



## Synthesis and Characterization of Polyurethane Matrix Nano Composites

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A gel-casting method was used to fabricate the polyurethane polymer matrix composites with commercially available molybdenum disulphide (5 to 20 wt. %) and nano particles of titanium dioxide (0.5 to 2 wt. %) were added to tetrahydrofuran. Polyurethane was added pellet wise to stirred suspension. To maintain feasible viscosity of the suspension, the concentration of the polyurethane had to be reduced in the solution. Variation was made in the concentration of polyurethane in tetrahydrofuran from 3.5 to 10 wt. %, the suspension was being continuously stirred for 1 h to ensure the complete dissolution of the pellets of polyurethane. The suspension was then cast into different specimen sizes and was characterized through transmission electron microscopy, scanning electron microscopy and powder X-ray diffraction for morphological properties. The mechanical strength properties were determined by impact test, fracture test, wear and the friction test.

**Keywords:** Polyurethane matrix composites, Nano titanium dioxide, Mechanical properties, Morphological properties.

### INTRODUCTION

Polyurethane is one of the most interesting synthetic materials in industries, which has been widely used in adhesives, coatings, synthetic leather, construction, automatic applications, *etc.* Nano composites are having polymers containing nanofillers<sup>1,2</sup>. The microstructure of nano composites are homogeneties in the scale range of nanometers. Nowadays in the application of polyurethane, researchers to search for higher performance of polyurethane. Polyurethane based nano composites exhibit remarkable improvements in mechanical, dielectric, magnetic, thermal, optical and acoustic properties compared with pure organic polymers<sup>3,4</sup>.

The main archetype is that a valuable nanocomposite is one with the largest possible surface of nanofiller. Nanoparticles are commercially available from different sources, avoiding aggregation of nano particles and exfoliation of nanoclays is important in synthesis. Nanoparticles tend to aggregate and have very poor dispersion in polymers<sup>5</sup>. To achieve good dispersion of nanoparticles and yield better compatibility between nanoparticles and polymer matrix, the use of various modification agents, such as trialkoxy, silane, stearic acid, CTAB are recommended for appropriate surface modification of nanoparticles<sup>6,7</sup>. Ultrasonic irradiation is also employed to overcome the disadvantages such as agglomeration of particles<sup>8</sup>. Suslick<sup>9</sup> have employed a variety of applications of ultrasound to materials chemistry.

The degree of exfoliation in a nanocomposite is increased by number of ways, such as *in situ* polymerization, solution blending, sonication, melt blending, high shear mixing, melt intercalation and some others<sup>10,11</sup>. The morphology of nanocomposites is studied by X-ray techniques, scanning electron microscopy and transmission electron microscopy<sup>12</sup>.

The micro fillers improve many physical and few mechanical properties of polymers and were usually beneficial in increasing the wear resistance under adhesive wear conditions. Sole and Ball<sup>13</sup> indicated that rigid fillers have a positive influence on creep performance and stiffness but exhibit a deleterious effect on ductility and tensile strength. These researchers also observed that under wear, where the applied load per particle was low, the wear behavior of filled polyurethane showed some dependence on the size and shape of the filler particles.

Molybdenum disulphide (MoS<sub>2</sub>) is a well-known solid lubricant<sup>14</sup>. Its lubrication capacity, *i.e.* easy cleavage and low friction characteristics, is intrinsic to its crystal layered structure<sup>15</sup>. Each crystal layer consists of two layers of sulphur atoms were separated by a layer of molybdenum atoms. The atoms lying on the same crystal layer were closely packed and strongly bonded to each other, the layers themselves were relatively far apart and the forces, *e.g.* vander Waals, that bond them were weak. Many studies compressing the effect of the addition of MoS<sub>2</sub> on wear and friction properties of different polymers, such as polytetrafluoroethylene (PTFE), polyamide

(PA), polyester (UP) and polyimide (PI)<sup>14,16,17</sup> are available in the literature. Bahadur and Gong<sup>14</sup> reported that wear was considerably reduced by the addition of MoS<sub>2</sub> to polytetrafluoroethylene, polyamide 66 and polyimide. They also reported that the filler proportion affect the wear resistance of composites: the wear rate of polyamide decreased initially with the increase in MoS<sub>2</sub> content but then increased again, with an optimum content about 15-20 wt. %. Peng *et al.*<sup>17</sup> found that MoS<sub>2</sub> decreased dry and water sliding wear rate of polyimide, finding again an optimum content of MoS<sub>2</sub> to be about 10-15 wt. %.

Titanium dioxide was extensively used in the industries such as additives in plastics, agglomerates for air/fuel ratio controller in automobile, attenuation of ultraviolet light, thermal sprays, catalysts and catalyst supports, demilitarization of chemical and biological warfare agents, energy converter in solar cells, gas sensors, electrode materials in lithium batteries, inorganic membranes, photo catalytic degradation of bacteria and grime, piezoelectric capacitors, solid oxide fuel cell, photochemical degradation of toxic chemicals, UV protection and waste water purification. Nanocomposites using thermoplastic polymers were well known for improving the mechanical, thermal, electrical and insulating properties. However, thermosetting polymer nanocomposite have not been studied so extensively<sup>18,19</sup> particularly using TiO<sub>2</sub>. We focused on the performance optimization of composites containing TiO<sub>2</sub> nanoparticles and to understand the role of nanoparticles. The mechanical and thermal performance of the nano-filled polymer matrix was evaluated as a function of the nanoparticle content (0.5-2 %). The overall properties of nanocomposites may open the way towards new applications of high performance polymers, leading to an innovative product development in the automotive industry, electronics for coatings and many other applications.

## EXPERIMENTAL

Polyurethane (DP385S) used is supplied by Bayer Material Science, Chennai, India. The Molybdenum disulphide and titanium dioxide are supplied Chenchems, Chennai, India. Tetrahydrofuran also purchased from Chenchems, Chennai, India

**Fabrication:** The solution mixing; shear mixing and mechanical stirring are used to infuse nanoparticles into polyurethane. Molybdenum disulphide and nano particles of titanium dioxide are added to tetrahydrofuran solvent, polyurethane was added pellet wise to stirred suspension. To maintain feasible viscosity of the suspension, the concentration of the polyurethane had to be reduced in the solution. Variation was made in the concentration of polyurethane in tetrahydrofuran from 3.5 to 10 wt. %, the suspension was being continuously stirred for 1 h to ensure the complete dissolution of the pellets of polyurethane was added in the mixture and mixing was continued for another 10 min using a high speed mechanical stirrer. The resin was precipitated layer by layer and was cured for about 8 h. The samples for various tests were prepared.

## RESULTS AND DISCUSSION

**Scanning electron microscopy:** To improve the properties of nanocomposites, filler dispersion with the polymer matrix

are very important. The most critical parameter to obtain the desired properties of polymer composites is to control the interface morphology of nanocomposites. Fig. 1(a) shows that the polyurethane matrix composites (92.5/7/0.5) have fine dispersion whereas in (b) the nanoparticles of TiO<sub>2</sub> are dispersed in polyurethane matrix (89/10/1) on nanoscale has strong tendency to form aggregation makes difficult to disperse uniformly.

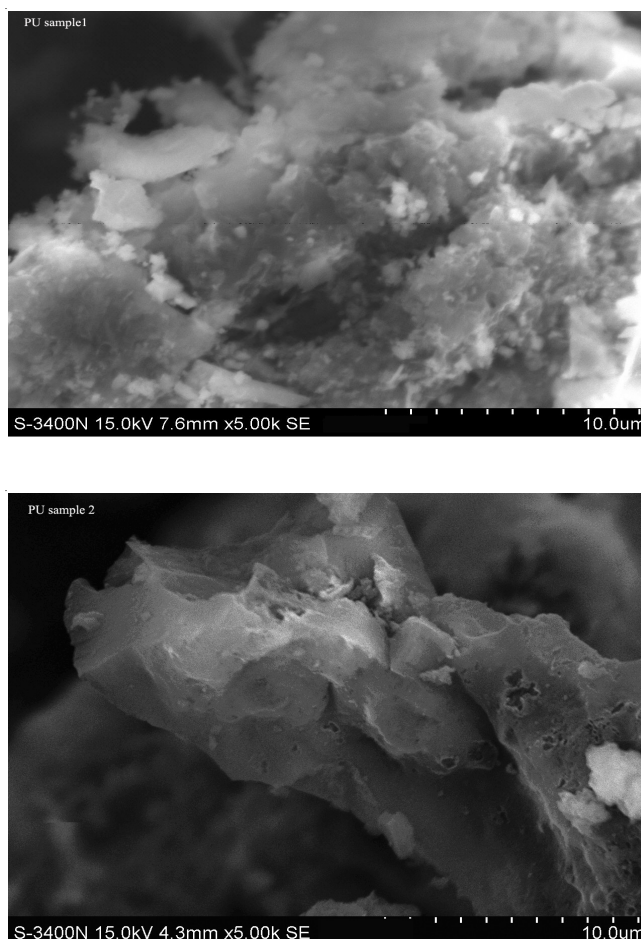


Fig. 1. Scanning electron micrographs of (a) PU/MoS<sub>2</sub> (7 %)/TiO<sub>2</sub> (0.5 %) and (b) PU/MoS<sub>2</sub> (10 %)/TiO<sub>2</sub> (1 %)

**Transmission electron microscopy:** Fig. 2 shows the transmission electron microscopy micrographs of polyurethane matrix (92.5/7/0.5) and (89/10/1) nano composites. Fig. 2(a) shows that the nanoparticles have some aggregation are clearly seen, whereas in Fig. 2(b) shows that the nanoparticles are dispersed in polyurethane matrix can be clearly on nanoscale, which indicates the formation of a nanocomposite and thus distribute in the polymer are homogeneous.

**X-ray diffraction:** Fig. 3 shows X-ray diffraction curves of the polymer, nanoparticle and composite is amorphous and does not exhibit any anisotropic behaviours<sup>20</sup>. Fig. 3(a) shows that most of the characteristic peaks at 2θ values of PU/MoS<sub>2</sub>/TiO<sub>2</sub> (92.5/7/0.5) are kept intact. According to the Debye-Scherrer formula, the average size of the nanoTiO<sub>2</sub> is calculated to be 30-35 nm. Whereas, the intensities of anatase peaks become weaker in of PU/MoS<sub>2</sub>/TiO<sub>2</sub> (89/10/1) and the peaks are widened.

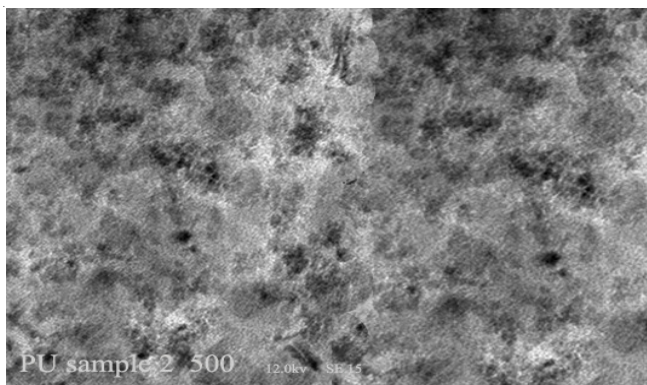
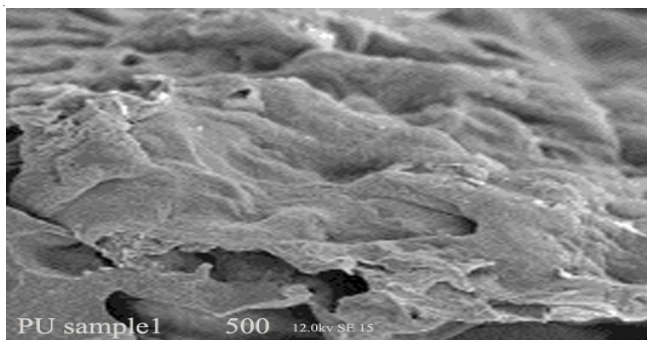


Fig. 2. Transmission electron microscopy micrographs of (a) PU/MoS<sub>2</sub> (7 %)/TiO<sub>2</sub> (0.5 %) and (b) PU/MoS<sub>2</sub> (10 %)/TiO<sub>2</sub> (1 %)

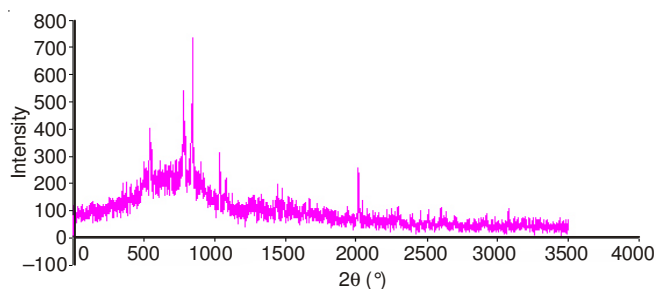
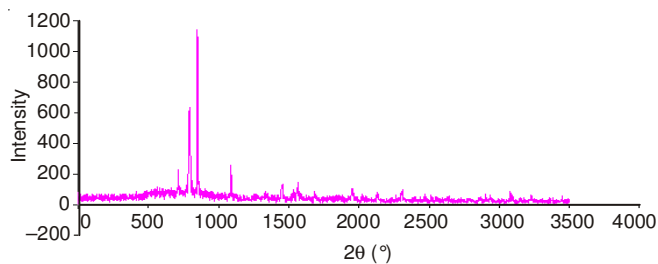


Fig. 3. X-ray diffraction patterns of ((a) PU/MoS<sub>2</sub> (7 %)/TiO<sub>2</sub> (0.5 %) and (b) PU/MoS<sub>2</sub> (10 %)/TiO<sub>2</sub> (1 %)

**Tensile properties:** The tensile properties of the polyurethane Matrix (PU/MoS<sub>2</sub>/TiO<sub>2</sub>) of varying proportions in samples 1 and 2 were shown in Table-1. The sample 1 has 7 % of molybdenum disulphide and 0.5 % of titanium dioxide were stirred mechanically with polyurethane to improve the homogeneity of the polyurethane matrix. The sample 2 of 10 % MoS<sub>2</sub> and 1 % TiO<sub>2</sub> has increase in tensile properties. Increase of percentage of TiO<sub>2</sub> has predominant increase in mechanical properties was shown in Table-1. The strength of the composites is decreased with addition of the particulate fillers is

observed by other workers<sup>21,22</sup>. The strong filler with matrix, adhesion would lead to enhanced strength of the composite. Accordingly, it is known that the tensile modulus of the composites has improved and also be interpreted as the improvement of the interfacial interaction.

Sample 1	Sample 2
19.984 M Pa	20.114 M Pa

**Compressive properties:** The compression properties of the polyurethane Matrix (PU/MoS<sub>2</sub>/TiO<sub>2</sub>) of varying proportions in samples 1 and 2 were shown in Table-2. Increase of TiO<sub>2</sub> in sample 2 increases the yield stress, whereas in sample 1 has lesser values. The fillers of MoS<sub>2</sub> and TiO<sub>2</sub> have increases the strength of the composites by increasing the adhesion with the polyurethane matrix. The strong molecular interaction of the filler with matrix improves the standard deviation of their yield stress. The sample 2 has increase in failure stress is tabulated as in Table-2.

Sample No.	Yield stress (MPa)	Standard deviation yield stress (MPa)	Stress at failure (MPa)	Standard deviation stress at failure (MPa)
1	52.12	5.21	48.72	6.14
2	54.79	5.74	51.13	6.89

**Wear:** Sliding tests were performed on polyurethane matrix composites with nanoscale TiO<sub>2</sub>, MoS<sub>2</sub> fillers. By varying the proportions of fillers, investigate the effect of filler on wear. The sliding velocity of 210 cm/s and normal load of 10 N were used to perform the wear test on polyurethane matrix composites. The wear rate on sample 1 (92.5/7/0.5) is less than the sample 2 (89/10/1) was shown in Table-3. With the increase of molybdenum disulphide and titanium dioxide increases the wear rate of the composites.

Sample No.	Sliding velocity (cm/s)	Normal load (N)	Wear rate (mm <sup>3</sup> /N-km)
1	210	10	1.0895
2	210	10	1.7897

**Fracture toughness:** The fracture toughness for various initial crack lengths was calculated in Table-4. For sample 1 (92.5/7/0.5) has lesser fracture toughness than sample 2 (89/10/1). When increases in titanium dioxide improves the fracture toughness of the polyurethane matrix composites. Several specimens were loaded to different displacements. The amount of crack extension which occurs during testing was determined using a profile projector.

**Impact properties:** The impact strength of polyurethane matrix (PU/MoS<sub>2</sub>/TiO<sub>2</sub>) composites of sample 1 (92.5/7/0.5) and sample 2 (89/10/1) were given in Table-5. Impact strength of sample 2 is higher than sample 1. Impact strength of polyurethane matrix increases by increasing the composition of the filler materials, the filler improves the impact properties of the matrix.



TABLE-4  
VALUES OF FRACTURE TOUGHNESS

Sample No	Initial Crack Length a (mm)	Fracture Toughness Gc (KJ/m <sup>2</sup> )	Avg. Fracture Toughness (KJ/m <sup>2</sup> )
Sample 1	10	0.418	0.418
	21	0.421	
	23	0.416	
	25	0.413	
	30	0.422	
Sample 2	10	0.526	0.5986
	21	0.596	
	23	0.651	
	25	0.624	
	30	0.596	

TABLE-5  
VALUES OF IMPACT STRENGTH

Sample	Impact strength (J/m)
Sample 1	400.12
Sample 2	421.73

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