



Degradation Analysis of Polyamide 6 Monofilament Fibers Coated with Thermoplastic Polyurethane Thin Films

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Abstract

Degradation studies were conducted on high performance polyamide (PA) 6 monofilament fibers prepared with various types of thermoplastic thin film coatings. Polyether, polyester and polycarbonate based polyurethane thin film coatings were used with changes in the molecular weight of the polyols and NCO index. It was found that the thermoplastic coating significantly protected the core PA6 monofilament fibers from degradation, analyzed through sliding abrasive wear and accelerated weathering irrespective of the type and nature of the thermoplastic polyurethane (TPU) thin film coating. The structural and physical changes were analyzed after exposure to degradation tests. Polycarbonate based TPU thin film coated PA6 monofilament fibers showed significant resistance towards degradation factors as compared to the polyether and polyester based TPU thin film coatings. The TPU thin film coated PA6 monofilament fibers are potential candidates as material for fishing gears.

Keywords: Polyamide 6 monofilament fiber, thermoplastic polyurethane, accelerated weathering, sliding wear, thin film coating

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Introduction

Polyamide 6 (PA6) is one of the most widely used industrial material, valued for its strength, melting point and processability and is commercially available in the form of fibers and films (Murthy et al., 2009; Palabiyik & Bahadur, 2000; Dong & Gijssman, 2010). PA6 monofilament fiber is a commonly used material in fishing gear sector. The presence of external factors like moisture, UV radiation and abrasion due to continuous use exert considerable influence on the physical and mechanical properties of PA6. There is extensive literature on the modification of the properties of PA6 monofilament fibers through structural modifications, blending with resistant polymers or adding molecules that can resist a particular aspect like UV radiation (Yarisheva et al., 1992). The development of high performance PA6 monofilament fibers by a polycarbonate based thermoplastic polyurethane (TPU) thin film coating improved the mechanical properties to a significant level without changing the inherent properties of the same. This was achieved through the structural changes from amorphous phase to crystalline phase through the influence of PU bondage, interface interaction and the cohesion role played by the micro-cracks formed on PA6 surface with the TPU coating (Motokucho et al., 2009; John et al., 2009c; 2009d; John & Furukawa, 2009a; 2009b). The significant features of TPUs are in the structure based on a soft segment formed with polymer glycol, where one can go any series based on ether/ester/carbonates, a hard segment formed with a diisocyanate and a chain extender (Petrovic & Ferguson, 1991; Furukawa et al., 2003; John & Furukawa, 2012).

The significant factors in weathering include moisture absorption due to the hydrophilic nature,

UV irradiation and abrasive wear while in use (Dong & Gijsman, 2010; Yarisheva et al., 1992; Friedrich & Reinicke, 1998; Sun et al., 1980). The decrease in the mechanical properties of PA6 is due to the diffusion of water molecules into the amorphous regions of the semi-crystalline polymer leading to plasticization and rupture of intermolecular hydrogen bonds (Cayer-Barrioz et al., 2003). UV irradiation results in breakage of CO-linkage, leading to degradation (Cerruti et al., 2003). The abrasion wear involves the tearing away of small pieces of materials with indentation type morphology in scar and low values of tensile strain to failure (Hailing, 1983). The most feasible way to combat and analyze degradation resistance factors are sliding wear which involves abrasion tribology and accelerated weathering tests where UV and moisture are significant parameters.

So our next focus was on the degradation resistance analysis of the high performance monofilament fibers developed, based on thin film TPU coating. In the present study, TPU thin film coated PA6 monofilament fibers were prepared by reactive-coating method (Motokucho et al., 2009; John et al., 2009c; 2009d; John & Furukawa, 2009a; 2009b). The prepared TPU were based on polyether, polyester and polycarbonate polyols as soft segments with changes in molecular weight and NCO index to analyze the impact of the same on degradation factors that restrict the outdoor application of PA6 monofilament fibers. The degradation was done by weatherometer and sliding wear apparatus and characterization was done by FTIR, tensile tester, SEM and dynamic viscoelastic measurements.

Materials and Methods

The polyols used for the preparation of TPU include poly (hexamethylene carbonate) glycol (PCG, $M_n=1076$, 2000 g mol⁻¹, Asahi Kasei Chemicals Co., Ltd, Japan), poly (oxytetramethylene) glycol (PTMG, $M_n=994$, 2000 g/mol, Nippon polyurethane Industry Co., Ltd, Japan) and poly (ethylene adipate) glycol (PEA, $M_n=995$, 2000 g mol⁻¹, Nippon polyurethane Industry Co., Ltd., Japan). The diisocyanate used was 4, 4'-diphenylmethane diisocyanate (MDI, Nippon polyurethane Industry Co., Ltd., Japan). 1, 4-Butanediol (BD, Wako Chemical, Co., Ltd., Japan) was used as a chain extender. PA6 monofilament ($f=520$ mm, Toray monofilaments, Japan) was taken as the basic fiber.

Synthesis of polyurethane adduct

TPU adduct was prepared from polycarbonate glycol (PCG 1k⁻¹), 4, 4'-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BD) by one-shot method. In one-shot method of preparation, the polyol directly mixed with diisocyanate and chain extender with varying [NCO]/[OH] ratio. PCG was bubbled with nitrogen gas at 100°C for 5 h to remove moisture. TPU was prepared at an [NCO]/[OH]_{PCG} ratio of 2.05 to 3.05 and an NCO index of [NCO]/[OH]_{PCG+BD} of 1.05. PCG was mixed with BD at 100°C and agitated for 3 min under nitrogen followed by the addition of MDI to the mixture and agitated for 30 s. The whole mixture was then stirred thoroughly in vacuum for 1 min. TPU adduct was also prepared with polyether (PTMG) and polyester (PEA) polyols. PCG2 PA, PCG3 PA, PTMG2 PA, PTMG3 PA, PEA2 PA and PEA3 PA, represents PCG, PTMG and PEA based TPU coated PA6 monofilament fibers with a K value of 2.05 and 3.05. The molecular weight of PCG based polyols was between 1000 and 2000 g mol⁻¹.

Preparation of TPU coated PA6 monofilament fibers

The PA6 monofilament fibers were cleaned using distilled water in an ultrasonic water bath for 15 min and dried at room temperature. The fibers were immersed in a TPU reactive adduct (based on PCG, PTMG and PEA) for less than a minute and were retrieved through a groove with a set thickness. The samples were then cured (at 100°C for PCG and 80°C for PTMG and PEA) for 24 h and stored in a desiccator.

The thickness (t) of the TPU-coated PA6 monofilament fiber was calculated as follows

$$t = [(\phi_{\text{coated fiber}} - \phi_{\text{uncoated fiber}})/2]$$

where f_{coated} fiber and f_{uncoated} fiber are the diameters of the TPU-coated and uncoated PA6 monofilament fiber, respectively

The detailed properties and characteristics of the TPU coated PA6 samples prepared are given in Table 1. The [NCO]/[OH] values taken for the study were 2.05 and 3.05 respectively. The TPU film coating on PA6 monofilament fiber was 40 mm and no substantial changes were observed on the PA6 fibers such as the glass transition temperature, melting point and density with the coating.

Table 1. Physical and mechanical properties of TPU thin film coated PA6 monofilament fibers

Fiber	TPU Coating thickness (μm)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	d (g cm^{-3})	T (MPa)	E	Y (GPa)
PA 6	40	55	220	1.22	646	0.33	2.85
PEA2 PA	40	55	222	1.22	810	0.77	3.33
PEA3 PA	40	54	221	1.23	875	0.59	3.51
PTMG2 PA	40	55	220	1.21	873	0.73	3.81
PTMG3 PA	40	53	220	1.23	880	0.58	3.92
PCG2 PA	40	55	218	1.22	769	0.67	3.55
PCG3 PA	40	54	248	1.23	810	0.84	3.81
PCG2 PA (2000)	40	53	220	1.21	805	0.65	3.48
PCG3 PA (2000)	40	52	220	1.22	817	0.56	3.51

T, E, Y represents the tensile strength at break, strain at break and Young's modulus respectively

Characterisation

The morphological and physical properties were evaluated by scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and a tensile tester.

Field emission SEM (FE-SEM) images were taken with a JEOL JSM-7500 scanning electron microscope (JOEL, Tokyo, Japan) operated at 5 kV. The samples were gold-sputtered prior to the examination. FTIR studies were conducted to analyze the structural changes in the PA6 monofilament fiber with various types of TPU coating. FTIR cross sectional scanning of the fiber was conducted through a microscope in attenuated total reflectance mode at an intensity range of 400-4000 cm^{-1} (UMA-600 FTIR microscope-FTS 3000 type, Bio-Rad Laboratories Inc. Hercules). Scan was taken with an inbuilt camera attached to the microscope and images were viewed on a computer screen. All the spectra were collected from 32 scans at a resolution of 4 cm^{-1} . The position for scanning was adjusted by viewing through a microscope.

Tensile tests were performed with an Instron type tensile tester (Tensilon, U-440 model, Orientec Co., Ltd., Tokyo Japan) at 20 $^{\circ}\text{C}$. The initial length and elongation rate were set at 30 mm and 10 mm min^{-1} , respectively. Accelerated weathering studies were conducted using a weatherometer (SC700-FA, Suga Machine Company Ltd, Japan) with a Xe arc lamp source (continuous irradiation of 180 W sq m^{-1} in the wavelength range of 200-300 nm). The

water spray was for 18 min and the interval between each raining was 120 min. The black panel temperature was 65 $^{\circ}\text{C}$ during irradiation and 45 $^{\circ}\text{C}$ during the spray. The total exposure time was 200 h and the samples were retrieved after every 50 h. The length of the fiber samples loaded on the experimental frame for exposure was 40 mm. All the TPUs possessed a flexible nature as confirmed from the glass transition temperatures (T_g) ranging from -33.7 for PEA2 PU to -9.4 for PCG3 PU. The T_g s of the TPUs showed a clear decrease with an increase in the NCO index of the same. With an increase in molecular weight of the polyols, T_g showed a decrease from -2.5 to -10.6 for PCG based TPUs. An indirect information regarding the degree of microphase separation between soft and hard segments can be derived from $\Delta T = T_m - T_g$. The degree of microphase separation was in the order PTMG > PEA > PCG based TPUs. The degree of microphase separation showed a decrease with an increase in the molecular weight of the polyol (PCG2 PU 1000 > PCG3 PU 2000). There was no significant variation in the microphase with a increase of NCO index from 2 to 3.

Experimental set-up of the fibers of indigenously designed sliding wear for the investigation is shown in Fig. 1. The abrasive surface was placed inside the groove of the pulley (inset image shown in Fig. 1). The water proof abrasive paper, SiC - G 600 was selected for the wear surface. The wear particles are silica particles of size varying from 30-50 μm . The

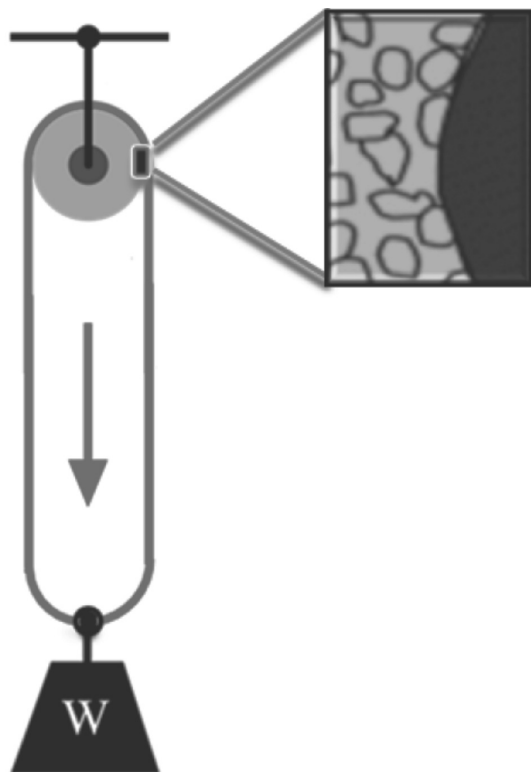


Fig. 1. Experimental set up for the sliding wear analysis of TPU thin film coated PA6 monofilament fibers. The inset shows the grit paper surface and fiber in contact. The arrow mark shows the downward tension from the applied load.

fiber was inserted in the loop region of the pulley and a tension load was loaded at the bottom region. Applied tensile load was in the order of 20×10^{-3} kg and the sliding rate was 0.15 m s^{-1} . The interval was set for sliding distances as multiples of 50 m. The fibers were retrieved after each sliding interval of 50 m and the mechanical properties were analyzed. Abraded surface of the fiber and the transfer film on the abrasion surface were analyzed using the FE-SEM after 150 cycles of rotation. PCG2 PU coated fiber was selected for sliding wear analysis as it showed very significant resistance in accelerated weathering experiments.

The specific wear rate of the specimens was evaluated by the equation (Bijwe et al., 2001)

$$K_o = (m_1 - m_2) \times 1000 / \rho N S \quad (1)$$

Where m_1 and m_2 are the initial and final masses of the sample before and after the sliding wear test, r is the specific gravity of the specimen, N is the normal load and S is the sliding distance.

Results and Discussion

Morphological features

Fig. 2. shows the morphological properties of the PA6 and PCG2 PA fibers before and after exposure to the accelerated weathering chamber for 200 h. T, E, Y represents the tensile strength at break, strain at break and Young's modulus respectively. The surfaces of the fibers were smooth and there were no features of degradation (Fig. 2a and 2c). A ridge like feature was observed on both the fibers, showing a slight shrinkage of the fiber with weathering exposure as shown in Fig. 2 and 3. This is due to the presence of moisture from the water spray in the chamber and the degree of shrinkage was less for TPU coated one as compared to the neat one (Larsen-Basse, 1988). Also the surface layer of the PA6 fiber and PCG2 PA showed a slight crack-like feature with 200 h weathering in the chamber. Similar morphological features were observed for the rest of the TPU thin film coated PA6 monofilament fibers.

Morphological features of PA and PCG2 PA fibers after sliding wear test are shown in Fig. 3. Fig. 3a, b and c show the PA6 monofilament fiber before and after sliding wear test. The microfibrils are seen on the PA6 monofilament fiber in the sliding wear

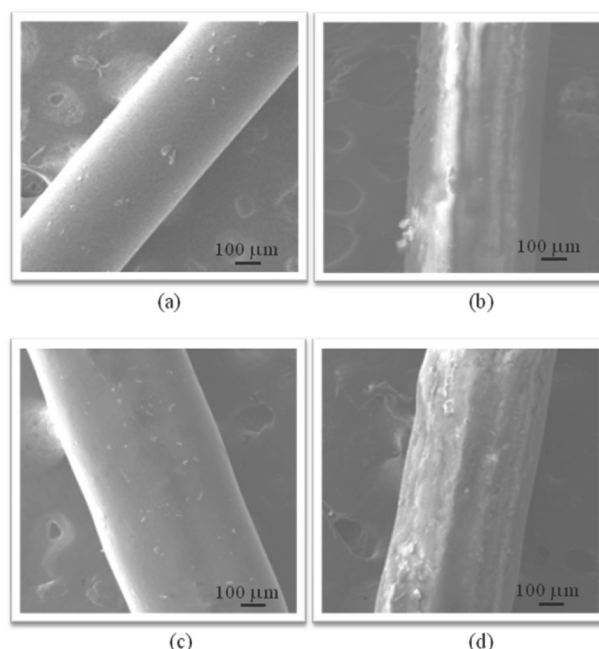


Fig. 2. FE-SEM images of the neat PA6 (a), (b) and PCG2 PA monofilament fibers (c), (d) before and after 200 h of exposure to accelerated weathering.

direction. The damage due to wear is drastic which might affect the performance of PA6 monofilament fiber for various applications. Fig. 3d, e and f show the effect sliding wear on the PCG2 PU coated PA6 monofilament fibers. The PCG2 PA fibers which have undergone sliding wear show three types of wear morphological features. The first is the outer PCG2 PU region, the second is the interface interaction region between the PCG2 PU with the PA6 monofilament fiber highlighted in the encircled

region and the third is the core PA6 monofilament region. The PA6 region shows microfibrils after the sliding abrasion similar to the one observed in the neat ones. The view of the PCG2 PU coating region shows a rubbery region with no microfibrils (Fig.3f). This clearly shows that the TPU coating can withstand wear and a similar feature was observed on other coated samples. Fig. 3g shows the abrasive surface of SiC paper of grit size 600 used in the sliding wear, where silica particles are clearly visible.

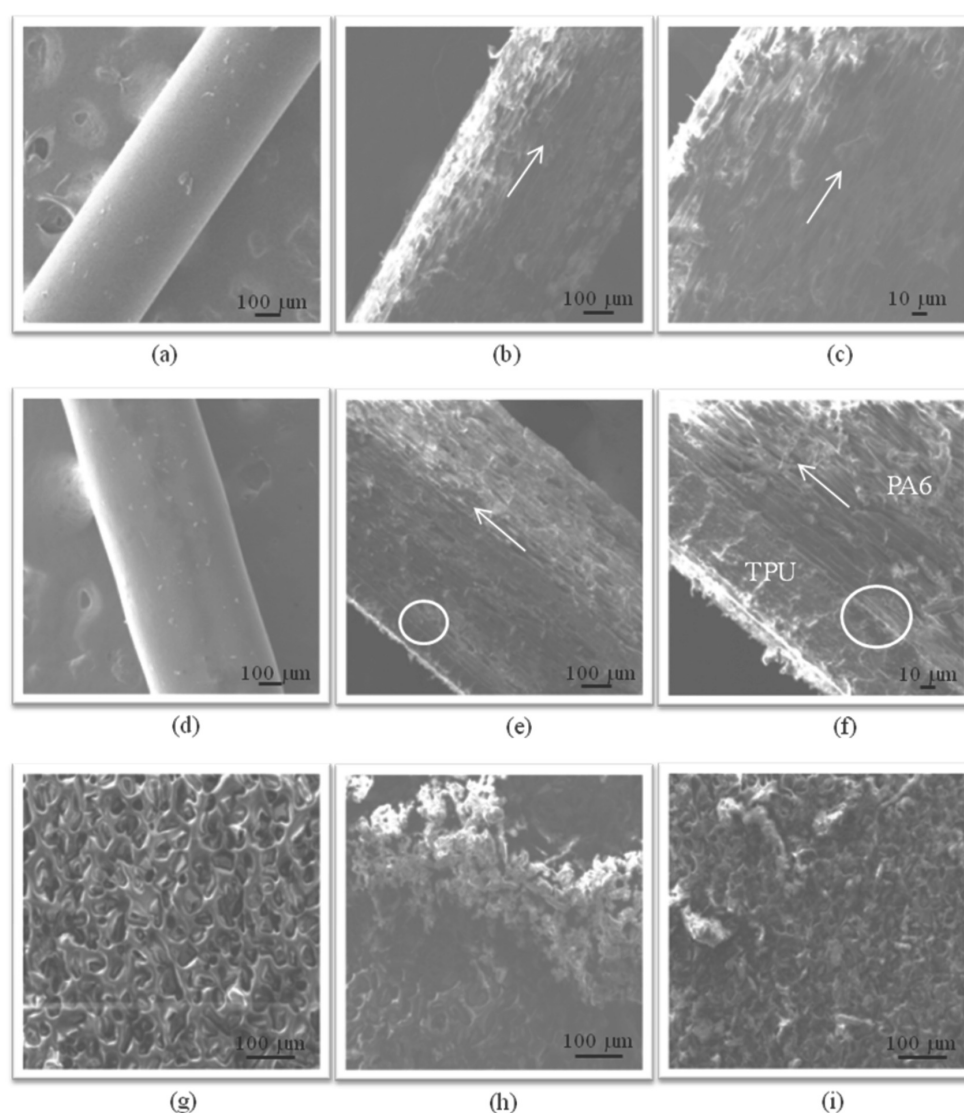


Fig. 3. FE-SEM images of (a) neat PA6 monofilament fiber, (b) surface of PA fiber after 200 m of sliding abrasion, (c) magnified image of abrasion surface showing the micro-fibrils on the fiber, (d) neat PCG2 PA fiber, (e) surface of PCG2 PA monofilament fiber after 200 m of sliding abrasion, (f) magnified image of abrasion surface showing the micro-fibrils in the PA6 region and rubbery nature observed in the TPU coating region, (g) surface of SiC paper of grit size 600, (h) transfer film of PA6 fibers after 200 m of sliding abrasion, and (i) transfer film of PCG2 PA monofilament fibers after 200 m of sliding abrasion. The arrow mark indicates the sliding direction and the circled region represents the interface-interaction region between the PA6 and PCG2 PU coating.

Fig. 3h shows the transfer film formed on the abrasion surface by the PA6 monofilament fiber after the wear test. In the case of PA6 transfer films, it appeared as a fine powder. Fig. 3i shows the transfer film formed on the abrasion surface by the PCG2 PA fiber after a sliding wear test. Here the transfer film that appeared as roll like structures due to rubbery nature is a mixture of PA6 and PCG2 PU particles. This difference in nature of the transfer film between the two samples is due to the difference in the cohesive energy densities of the surfaces where one is of PA6 monofilament fiber and the other PCG2 PU coating (Bahadur, 2000).

Transfer film is another feature which occurs when polymers slide against metal or hard counterfaces. It can also occur when sliding occurs between a polymer and another polymer with varying densities. The transfer film formed on a non-polymer counterface is governed by the counterface material, roughness, and the sliding conditions. The transfer films affect the friction and wear behavior of sliding pairs. The role of transfer film in polymer-hard surface sliding contacts is responsible for the gradual transition from a transient wear behavior to steady state wear behavior. However, the role of sliding variables such as velocity, load and temperature on the transient wear behavior as well as their effect on transfer film is not clear. As for the role of transfer films, it is widely believed that transfer films provide shielding of the soft polymer surface from the hard metal asperities.

FTIR Analysis

FTIR studies were conducted to analyze the structural changes in the TPU coated and neat PA6 monofilament fiber after exposure to accelerated weathering. PA6 is a semi crystalline polymer, which has stable α , γ forms and an unstable β form. The hydrogen bonds are between the antiparallel chains in the α form and between the parallel chains in γ form. An important difference between these two structures is that the chain-axis repeat is 1.724 nm in the α form due to its extended planar conformation and for the γ form, it is 1.688 nm due to twisted helical transformation. The β form is said to be a variant of the γ form in which the chains have a disordered conformation with no definite chirality and the chain-axis repeat of this phase is 1.67 nm (Rotter & Ishida, 1992). The peaks at 830, 930 and 960 cm^{-1} show the characteristic α crystalline form, while the peak at 980 cm^{-1}

represent γ -crystalline form, all in CO-NH in the plane stretching region (Xenopoulos & Clark, 1995). The crystalline structures are interchangeable in such a way that the α -crystalline form can be changed into the γ -crystalline form by treating in a mixture of aqueous iodine and potassium iodide. The γ -crystalline form can be transformed into the α -crystalline form through a treatment with an aqueous phenol solution (Maillo et al., 2005). During the process of fiber spinning, crystallization occurs from the amorphous phase to the α form and from γ to α transformations. During annealing, transformation occurs only from the amorphous phase to the α form (Rotter & Ishida, 1992).

Fig. 4 shows the FT-IR spectra of the PA6, PCG2 PA, PTMG2 PA and PEA2 PA monofilament fibers after exposure to accelerated weathering. The peak at 1070 cm^{-1} (CO-NH in skeletal motion) is often taken as indicator of C=O bond breakage due to UV irradiation. All the coated fibers showed an increase in intensity of 1070 cm^{-1} peak, which is a confirmation of cleavage of C=O bond by UV irradiation in weathering chamber (Sharkey & Mochel, 1959). The PA6, PCG2 PA, PTMG2 PA and PEA2 PA fibers possessed peaks at 830, 930 and 960 cm^{-1} showing the characteristic α crystalline form before exposure to weathering. The peak at 980 cm^{-1} which represents the γ crystalline form was absent. After initial exposure of about 100 h to weathering chamber, the PA6, PTMG2 PA and PEA2 PA fibers (Fig. 4a,c,d) showed the same trend and in the case of the PCG2 PA fiber (Fig. 4b) a peak at 980 cm^{-1} peak was observed, which represents the formation of γ -crystalline form. All the fibers except PCG2 PA showed a transformation from α -crystalline form to amorphous phase and in the case of PCG2 PA it was from α -crystalline form to γ -crystalline form and to amorphous phase. The presence of ionic groups or radicals is very much necessary for α to γ crystalline transformation (Rotter & Ishida, 1992). But, in the case of PCG2 PU coating there is no possibility of the occurrence of ionic radical or groups. The UV irradiation from weathering softened the PCG2 PU coating and thereby the changes had occurred in the elastomeric chains in the coating with the breakage of C=O bonds. These broken bonds reacted with water molecules forming C=O...OH ionic system, which might have influenced the PA6 lamellar structures causing the crystalline transformation (Petrovic & Ferguson, 1991). In the case of PTMG and PEA based TPU coating, the presence of free C=O bonds are

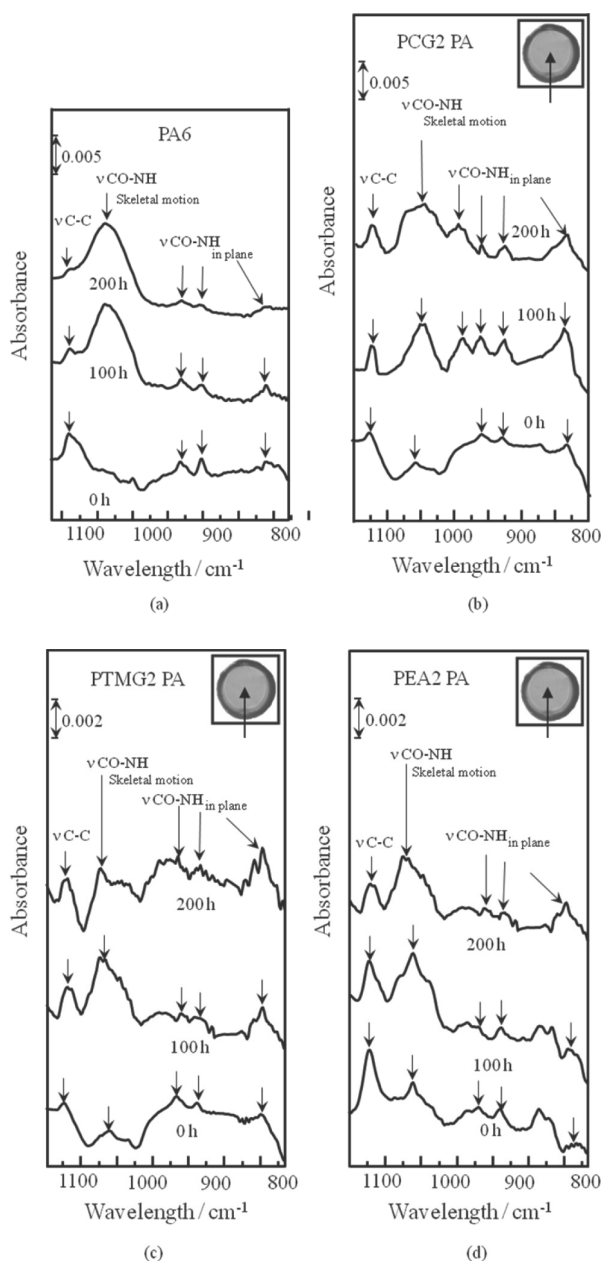


Fig. 4. FT-IR spectra of (a) PA6, (b) PCG2 PA, (c) PTMG2 PA, and (d) PEA2 PA fibers before and after exposure to weathering.

few compared to the PCG based TPU coating. Also, the mechanical strength loss after exposure is an indirect indication of the increase in the amorphous nature of the uncoated and TPU thin film coated fibers, which shall be discussed in the later section.

Mechanical properties after degradation

Mechanical properties of PA6 and TPU thin film coated PA6 monofilament fibers for various

intervals of accelerated weathering exposure are given in Table 2. Fig. 5 shows the variation of stress and strain of TPU coated PA6 monofilament fibers and with different molecular weights of PCG polyols ranging from 1000 to 2000 with NCO/OH values of 2.05 and 3.05.

Table 2. Mechanical properties of TPU film coated PA6 monofilament fibers after weathering

Fiber	Weathering (h)	T (MPa)	E	Y (GPa)
PA 6	200	316	0.17	1.54
Ann PA	200	313	0.15	1.66
PEA2 PA	200	551	0.28	3.22
PEA3 PA	200	753	0.37	3.39
PTMG2 PA	200	786	0.39	3.62
PTMG3 PA	200	711	0.30	3.72
PCG2 PA	200	686	0.28	3.33
PCG3 PA	200	794	0.43	3.42
PCG2 PA (2000)	200	703	0.34	3.36
PCG3 PA (2000)	200	569	0.24	3.38

T, E, Y represents the tensile strength at break, strain at break and Young's modulus respectively

The mechanical properties of PA6 monofilament fiber showed a marked decrease in strength after 200 h of exposure to weathering. The strength of the PA6 monofilament fiber decreased more than 50% of the original strength which is cut off value for the fiber. In the case of PCG, PTMG and PEA based PU coated thin film coated PA6 fibers; the mechanical strength on an average of 60% of the original strength was retained even after 200 h of weathering exposure. In the case of PCG based TPU based TPU coated PA6 monofilament fibers the strength showed an increase (an average of 10%) during the initial hours of exposure to weathering. The UV irradiation from weathering softened the PCG2 PU coating and thereby the changes had occurred in the elastomeric chains in the coating with the breakage of C=O bonds. These broken bonds reacted with water molecules forming C=O...OH ionic system, which might have influenced the PA6 lamellar structures causing the crystalline transformation as discussed earlier in the FT-IR section. The retention of tensile strength was in the order PCG>PTMG>PEA based TPU coated PA6 monofilament fibers. For all the intervals of exposure and types of fibers, the elongation at break showed a decrease. This was due

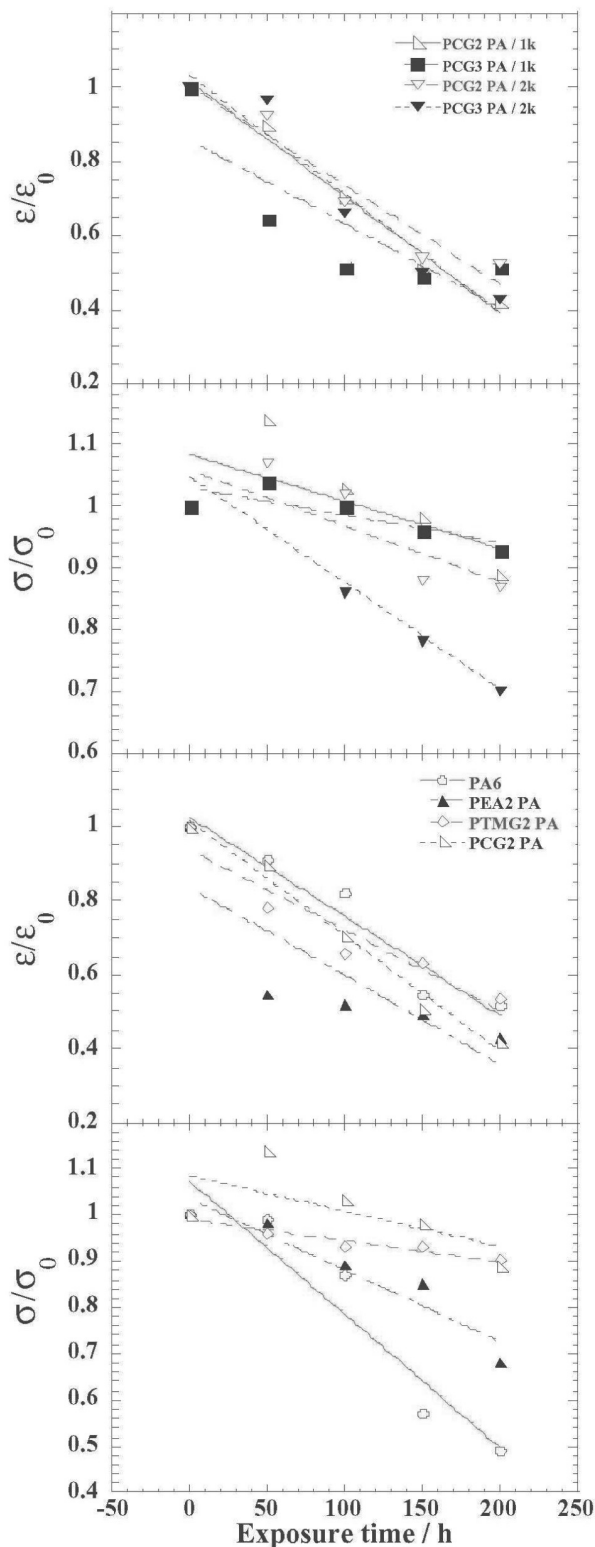


Fig. 5. Variation of stress and elongation of TPU coated and uncoated PA6 fiber samples after exposed to weathering.

to the shrinkage effect, an inherent property of PA6 fiber in the presence of water (Larsen-Basse, 1988).

For PTMG and PEA based TPU coated PA6 fiber, Young's modulus showed a slight decrease with various intervals of exposure except for PCG based coated ones, which showed a slight increase and then a decrease. The molecular weight of the polyol and the $[NCO]/[OH]$ values of the TPU had no significant effect in the mechanical property of TPU coated PA6 monofilament fibers exposed to weathering (Fig. 5). The loss of the tensile strength of PA6 monofilament fibers with weathering is due to the degradation of the crystal structure and the transformation of the same to amorphous state with weathering exposure. In the case of TPU coated PA6 monofilament fibers with PTMG, PEA and PCG based polyols, the degree of degradation was low by the protective TPU coating. For PCG based TPU coated PA6 monofilament fiber, the formation of g-crystalline form resulted in initial improvement of tensile strength.

Cross sectional view of PA6 (Fig. 6a, b) and PCG2 PA fibers at break (Fig. 6c, d), before and after exposure to weathering show significant morphological features. Before weathering exposure, the

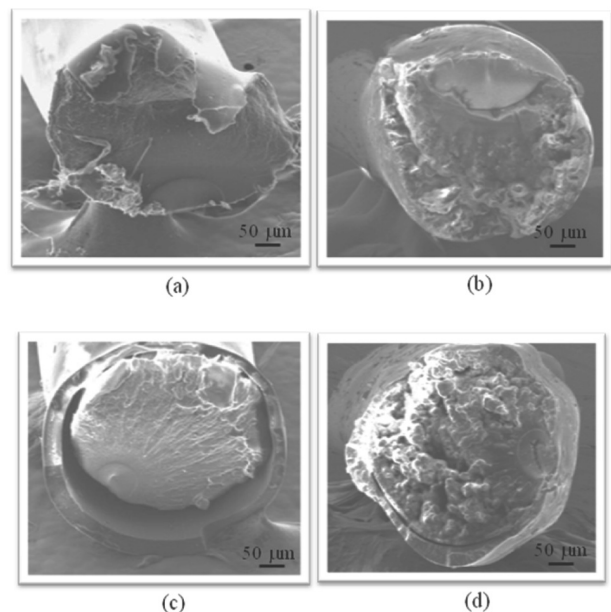


Fig. 6. Cross sectional FE-SEM images of the PA6 monofilament fiber at break (a) before and (b) after exposed to 200 h of weathering and PCG2 PA monofilament fiber at break (c) before and (d) after exposed to 200 h of weathering.

natures of break for PA6 and PCG2 PA fibers were 'plastic' and 'metallic' respectively (John et al., 2009a). But after the exposure to weathering, the break for both fibers showed a 'plum cake' like feature with degradation. A significant feature of PCG2 PA fiber is adherence of coating with the PA6 fiber surface after 200 h of weathering exposure.

The impact of sliding wear for different sliding intervals on the mechanical properties of the neat and coated PA6 monofilament fibers are shown in Table 3 and Fig. 7. The specific gravity of fibers showed no variation with abrasion as it is inherent property of the material with a physical degradation like sliding wear. The most important parameter to be analyzed with abrasion analysis is the specific wear rate, which represents the mass of the material lost with the sliding distance.

The specific wear rate of PA6 monofilament fiber was high and easily vulnerable to sliding wear as seen from Fig. 7a. The PTMG2 PA and PEA2 PA monofilament fibers showed higher wear resistance as compared to the PA6 fibers but far behind the PCG2 PA fibers. PCG2 PA possessed the least specific wear rate and thus the highest wear resistance. PCG2 PU and PCG3 PU are more of thermoplastic nature than PEA and PTMG counterparts. The role played by compatibility and interface interaction in TPU also played a significant role in keeping wear to a minimum level irrespective of the type of TPU coating. The quality of fiber is said to be lost when it loses 50% of strength (Fig. 7b). So taking into account this parameter, the loss of 50% of tensile strength (s_{50}) with sliding distance is an important factor. The s_{50} values for PA6, PEA2 PA, PTMG2 PA, CG2 PA fibers were 32.1, 370.1, 410.8 and 365.1 MPa for sliding distances of 100, 150, 200 and 300 m respectively (Table 3). So the percentage improvement of wear resistance with TPU thin film coated ones to the neat PA6 fibers were 300, 100, and

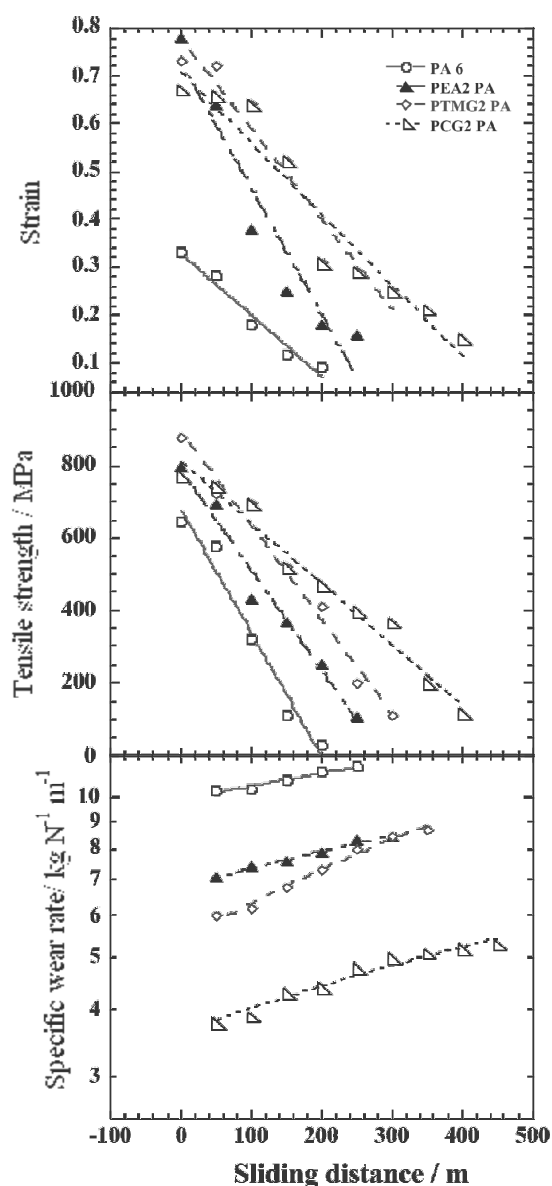


Fig. 7. Variation of specific wear rate and tensile strength with sliding distance of TPU coated PA6 monofilament fibers.

Table 3. Impact of sliding wear on the mechanical properties of TPU thin film coated PA6 monofilament fibers

Fiber	Sliding distance (m)	Specific gravity	Specific wear rate (Kg Nm ⁻¹) x 10 ⁻⁶	Tensile strength (MPa)	Strain at break
PA6	100	1.13	10.4	321.10 (s_{50})	0.18
PCG2 PA	300	1.14	5.0	365.1 (s_{50})	0.25
PTMG2 PA	200	1.14	7.3	410.8 (s_{50})	0.31
PEA2 PA	150	1.14	7.6	370.4 (s_{50})	0.25

50% for PCG2 PA, PTMG2 PA and PEA2 PA respectively (Fig. 7b).

On the application side, the TPU thin film coating improved wear and weathering resistance of PA6 fibers and coatings can be selected according to the need for various marine applications. Polycarbonate (PCG2 PA) and polyether based (PTMG2 PA) TPU coated PA6 monofilament fibers are more durable in the tough conditions of marine environment. Biodegradable polyether (PEA2 PA) based PA6 monofilament fiber is biodegradable. PA6 monofilament fiber is notorious for its non-degradable nature. Recent studies have reported degradation of PA6 fibers on land and in marine environment by certain species of microbes (Huemann et al., 2006; Klun et al., 2003; Sudhakara et al., 2007; Cosgrove et al., 2007; Nakajima-Kambe et al., 1997). But the process is extremely slow. The same biological species can degrade polyester based TPU as it is biodegradable.

The TPU thin film coated PA6 monofilament fibers are resistant to degradation than their neat counterparts. The thin film coating acted as a protection barrier against the impacts of the forces of degradation through structural changes in crystalline and amorphous regions. The polycarbonate (PCG2 and PCG3 PU) based thin film coating showed the best performance among all the types of TPU coatings with high degree of sliding and weathering resistances. The TPU coating for the PA6 monofilament fibers can be selected according to the type of applications and the nature of degradation forces that come along with it. The process of fast biological degradation is possible with the biodegradable coating. Thus the problem of 'ghost fishing' in oceans can be addressed to a great extent with the use of this material.

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References

- Bahadur, S. (2000) The development of transfer layers and their role in polymer tribology. *Wear*, 245: 92-99
- Bijwe, J., Indumathi, J., Rajesh, J. J. and Fahim, M. (2001) Friction and wear behavior of polyetherimide composites in various wear modes. *Wear*, 249: 715-726
- Cayer-Barrioz J, Mazuyer D, Kapsa P, Chateauminois A, Bouquerel F. (2003) On the mechanisms of abrasive wear of polyamide fibres. *Wear*, 255: 751-757
- Cerruti, P., Carfagna, C., Rychly, J. and Matisova-Rychla, L. (2003) Chemiluminescence from oxidation of polyamide 6,6. I. The oxidation of pure polyamide. *Polym. Degrad. Stab.* 82: 477-85
- Cosgrove, L., Mc Geechan, P. L., Robson, G.D. and Handley, P. S. (2007), Fungal communities associated with the degradation of polyester polyurethane in soil. *Appl. Environ. Microbio.* 73, 5817-5824
- Dong, W. and Gijsman, P. (2010) Influence of temperature on the thermo-oxidative degradation. *Polym. Degrad. Stab.* 95: 1054-1062
- Friedrich, K. and Reinicke, P. (1998) Friction and wear of polymer based composites. *Mech. Compos. Mater.* 34: 503-514
- Furukawa, M., Hamada, Y. and Kojio, K. (2003) Aggregation structures and mechanical properties of functionally graded polyurethane elastomers. *J. Polym. Sci. Part B: Polym. Phys.* 41: 2355-2364
- Hailing, J. (1983) Towards a mechanical wear equation. *J. Tribol. Tech.* 105: 212-20
- Huemann, S., Eberl, A., Pobeheim, H., Lieminger, S., Fischer-colbrie, G., Almansa, E., Cavaco-Paulo, A. and Gubitz, G. M. (2006) New model substrates for enzymes hydrolyzing polyethyleneterephthalate and polyamide fibers. *J. Biochem. Biophys. Methods*, 69, 89-99
- John, B. and Furukawa, M. (2009a) Enhanced mechanical properties of polyamide 6 fibers coated with a polyurethane thin film. *Polym. Eng. Sci.* 49: 1970-1978
- John, B. and Furukawa, M. (2009b) High performance polyamide 6 fibers using thermoplastic polyurethane coatings. *J. Rubber. Res.* 12: 151-163
- John, B. and Furukawa, M. (2012) Structure and mechanical behaviors of thermoplastic polyurethane thin film coated polyamide 6 fibers part II. A solution coating method. *J. Polym. Res.* 19: 9764-9776
- John, B., Kojio, K. and Furukawa, M. (2009c) High performance polyamide 6 fibers using polycarbonate based thermoplastic polyurethane thin film coatings-a novel method. *Polym. J.* 41: 319-326
- John, B., Motokucho, S., Kojio, K. and Furukawa, M. (2009d) Polyamide 6 fibers with superior mechanical properties: TPU coating techniques. *Sen-I Gakkaishi.* 65: 236-240

- Klun, U., Friedrich, J. and Krzan, A. (2003), Polyamide-6 fiber degradation by a lignolytic fungus. *Polym. Degrad. Stab.*, 79, 99-104
- Larsen-Basse, J. (1988) Slurry abrasion of polymers under simulated submarine conditions. *Wear*, 122:135-49
- Maillo, J., Pages, P., Vallejo, E., Lacorte, T. and Gacen J. (2005) FTIR spectroscopy study of the interaction between fibre polyamide6 and iodine. *Eur. Polym. J.* 4: 753-59
- Motokucho, S., Kojio, K., Furukawa, M. and John, B. (2009) High Performance Polyamide 6 Fibers Using Thermoplastic Polyurethane Coatings. Japan patent, 127154
- Murthy, N.S., Curran, S.A., Aharoni S.M., and Minor H. (2009) Premelting crystalline relaxations and phase transitions in nylon 66 and 6, 6. *Macromolecules* 24: 3215-3220
- Nakajima-Kambe, T., Onuma, F., Akutsu, Y. and Nakahara, T. (1997) Determination of the polyester polyurethane breakdown products and distribution of the polyurethane degrading enzyme of *comamonas acidovorans* strain TB-35, *J. Ferment. Bioeng.* 83, 456-460
- Palabiyik, M. and Bahadur, S. (2000) Mechanical and tribological properties of polyamide 6 and high density polyethylene blends with and without compatibilizer. *Wear*, 246: 149-158
- Petrovic, Z.S. and Ferguson, J. (1991) Polyurethane elastomers. *Prog. Polym. Sci.* 16: 695-836
- Rotter, G. and Ishida, H. (1992) FTIR separation of nylon-6 chain conformations: clarifications of the mesomorphous and g-crystalline phases. *J. Polym. Sci. Part B Polym. Phys.* 30: 489-95
- Sharkey, W.H. and Mochel, W.E. (1959) Mechanism of the photooxidation of Amides. *J. Am. Chem. Soc.* 81: 3000-3005
- Sudhakara, M., Priyadarshini, C., Doble, M., Murthy, P. S. and Venkatesan, R. (2007), Marine bacteria mediated degradation of nylon 66 and 6. *Int. Biodete. Biodegr.* 60, 144-151
- Sun, N. P., Sin, C. H. and Saka, N. (1980) *Fundamentals of Tribology*. 493p. MIT Press, USA
- Xenopoulos, A. and Clark, E. S. (1995) In *Nylon Plastics Handbook*, 107p. Kohan, M.I., Ed; Hanser Publishers: New York
- Yarischeva, L.M., Kabal'nova, LYu, Pedy A.A. and Volynskii, A.L. (1992) Thermal effects accompanying nylon-6 degradation. *Therm. Anal. Calorim.* 38: 1293-1297