing chipping off of materials from the impact zone. (b) Water treated—eroded at 30° angle surface showing fibrillation to some extent. (c) Untreated—eroded at 90° angle showing network of microcracks.



(a)



(b)



(c)

Figure 6 SEM micrographs of eroded surfaces of PA 6. (a) Untreated—(at 90° impact angle) showing network of microcracks. (b) Water treated—(at 90° impact angle) showing large cavity, deep cracks and rough topography of the impact zone. (c) Untreated—(at 30° impact angle) showing formation of patches due to repeated bouncing of particles.

the difference between the topography of the eroded (untreated) surfaces at 90° and 30° impact angles respectively. At 90°, the surface is full with a network of fine microcracks while at oblique impact the central portion of the surface shows the evidence of bouncing of the particles as discussed in the case of PA 12.

4. Conclusions

It was concluded that in the case of PA 6 and PA 12, erosive wear performance and mechanical properties were influenced by water absorption. The deterioration in strength properties led to deterioration in erosive wear performance. In the case of PA 12 water treatment, increase in strength properties and hardness led to improvement in erosive wear performance. The exact role of water in this case, however, was not clear.

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