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Effect of Thermoplastic Polyurethane content on properties of PC/TPU blend filled with Montmorillonite

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The present study was taken up to investigate the effect of addition of Montmorillonite (MMT) to Poly carbonate/Thermoplastic polyurethane (PC/TPU) blends. A master batch of PC/MMT (70/30) was prepared using Hake Rheomixer and PC/TPU blends filled with MMT of different compositions (90/10/5, 80/20/5, 70/30/5) were prepared by melt mixing using required quantities of master batch, PC and TPU in a twin screw extruder (TSE). Blends of PC/TPU of similar compositions (without MMT) were also prepared using twin screw extruder. The test specimens were prepared by injection molding. The samples were characterized in terms of mechanical (as per relevant ASTM standards), thermal and dynamic mechanical properties. It was observed that addition of 5 phb of MMT to PC/TPU system improves tensile strength by 34 %, flexural strength by 8.6 % and flexural modulus by 16.7 %, storage modulus by 25 % and Shore D hardness by 16 % in all the compositions containing MMT. Differencial Scanning Calorimetric (DSC) and Dynamic Mechanical Analysis (DMA) studies revealed that the Tg shift towards lower values when compared with neat PC.The heat deflection temperature (HDT) of blends with MMT was found to increase with the reinforcement.

Keywords : Montmorillonite, Polycarbonate, Polyurethane, blends.

1. Introduction : Polycarbonates (PC) known by the trademarked names Lexan, Makrolon, Makroclear and others, are a particular group of thermoplastic polymers. Polycarbonates received their name because they are polymers containing carbonate groups (-O-(C=O)-O-). They are easily worked, molded and thermoformed [1]. PC is a tough, transparent, impact-resistant thermoplastic engineering polymer with a very wide range of service temperatures. One of the biggest advantages of polycarbonate is its impact strength. However, it suffers from its high melt viscosity, which causes difficulties in processing (e.g. injection molding) and its low fatigue strength, which generates cracks at points of concentrated residual stress. A balance of useful features including temperature resistance, impact resistance and optical properties position polycarbonates between commodity plastics and engineering plastics [2]. Thermoplastic polyurethanes (TPU) are high-tech materials with a unique combination of very useful properties. They have high abrasion resistance, flexibility and shock absorbing capability. It has certain disadvantages, including high cost, moderate thermal stability and mechanical strength [3]. Montmorillonites (MMT) are nanoparticles of layered mineral silicates. It consists of stacked, layered silicates about 1-nm thickness including two tetrahedral sheets sandwitching an edge-shared octahedral sheet of either aluminium or magnesium hydroxide [4]. The literature study revealed that the polycarbonate nanocomposites showed rather good dispersion of MMT with a mixture of exfoliated, intercalated and confined morphology. The effect of MMT on the mechanical response of specimens is subjected to tensile and impact loading was investigated results in increased young's modulus and yield strength. Impact strength decreases significantly as the MMT content increases from 1 to 5% and thermal analysis demonstrated that addition of MMT leads to decreased thermal stability of Polycarbonate [5]. In another study Polycarbonate reinforced with silica nanofiller revealed that there was a strong improvement in impact strength compare to unmodified PC [6]. PC nanocomposites were prepared using organically modified clays and nano-TiO_2. There was a modulus enhancement with MMT filled material than TiO_2 nanocomposites. The mechanical and thermal properties are improved up to a 5 wt% loading. DMA results indicate improvement in storage modulus [7]. Influence of ZnO nanoparticles on the properties and wear resistance of PC was studied by F.J.Carrion and co-workers [8]. Z.Wang and co-workers studied the rheology enhancement of PC/$CaCO_3$ nanocomposites [9].

From the literature survey it is concluded that MMT is added to either PC or TPU. However no studies on effect of MMT on properties of PC/TPU blends are reported in the literature. In view of this, the present study was taken up to investigate the effect by addition of MMT 5 parts per hundred parts of blend. The TPU content in PC/TPU blend was varied from 10% to 30%. PC/TPU blends of similar composition without MMT were also prepared and their mechanical, thermal and dynamic mechanical properties were compared with PC/TPU/MMT compositions.

2. Experimental :

2.1 Materials and specimen preparation : PC was procured from by SABIC Innovative Plastics (grade Lexon 143 R, melt flow rate - 11 g/10 min at 300^0C / 1.2 kg). The ester based Thermoplastic Polyurethane (TPU) was procured from Bayer Material Science (grade Desmopan 385L, MFI 33.90 g/10 min at 190^0C/1.2kg). The layered silicate Montmorillonite (MMT) (molecular weight 549.07, density 2-2.7g/cm^3) was procured from Nanocor.

Table (1) : Formulation details of blends with and without MMT

Sample Designation	Composition		MMT Phb*
	PC (wt %)	TPU (wt %)	
PC	100	0	0
90/10	90	10	0
80/20	80	20	0
70/30	70	30	0
90/10/5	90	10	5
80/20/5	80	20	5
70/30/5	70	30	5
TPU	0	100	0

* phb – parts per hundred parts of blend

The blends of PC/TPU were prepared by melt mixing the components in counter rotating twin screw extruder (Haake Rheocord, screw diameter 16mm, L/D ratio;40). The TPU in PC/TPU blend was varied from 10-30%. In case of filled systems, MMT content was fixed at 5 phb.

Table (2) : Mechanical and HDT properties of different compositions.

Compositions	Tensile Strength at yield (MPa)	Tensile Modulus (MPa)	Elongation at break (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Hardness (Shore D)	Abrasion loss (cm^3)	HDT (^0C)
PC	70.8	2840	0.4	90.96	2209.8	62	0.05	135
90/10	57	2200	24.6	78.00	2000	52	0.045	119
80/20	45	1498	29.7	70.01	1923	50	0.042	115
70/30	30	1200	60.3	52.50	1424.8	43	0.039	112
90/10/5	60.1	2433	0.9	80.02	2100.6	56	0.042	126
80/20/5	55.8	2389	7.4	73.65	2090.6	52	0.038	120
70/30/5	40.1	1733	9.9	57.01	1662.6	50	0.035	116
TPU	4.5	0.4	100+	-	-	27	0.03	--

To prepare MMT filled PC/TPU blends, initially a master batch of PC/MMT was prepared using an internal mixer (Haake Rheomix 600P, fitted with roller rotor) maintained at 240^{0}C and operated at a rotor speed of 100 rpm for 6min. The master batch and PC were dried at 100^{0}C for 4hours and TPU at 70^{0}C for 3 hours in a hot air oven. The required quantities of PC, TPU and master batch were mixed together and extruded using TSE by maintaining temperature in the range of 180-240^{0}C and screw speed 20rpm. The blends with and without MMT prepared were designated as shown in Table (1).

The specimens for tensile test, flexural test, hardness, abrasion test and HDT were molded using a Windsor SP80DD Injection molding machine and the tests were conducted as per relevant ASTM standards. Due to the elastic behavior of TPU, the speed of tensile testing applied was 500mm/min and for other compositions 50mm/min was employed as per the ASTM D 638. DSC measurements were carried out on a TA instruments DSC Q200 thermal analysis system. The sample size used was 5 to 6 mg and was heated at 10^{0}C/min from -100 to 160^{0}C for TPU and 40^{0}C to 160^{0}C for other compositions. The HDT test was carried out according to ASTM D 648. DMA measurements were carried out on a TA instruments DMA Q800 in a dual cantilever mode (frequency 1Hz, amplitude 30μm) and test was carried out from room temperature to 200ºC at a rate of heating 3ºC/min.

3. Results and Discussion :

3.1 Tensile properties : The tensile properties evaluated as per ASTM D 638 and resulting stress vs strain plots are shown in Figure (1). It is clear from Figure (1) that PC shows a brittle failure (Elongation at break=7%) and TPU shows highly elastic nature (Elongation at break>100%). Incorporation of MMT induces brittleness within the PC matrix whereas incorporation of TPU improves flexibility. It was observed that there is an improvement in elongation with an increase in TPU content in case of PC/TPU blends.

Addition of 5 phb of MMT results in lower elongation at break. Similar results were reported for PC/MMT by Jayavani and co-workers [6].The mechanical properties namely tensile, flexural, hardness, abrasion loss and HDT of PC/TPU blends and PC/TPU with MMT are presented in Table (2).

From the results, it was observed that there is an improvement in tensile properties of PC/TPU blends reinforced with MMT compare to non reinforced blends. It was observed that addition of 5phb MMT to PC/TPU system improves tensile strength by 34% and tensile modulus by

59%. The elongation decreased in all the compositions reinforced with MMT. Similar observation was made by P.S.Archondouli and co-workers and others **[2, 14, 17].**

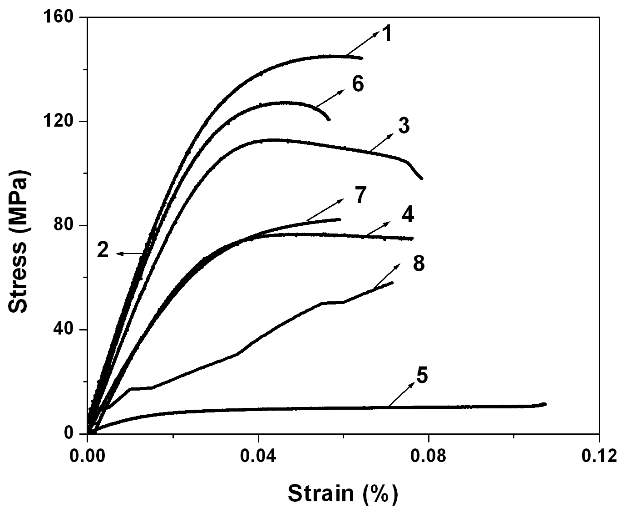

Figure (1) : Stress vs. Strain plots of 1) 90/10/5, 2) 80/20/5, 3) 70/30/5, 4) PC, 5) TPU, 6) 90/10, 7) 80/20, 8)70/30

3.2 Flexural properties : The Effect of TPU content on flexural strength and modulus are presented in Table 2. The addition of rubbery TPU to PC matrix decreases the flexural Properties. This can be attributed to the involvement of the elastomeric nature of the TPU molecular structure. Further it was observed that there is an improvement in flexural strength (by 8.6 %) and modulus (by 16.7%) values in all the compositions containing MMT. Similar behaviour is observed in the research papers **[2, 14]**.

3.3 Hardness : Addition of TPU to PC results a gradual decrease in hardness (PC- 62 Shore D, 70/30 - 40 Shore D). This is due to the presence of soft elastomeric segments in TPU. It was observed that there is an improvement in hardness values by about 4-16% for PC/TPU blends reinforced with MMT compare to non reinforced blends. Similar observation was made by P.S.Archondouli and co-workers **[2]**.

Incorporation of organically modified clay results in improvements in mechanical properties. The primary cause for such improvements is due to the presence of immobilized or partially mobilized polymer phases as a consequence of interaction of polymer chains with organically modified clays and large number of interacting molecules due to the dispersed phase volume ratio characteristics of largely exfoliated nanocomposites **[6]**.

3.4 Abrasion test : The average weight loss of the PC/TPU blends with and without MMT is shown in Table 2. The weight loss of PC/TPU blends filled with MMT and PC/TPU blends differs by about 10%. In other words, there is a slight increase in abrasion resistance of the PC/TPU blends containing MMT. Simillar behaviour was observed in surface-modified silica nano particle–reinforced poly (ethylene 2,6-naphthalate) system **[15]**.

3.5 Heat Deflection Temperature : The HDT of PC/TPU blends was found to decrease with increase in TPU content in both filled and unfilled compositions. As TPU content increases, it makes the material softer due to soft elastomeric segments which lead to lower HDT values. It was observed that there is an improvement in HDT values by about 3.5% - 5.8% for PC/TPU blends reinforced with MMT compare to unfilled blends **[10]**.

3.6 Differential Scanning calorimetry : DSC analysis of different compositions is shown in the Figure (2). The T_g values obtained from these thermograms are presented in Table (3). The T_g s of PC and TPU were found to be 150^oC and -40^oC. The T_g of prepared compositions were significantly lower compare to the tough pure PC. It is reported that in presence of MMT filler, the molecular weight of PC matrix reduces thereby the polymer chain mobility increases as explained by others **[5, 12, 13]**. Another reason behind the decrease in T_g may be due to the reduction in density which cause chain end localization and reduced chain entanglement compare with the bulk matrix [6, 10]. Our observations agree well with previous studies on PC/nanoclay and PC/TiO_2 [8, 9].

Table (3) : T_g values obtained from DSC and DMA of different compositions.

Compositions	T_g (°C) from DSC	T_g (°C) from DMA
PC	150	152
90/10	138	127
80/20	135	125
70/30	131	123
90/10/5	125	125
80/20/5	123	120
70/30/5	120	119
TPU	-40	-

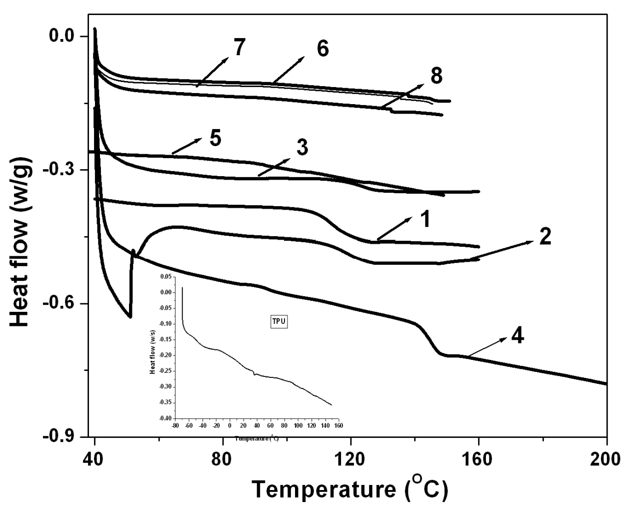

Figure (2) : DSC thermograms of 1) 90/10/5, 2) 80/20/5, 3)70/30/5, 4) PC, 5) TPU, 6) 90/10, 7) 80/20, 8) 70/30.

3.7 Dynamic mechanical analysis : The variation of storage modulus and loss modulus with temperature are shown in Figures (3) and Figure (4). From the storage modulus plot, the T_g values are obtained for all compositions (Table 3). It was observed that there was reduction in T_g values. The reason for reduction in T_g may be due to enhanced mobility of confined change in an intercalated system. Thus the damping value decreases due to the incorporation of inorganic clay platelets thereby PC/TPU blends become slightly brittle. Our observation agrees well with previous studies [6, 11].

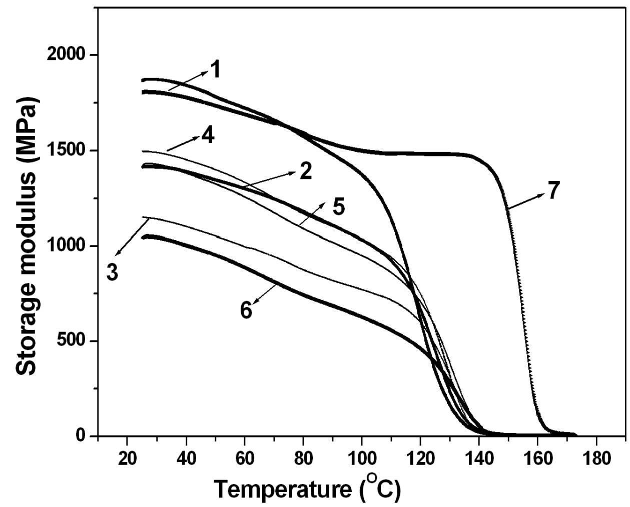

Figure (3) : Storage modulus vs. temperature of 1) 90/10/5, 2) 80/20/5, 3) 70/30/5, 4) 90/10, 5) 80/20, 6) 70/30, 7) PC.

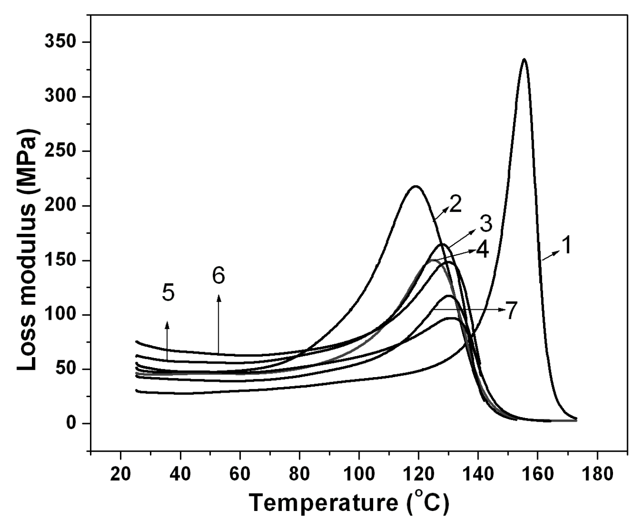

Figure (4) : Loss modulus vs. temperature of 1) PC, 2) 90/10/5, 3) 80/20/5, 4) 70/30/5, 5) 90/10, 6) 80/20, 7) 70/30.

The storage and loss modulus values of different compositions are presented in Table (4) at 35°C and 75°C. It is observed that there is an increase in modulus values in the compositions containing MMT compare to unfilled materials. The storage modulus values were increased by 25% compare to unfilled compositions. Improvement in the modulus values is due to the reinforcing effect of MMT which makes the material stiff. Our observations agree well with previous studies [7, 16].

Table (4) : Storage and loss modulus values of different compositions

Composition	Storage Modulus (MPa)		Loss Modulus (MPa)	
	35^0C	75^0C	35^0C	75^0C
PC	1794	1624	28.1	32.8
90/10	1491	1248	59.7	58.0
80/20	1421	1158	69.5	63.8
70/30	1041	799	50.1	48.8
90/10/5	1865	1631	45.3	55.6
80/20/5	1775	1492	58.3	63.6
70/30/5	1133	927	41.5	41.6
TPU	-	-	-	-

4. Summary and conclusions : This work investigates the effect of TPU content on PC reinforced with and without MMT. The different compositions of PC/TPU/MMT with varying TPU content from 10 – 30 % and 5phb MMT were prepared. It was observed that there is an improvement in mechanical properties like tensile, flexural, hardness and abrasion resistance in case of PC/TPU blends filled with MMT. Addition of 5phb MMT to PC/TPU system improves tensile strength by 34 %, flexural strength by 8.6 %, flexural modulus by 16.7 %, Shore D hardness by 16 % and the storage modulus values by 25%. DSC and DMA studies revealed that the T_g shift towards lower values when compared with neat PC. The HDT of PC/TPU blends filled with 5phb MMT increased by 6 % when compared to unfilled blends.

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