Effect of organoclay addition on the two-body abrasive wear characteristics of polyamide 6 nanocomposites

G. Srinath · R. Gnanamoorthy

Abstract Polymer clay nanocomposites (PCN) exhibit improved mechanical properties due to nanolevel dispersion of clay in the polymer matrix. They also exhibit good tribological performance under dry sliding conditions. Abrasive wear behaviour of these materials would be different from dry sliding behaviour as the mechanisms of the both are entirely different. Hence the abrasive wear behaviour of these materials needs to be investigated. The abrasive wear characteristics of polyamide 6 nanocomposites, with 1, 3 and 5% (wt.) clay prepared by melt intercalation technique, under two-body abrasive wear conditions have been reported. Abrasive wear tests were conducted using a pin-on-disc tribometer containing an abrasive counterface. All the polyamide nanocomposites investigated exhibited a low abrasive wear resistance compared with pristine Nylon. The wear performance of the nanocomposites was correlated with the mechanical properties. Dominant ploughing and cutting wear were observed in polymer clay nanocomposites. The amount of clay present alters the wear mechanism.

Introduction

Polymer nanocomposites are a new class of reinforced polymers in which at least one dimension of the reinforcing phase is in the nanometer range [1]. Typical inclusions with at least one dimension in the nanometer range, that produce a commonly termed nanocomposite, are e.g. spherical silica, nanotubes, whiskers, layered silicates etc. [2]. Among the potential precursors to produce nanocomposites, silicate clays like montmorillonite, hectorite, and saponite are widely investigated [1–3]. The silicate clays have a stacked structure of 1 nm thick silicate sheets with a variable basal distance. The polymer molecules may penetrate/diffuse into the galleries and thus increase the clay gallery spacing. The intercalated galleries are finally dispersed or exfoliated into monolayers by shear forces during processing. Dispersion of layers or agglomerated tactoids into discrete monolayers, can be achieved by various methods including melt intercalation. As the layered silicate clays are hydrophilic, it makes them poorly suited for mixing and intercalation with most polymer matrices. Hence they are organically modified through substitution of sodium ions with organic onium ions, to make the clay compatible with the organic matrix [3]. These organically modified clays or organoclays help in better intercalation and exfoliation. Nanolevel dispersion in thermoplastic matrices such as polyamides and polyolefins was reported to improve the tensile properties, barrier properties; resistance to solvent intake; thermal stability and flame retardancy [2]. Hence these materials are given much attention recently and represent an emerging class of specialty plastic compounds [3].

The changes in the mechanical properties such as strength, elongation and modulus of base polymer/composite due to the reinforcements affect the tribological behaviour under dry sliding conditions. Low nanometer silicon nitride filled epoxy composites,

G. Srinath · R. Gnanamoorthy (✉)
Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai 600 036, India
e-mail: gmoorthy@iitm.ac.in

nano-sized SiO_2-filled PEEK and nano-sized ZnO-filled PTFE showed an appreciable improvement in friction and wear characteristics compared to the pristine polymer under dry sliding conditions [4–6]. In the earlier work of the authors, polyamide 6 nanocomposites showed improved friction and wear properties in comparison to the pristine polyamide when tested against a ground stainless steel counterface under dry sliding conditions [7].

Under abrasive conditions these materials behave differently as the mechanisms of adhesive sliding wear and abrasive wear are entirely different. Presence of reinforcements in polymer matrix composites has both detrimental and beneficial effects depending upon the reinforcement and the matrix. Reinforcing polyetherimide (PEI) with glass fibres and polyethersulphone (PES) with carbon fibres resulted in a decrease in the specific wear rate under abrasive mode while wear resistance increased under adhesive conditions compared to neat PEI and PES, respectively [8, 9]. Liu et al. [10] reported that the abrasive wear resistance of ultrahigh molecular weight polyethylene (UHMWPE) improved significantly by reinforcing it with quartz powder. The abrasive wear characteristics of polymer clay nanocomposites are not reported in literature. This paper describes the effect of organoclay content on the abrasive wear behaviour of the polyamide clay nanocomposites. The wear behaviour is correlated with the mechanical properties.

Materials and experimental procedure

Materials

Polyamide nanocomposites with 1, 3 and 5% (wt.) organoclay were prepared by melt mixing polyamide 6 pellets (obtained from GSFC Ltd, India) using a twin-screw extruder. The organoclay (Bentone 105) was obtained from Elementis Specialties, USA. The organoclay used was montmorillonite clay modified with two methyl, two hydrogenated tallow quaternary ammonium chloride. The individual platelet size of the clay ranged from about $0.5 \times 0.5 \times 0.001$ μm to about $0.8 \times 0.8 \times 0.001$ μm while the clay bundles were of the order of about 75 μm [11]. Polyamide 6 granules were preheated at 333 K for 4 h to remove moisture. The specimens for tensile tests (dumbbell shaped with a gauge length of 7.62 mm (ASTM D 638 Type V)) and wear tests were injection moulded using an injection-molding machine at an injection pressure of 125 MPa. All the test specimens are thoroughly dried to remove moisture prior to testing.

Characterisation and tensile test procedure

X-ray diffraction (XRD) studies were carried out on the injection-moulded nanocomposite specimens and the organoclay with Cu K_α radiation at a wavelength of 1.542 nm. Figure 1 shows the X-ray diffraction data of the organoclay and polyamide nanocomposites investigated. The XRD data of organoclay shows a peak at 3.6° corresponding to the gallery spacing of the clay layers. This peak was not detected in the nanocomposites indicating that clay layers are well exfoliated and dispersed in the matrix. Tensile tests were carried out on polyamide and polyamide nanocomposites according to ASTM D 638 [12]. Tests were conducted at a crosshead speed of 2 mm/min in an Instron tensile testing machine at room temperature (305 ± 3 K, RH 57 ± 5%).

Abrasive wear test details

The abrasive wear tests were conducted on a pin-on-disk machine modified to test under abrasive mode (schematically shown in Fig. 2). Grade #80 SiC
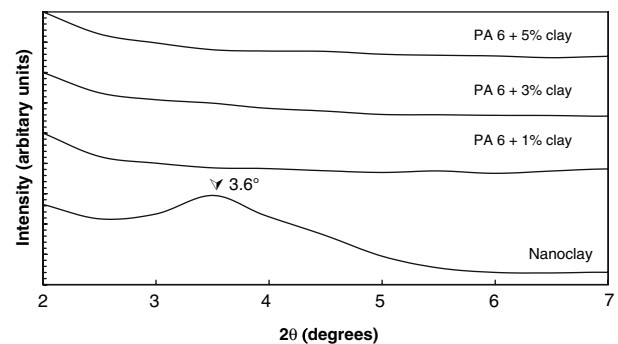
Fig. 1 X-ray diffraction curves of the organoclay and polyamide nanocomposites with peak at 3.6°
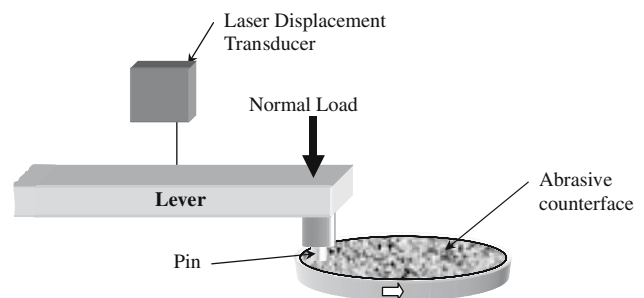
Fig. 2 Schematic of the pin-on-disk tribometer used in abrasive wear studies

waterproof emery paper (with particle size of about 192 μm) was rigidly affixed to the disk using ethyl cyanoacrylate-based adhesive. Injection-moulded cylindrical pin specimens of 7.8 mm in diameter and 20 mm in length were used as test specimens. The friction force was measured by using a force transducer fixed on the loading lever arm. A non-contact laser displacement transducer was used to measure the linear wear. Friction and wear tests were conducted at a normal load of 5 N and at a constant sliding velocity of 0.2 m/s. Tests were conducted under laboratory conditions (305 ± 3 K, RH 57 ± 5%). Friction force and linear wear were measured continuously and data were stored using a personal computer-based data acquisition system.

The test pins were cleaned before testing and the initial mass of pins was measured using an electronic balance with 0.1 mg accuracy. The centre line average surface roughness (R_a) of the pin was measured using a perthometer. Tests were run up to a sliding distance of 180 m. Three tests were conducted under each test condition and the average values of measured friction force, linear wear and mass loss were used for further analysis. The wear loss is quantified by both mass loss, and dimensional loss. The wear volume loss K_m (mm^3) was calculated from mass loss, using Eq. 1

$$K_m = \frac{(m_1 - m_2) \times 1000}{\rho} \tag{1}$$

where m_1 and m_2 are mass (g) of specimen before and after testing and ρ (g/cm^3) density of the material.

The wear by dimension change is measured on-line using the laser displacement transducer, which directly gives the change in the length of the specimen during the wear process. The dimensional changes that occur on the disc surface are negligible. From the change in the length, the wear volume, K_d (mm^3), is calculated using Eq. 2

$$K_d = \frac{\pi d^2 h_0}{4} \tag{2}$$

where d is the diameter of the pin (mm) and h_0 is the change in the length of pin during wear (mm). The

worn-out surfaces of the pin and the wear debris were observed using a scanning electron microscope.

Results and discussion

Tensile behaviour

The nanocomposites show improved tensile properties (Table 1) due to clay dispersion. Addition of 5% clay increases the tensile strength by 14%, while 3% clay addition leads to a 6% increase in the tensile strength. The high aspect ratio of the clay and molecular level interactions due to nanolevel dispersion are responsible for the property enhancement [2, 13, 14]. A detailed discussion of the tensile behaviour is provided elsewhere [7]. Addition of the clay imparts brittleness to the nanocomposite. With increase in the clay addition the ductility or the strain at break drops drastically (Table 1).
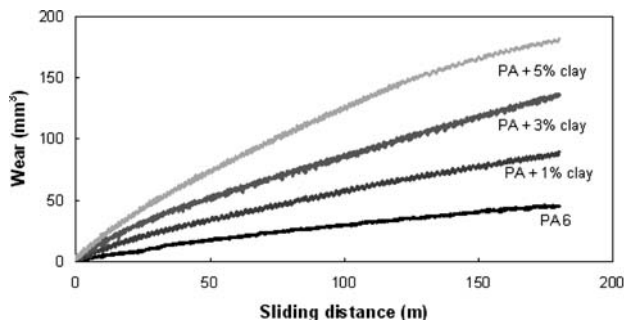
Wear loss and coefficient of friction

The effect of clay addition to polyamide 6 on the wear loss under abrasive conditions is shown in Figs. 3 and 4. Figure 3 shows the effect of amount of clay on wear quantified by the mass loss. Pristine polyamide exhibits the lowest wear loss while the polyamide nanocomposite with 5% clay exhibits the highest wear loss.
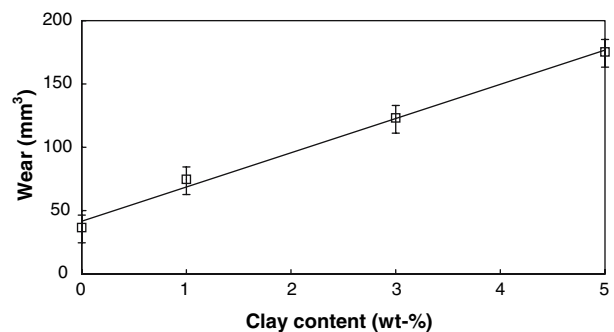
Fig. 3 Effect of clay addition on wear of polyamide and polyamide nanocomposite by mass loss quantification (0% clay represents pure polyamide) at a normal load of 5 N and a sliding distance of 0.2 m/s

Table 1 Tensile stress and strain at break of polyamide and polyamide nanocomposites

Weight percentage of clay in nanocomposite	Tensile stress (MPa)	Tensile stress at break σ_b (MPa)	Strain at break ε_b
0	44.6	44.1	3.84
1	43.6	41.0	2.66
3	47.1	46.9	2.03
5	50.8	50.1	0.95

Fig. 4 Effect of sliding distance on wear by dimension loss of polyamide nanocomposites at a normal load of 5 N and a sliding distance of 0.2 m/s

Addition of clay tends to deteriorate the wear resistance of Nylon. With 5% addition of clay the wear drastically increases by about five times. The increase of the wear with the percentage of clay in the nanocomposite is almost linear. The effect of the sliding distance on the wear quantified by the length change is shown in Fig. 4. The effect of clay addition is apparent as it reduces the wear resistance of Nylon.

Many models have been proposed [15, 16] to explain the wear behaviour of polymers and composites under abrasive conditions. Among those the model proposed by Ratner–Lancaster [17] was found more suitable to correlate the wear behaviour and the mechanical properties of the polymer and polymer composites [8, 18–20]. The model proposes that the energy required to remove a unit volume of the material from the surface is proportional to the bulk fracture energy of the material. According to the Ratner–Lancaster correlation, the wear is inversely proportional to the product of tensile stress at break (σ_b) and strain at break (ε_b). Though the model was proposed to explain the behaviour in single pass condition, the application of the model for the present study was found suitable to explain the behaviour of the clay reinforcement in polyamide nanocomposites. Figure 5 shows the Ratner–Lancaster curve of polyamide nanocomposites. The inverse product of the tensile stress and strain of the polyamide nanocomposite with 5% clay (i.e., the Ratner–Lancaster factor of polyamide nanocomposite with 5% clay) is high and hence the abrasive wear is also high. The product $\sigma_b\varepsilon_b$ represents the energy required to cause tensile rupture for polymers. In the present case, addition of the clay reduces the ductility or the strain to break of the nanocomposite. As the ductility decreases, the energy to rupture the polymer also decreases and thereby increases the material removal from the surface. Addition of clay imparts brittleness to the polymer. With 5% clay addition, the ductility or the strain at break drops almost by a factor of about five. Hence, the decrease in the ductility of the nanocomposite due to clay addition causes the increase in the abrasive wear of polyamide nanocomposites.

Due to the multipass testing procedure followed in the current studies, i.e., the passage of the pin over the same wear track, the wear debris formed accumulates between the spaces between the abrasive grits, termed as clogging of the abrasive grits [21, 22]. Figure 6 shows the clogging of the abrasive grits with wear debris of polyamide with 5% clay. Clogging of the abrasive grits has a dominant effect on the wear rate of polyamide and nanocomposites. Figure 7 shows the effect of the sliding distance on the wear rate (volume loss per unit sliding distance.). The data presented are obtained by differentiating, with respect to the sliding distance, the wear loss-sliding distance curve (Fig. 4) at various

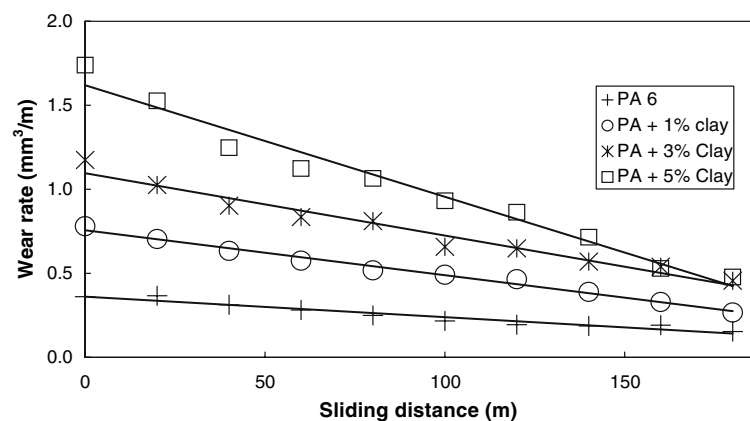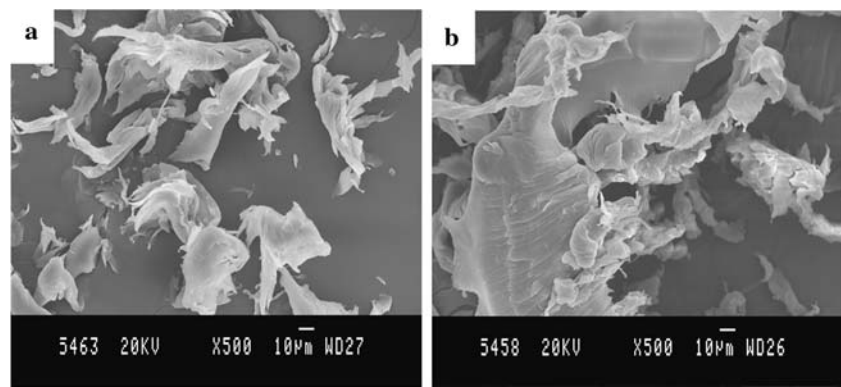**Fig. 5** Ratner–Lancaster factor of polyamide nanocomposites
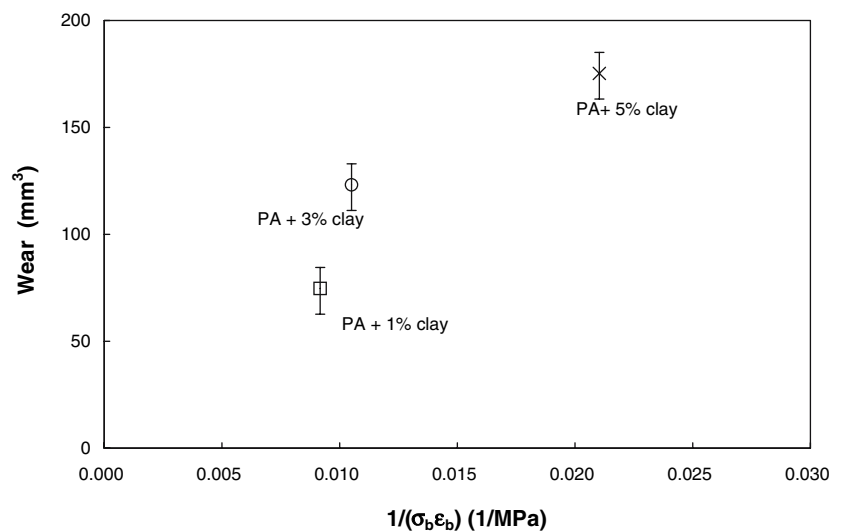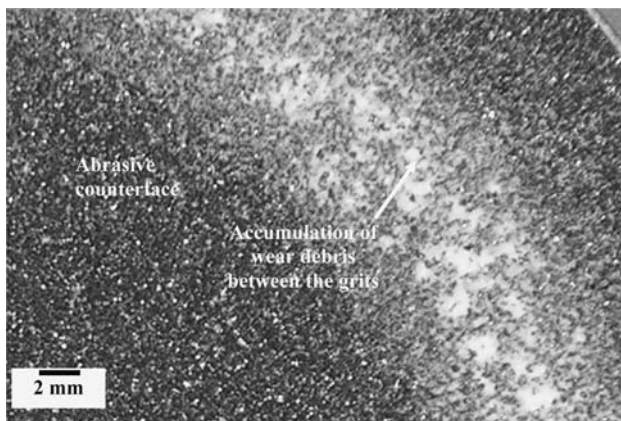
Fig. 6 Clogging of the abrasive grits by polyamide nanocomposite with 5% clay

sliding distances. The wear rate of all the materials tested decreases with sliding distance. Initially the wear rate is high due to the presence of fresh abrasive medium. Wear rates tend to decrease with sliding distance due to the progressive clogging of the abrasive grits by wear debris. Addition of hard clay particles also affects the rate of decrease in the wear rate.

Pristine polyamide shows the lowest decrease in the wear rate while polyamide with 5% clay shows a steep fall of the wear rate. However, the overall wear rates of the clay-filled materials are higher than that of unfilled Nylon. The size of the wear debris generated in polyamide nanocomposite with 5% clay is less (Fig. 8a) than that generated in pristine polyamide (Fig. 8b). The fine debris more effectively clogs the abrasive grits and results in the rapid decrease in wear rate compared to other materials.

The coefficient of friction under abrasive conditions depends on the materials in contact. Figure 9 shows the variation of the coefficient of friction during sliding. The initial coefficient of friction at the beginning of test is nearly the same for all the materials investigated. As the sliding distance increases, polyamide nanocomposite with 5% clay shows a least coefficient of friction due to efficient clogging of the grits by the wear debris. Nanocomposites with 1 and 3% clay exhibited a less steady state coefficient of friction compared with the pristine Nylon. The accumulation of the wear debris between the abrasive grits is not uniform and it depends on the size and amount of the wear debris produced during sliding. Under dry sliding conditions

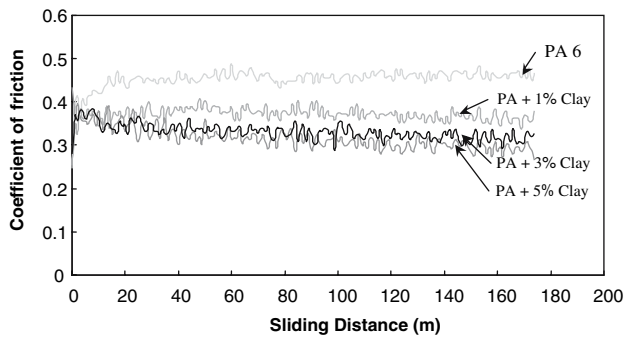**Fig. 7** Effect of sliding distance on wear rate of polyamide and polyamide nanocomposites

Fig. 8 Abrasive wear debris morphology generated in (**a**) polyamide nanocomposite with 5% clay and (**b**) pristine polyamide
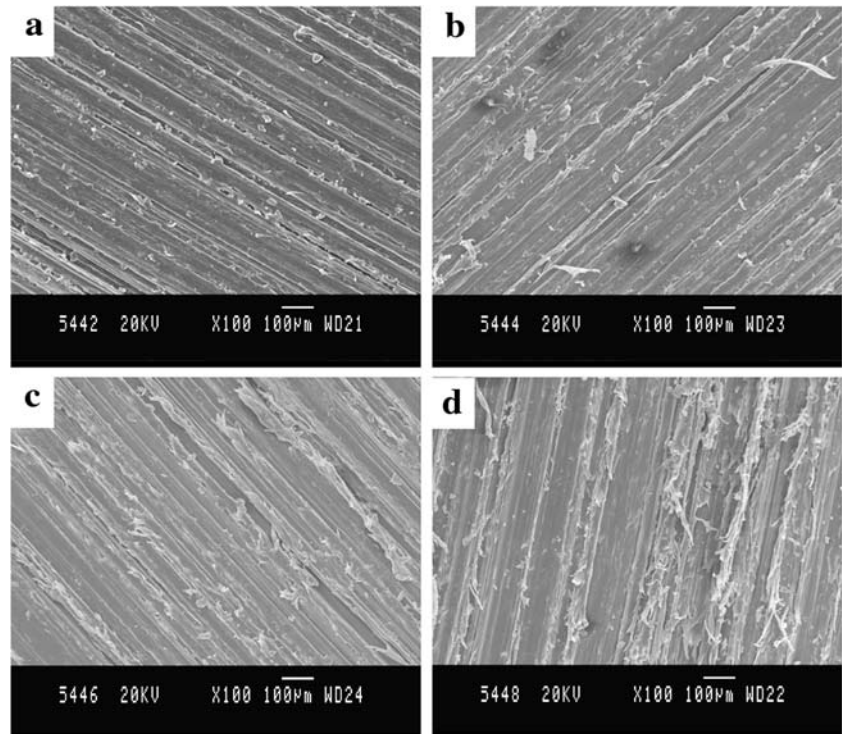
Fig. 9 Variation of coefficient of friction of polyamide and polyamide nanocomposites under abrasive conditions during sliding for test materials at a normal load of 5 N and a sliding distance of 0.2 m/s

when sliding against stainless steel, the polyamide nanocomposite with 5% clay showed a decrease in the coefficient of friction compared to pristine polyamide [7]. The coefficient of friction reported is lower than that under the abrasive conditions [7].
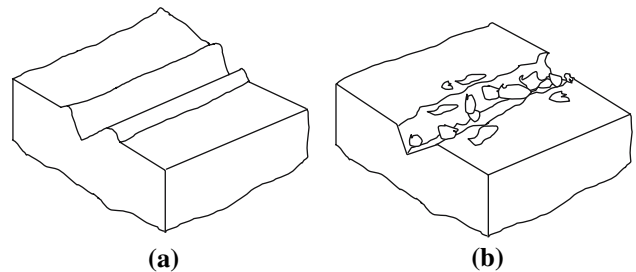
Abrasive wear mechanism

Figure 10 shows the scanning electron micrographs of the abraded surface of polyamide and polyamide nanocomposites pins. Ploughing and cutting action by abrasive grits on the pin surface were found dominant. Ploughing action is characterized by formation of grooves while cutting mode is characterized by both

particle and groove formation [11, 23] as shown schematically in Fig. 11. The cutting mechanism involves both geometrical change and material loss while ploughing mechanism involves only geometrical change. Hence quantification of wear by both mass loss and dimension loss is necessary for abrasive wear quantification. Table 2 shows the wear volumes estimated by both methods and difference between the two methods. Grooves formed in the polyamide 6 pins (Fig. 10a) are smoother with less particle formation indicating that ploughing is more prevalent in this material. As ploughing action is more visible in polyamide 6, quantification of wear by dimensional loss is the suitable wear characterization. Hence the highest deviation (~18%) was observed between the wear loss quantification by mass loss and dimensional

Fig. 11 Schematic representation of worn surface indicating abrasive wear mechanism (**a**) Ploughing and (**b**) cutting

Fig.10 SEM images of worn pins (**a**) polyamide (**b**) polyamide nanocomposite with 1% clay (**c**) polyamide nanocomposite with 3% clay and (**d**) polyamide nanocomposite with 5% clay

Table 2 Comparison of wear quantification by mass loss and dimensional loss

Weight percentage of clay in nanocomposite (%)	Wear by mass loss (mm³)	Wear by dimension loss (mm³)	Percentage variation (%)
0	36.64	44.44	17.56
1	74.68	86.95	14.11
3	123.16	129.52	4.92
5	175.26	178.07	1.57

Fig. 12 Final surface roughness of the tested pins
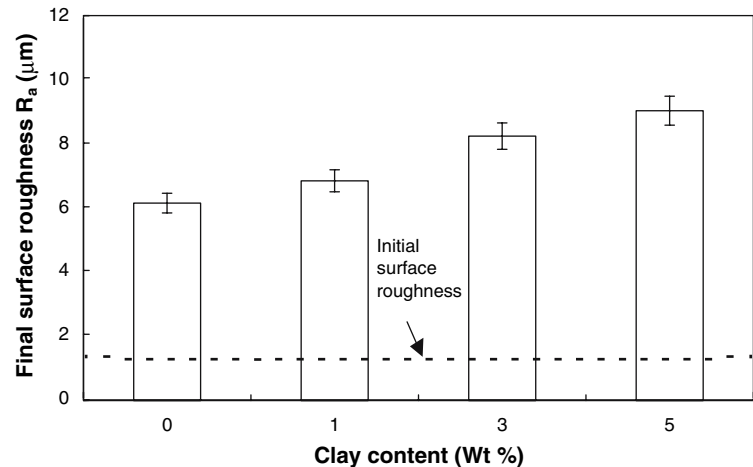
loss measurements. As the clay content increases in the polymer matrix cutting action predominates. Worn surface of the polyamide nanocomposite with 5% clay (Fig. 10d) had both grooves and fractured particles. The wear damage area is also more indicating the brittle nature of the nanocomposite [22, 23]. This effect is also verified by measuring the final surface roughness of the pins. Figure 12 shows the surface roughness of tested pins. Polyamide with 5% clay shows a maximum centerline average roughness (R_a) of 9.1 μm among the pins indicating a severe damage to the pin surface and high wear of the material.

Conclusions

The abrasive wear behaviour of polyamide clay nanocomposites with different clay content was investigated. Abrasive wear resistance decreases with the addition of clay to Nylon. The Ratner–Lancaster wear model was used to explain the wear behaviour of polyamide nanocomposites. Addition of clay increased the Ratner–Lancaster factor ($1/\sigma_b\varepsilon_b$) and hence the wear. Decrease in ductility due to the addition of clay increases the Ratner–Lancaster factor. Clogging tends to decrease the wear rate during sliding. The decrease

in wear rate is highest in Nanocomposite with 5% clay. Clogging also reduces the coefficient of friction of polyamide nanocomposites. Due to efficient clogging of the grits during sliding in the polyamide nanocomposite with 5% clay, the coefficient of friction is least. Ploughing and cutting action is prevalent on the pin surface. In polyamide nanocomposites cutting action is more dominant and it increases with clay content. Hence quantification of wear loss by both mass loss and and dimension change is necessary. Due to the decrease in ductility of the nanocomposites, the damaged area of the pin is more, which is indicated by an increase in the final surface roughness of the polyamide containing clay.

References

1. Lebaron PC, Wang Z, Pinnavaia TJ (1999) Appl Clay Sci 15:11
2. Alexandre M, Dubois P (2000) Mater Sci Eng 28:1
3. Dahman SJ (2001) In: White paper on nylon 6 nanocomposites. RTP Company, Winona, p 1
4. Shi G, Zhang MQ, Rong MZ, Wetzel B, Friedrich K (2003) Wear 254:784
5. Wang QH, Xu J, Shen W, Xue Q (1997) Wear 209:316
6. Li F, Hu K-A, Li J-L, Zhao B-Y (2001) Wear 249:877
7. Srinath G, Gnanmoorthy R (2005) J Mater Sci 40:2897
8. Bijwe J, Indumathi J, Rajesh JJ, Fahim M (2001) Wear 249:715

9. Bijwe J, Rajesh JJ, Jeyakumar A, Gosh A, Tewari US (2000) Tribol Int 33:697

10. Liu C, Ren L, Arnell RD, Tong J (1999) Wear 225–229:199

11. Bentone 105-Technical Information (2003) Elementis Specialties Inc., Highstown

12. ASTM D 638 (2002) Standard test method for tensile properties of plastics, vol 8.01. ASTM International, West Conshohocken, p 45

13. Yasue K, Katahira S, Yoshikawa M, Fuijimoto K (2001) In: Pinnavaia TJ, Beall GW (eds) Polymer-clay nanocomposites. John Wiley & Sons, Chichester, p 111

14. Jeffery J, Jacob KI, Tannaenbaum R, Sharaf MA, Jasiuk I (2005) Mater Sci Eng A 393:1

15. Rajesh JJ, Bijwe J, Tewari US (2002) Wear 252:769

16. Bundisnki KG (1997) Wear 203–204:302

17. Lancaster JK (1969) Wear 14:223

18. Shipway PH, Ngao NK (2003) Wear 255:742

19. BriscoeB, (1981) Tribol Int 14:231

20. Sinha SK (2002) In: Becker WT, Shipley RJ (eds) ASM handbook vol 11 failure analysis and prevention. ASM International, Ohio, p 1020

21. Rabinowicz E (1995) In: Friction and wear of materials. John Wiley & Sons, New York, p 194

22. Bayer RG (1994) In: Mechanical wear prediction and prevention. Marcel Dekker Inc., New York, pp 23

23. Stachowaik GW, Batchelor AW (2000) In: Engineering tribology Butterworth-Heinemann, Boston, p 483