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Effect of Heat aging on Mechanical Performance of MMT Clay Reinforced Thermoplastic Polyurethane (TPU)/EPDM Rubber Blends based Nano Composite

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ABSTRACT

The high temperature resistant polymer-nanocomposite was prepared using montmorillonite nanoclay as reinforcing fillers in polyester-based thermoplastic polyurethane/EPDM blends and the effect of increasing nanoclay loadings on physico-mechanical properties like hardness, tensile strength, modulus and Elongation at break was studied. Changes in mechanical and physical properties of polyurethane thermoplastic during aging at 70°C for 168 hours were investigated. The mechanical properties of nanocomposite after heat ageing studies at 70°C for 168 hours showed improved thermal resistance and increases with loading of nanoclay. The prolongation of the thermal exposure time, leads to a progressive increase in tensile strength. These results can be explained by the increase of thermal stability due to the increase of material rigidity and the decrease in chain mobility. The evaluation of the mechanical properties from tensile tests seems to be well correlated to the creep behaviour. The dispersion of the MMT nanoclay filler in the TPU/EPDM blends was achieved using aminopropyltriethoxysilane as coupling agent and investigated by SEM. The functionalized clay indicating improved interfacial bonding between clay and polymer matrix.

Key words: Thermoplastic Polyurethanes (TPU), Ethylene propylene diene monomer (EPDM), nanoclay, heat aging, nanocomposite, mechanical properties

INTRODUCTION

Recently, many scientists and researchers attracted towards layered silicate based polymer nanocomposite because the goal of polymer-clay nanocomposites is to help, not only improve outstanding mechanical performance [1-6] but also our control over thermal resistance [6] and cost effective due to small amount of filler loading. Polymer nano-composites contain nanofiller having dimension in the 10^{-9} m (nm) scale in a given matrix [7]. Common clays are naturally occurring minerals and 2:1 ratio of the tetrahedron to the octahedron results in mineral clays, the most common of which is montmorillonite. The montmorillonite layers (platelets) having high aspect ratio of 100 – 1500 and thickness of layers (platelets) is 1 nm with high ion exchange capacity [8]. The small amount of nano-sized montmorillonite platelets can increase physical properties of polymers and impact property [9]. The thermoplastic polyurethanes (TPU) are an essential class of polymers having many beneficial properties, comprising high impact strength, high elasticity, and good adhesion. At present, these are used for the surface protection of materials like plastics, glass fiber, wood and aircraft industry. Drawback of TPU is liable to degradation, which leads to discoloration and degradation. Therefore, its usage in outdoor applications is limited. It was necessary to impart light stability to the TPU films by adding additives.

Different types of UV absorbers (UVAs) which can absorb ultraviolet light or initiate photo oxidation were added in past. Due to high loss rate by continuous conversion to radicals and limited absorption peaks in narrow UV ranges inorganic UVAs have wider absorption regions and applications. Nanoparticles such as zinc oxide and cerium Oxide were used for photo stabilization of polymers [10-16]. In the recent years, thermoplastic polyurethane is widely using as hydraulic seals and gasket in automotives and various industrial purposes, manufactured through reaction of diisocyanates and difunctional polyols [17]. The polyester-diol based TPU contains an outstanding high thermo-mechanical strength shared with high resistance to mineral oil and hydraulic fluids. However, due to saturated hydrocarbon backbones, Ethylene propylene diene monomer (EPDM) rubber has significantly good weathering oxidation and chemical resistance in severe wet conditions [18-19]. In this present work, through blending of EPDM with TPUs a composite with excellent overall mechanical performance is produced.

The Plastic materials exposed to heat may be subject to many types of physical and chemical changes. The severity of the exposures in both time and temperature determines the extent and type of change that takes place. So the scope of this work is found out the effect of heat aging on mechanical properties of nanocomposite.

EXPERIMENTAL METHODOLOGY

Materials

Aromatic Polyester- based Thermoplastic polyurethane (Texin® 255) having specific gravity of 1.21 g/cm3 and Glass Transition Temperature (Tg = -26^{0}C) was supplied by Bayer Material Science Chennai, India were used to this studies. EPDM (KEP-960) having the specific gravity of 0.87 and a Mooney viscosity of 49(ML 1+4 at 125^{0}C) with ethylene content = 70 wt.% , propylene content = 23.85 wt.% and ethylene norbonenen of 5.7 wt.% was provided by Kumho Polychem. Co. Ltd., Korea.

Montmorillonite Nanoclay (Nanomer 1.31 PS) surface modified- contains 0.5-5 wt. % aminopropyltriethoxysilane, 15-35 wt. % octadecylamine (Sigma Aldrich, Saint Louis, USA) having bulk density 200-500kg/m3 with ≤ 20 micron in size of clay were used in this project work.

Preparation of Nanocomposite

Compounding of nanocomposite was carried out in two stages. In the first stage, the removal of moisture was carried out at 100^{0}C in electric blast oven for 2 hours. After predrying the TPU, EPDM rubber were mixed in different weight % loading 4,8,12 and 16 were mixed at ambient melt temperature 190^{0}C to 230^{0}C and the screw speed was maintained at 240 rpm in to high performance co-rotating intermeshing twin screw extruder (diameter of screw = 21 mm, L/D ratio=40, model ZV20, manufactured by Specifiq Engineering, Vadodara, India) for melt extrusion. In the second stage, nanoclay were mixed in different loading at 1, 2, 3, and 4 Phr into optimised TPU/EPDM rubber blend at 8 wt. %. The compounded materials passed through the different zones of the extruder and cooling water bath were finally collected in pelletized form. TPU/EPDM blend and MMT clay nanocomposite was dried in hot air circulating oven at 100^{0}C for 2 hours. The test specimens i.e. dumbbell specimens injection moulded by high performance injection molding machine (Model - endura, Clamping tonnage = 90 Ton, L/D ratio = 20 manufactured by Electronica Plastic Machine Ltd. Pune, India).

TESTING

Heat Aging of Samples

This practice recommends procedures for comparing the thermal aging characteristics of materials at a single temperature. Samples for each different blending ratio and filler volume fraction were prepared and cut into bar shape and thermal aged according to ASTM D- 3045 in the hot air circulating oven at 70°C for 7 days. The samples were aged in the heating condition of 70°C in order to accelerate thermal aging and attain a boundary limit, which is the beginning of thermal degradation.

Mechanical Properties

The test specimens are conditioned for analysing the mechanical properties at 23±20C and 50± 5%RH for 24 hr. prior to testing.

Tensile Strength

Analysis of the tensile properties was done using an INSTRON 3382 universal testing machine. To ensure that a representative sample of each composition was tested, five tensile tests were performed for each material. The dimensions of the dumbbell shaped sample were evaluated according to ASTM D 638 [20].

Flexural Strength

The specimens used for flexural testing are bars of rectangular cross section and molded shapes. The 3 point flexural test was carried out by using Inston 3382 Universal Testing Machine (UTM), with cross-head speed of 2.38mm/min. The samples were measured as per ASTM D790 [21].

Hardness

The hardness was determined according to ASTM D2240 using Durometer (shore-D) hardness tester. The test is carried out by placing specimens on a hard flat surface. The pressure foot of the instrument is pressed onto the specimen, making sure that it is parallel to the surface of the specimen. The durometer hardness is read within 1sec after the pressure foot is in firm contact with the specimen.

Abrasion Resistance

Abrasion resistance was performed according to ASTM D 1044 with the test machine (ABRASER 5131 by Taber® Industries. N.Y., USA). The test specimen is usually a 4-in.-diameter disc or a 4-in.2 plate having both surfaces substantially plane and parallel. A 1/2-in.-diameter hole is drilled in the centre. Specimens are conditioned employing standard conditioning practices prior to testing.

Table -1 Mechanical Properties of TPU/EPDM Blends

Sample Code	TPU/EPDM (wt. %)	Hardness (Shore-D)	Abrasion Loss (mg)	Flexural Strength (Mpa)	Tensile Strength (Mpa)	Elongation at break (%)
Before Heat aging						
A	100/0	58	48.9	16.39	16.1	446.08
B	96/4	54	38.8	13.11	16.36	459.08
C	**92/8**	**52**	**32.1**	**12.58**	**17.06**	**471.70**
D	88/12	51	35.3	11.12	14.03	454.51
E	84/16	51	37.7	10.72	12.41	437.45
After Heat aging						
A_1	100/0	62	23.5	20.84	18.73	284.14
B_1	96/4	60	24.7	16.03	19.03	237.19
$\mathbf{C_1}$	**92/8**	58	25.3	13.51	19.81	230.08
D_1	88/12	53	28.2	15.27	15.91	223.09
E_1	84/16	55	29.5	15.52	14.03	227.05

Table -2Mechanical Properties of TPU/EPDM/MMT Nanoclay Nanocomposites

Sample Code	TPU/EPDM/MMT clay (Phr)	Hardness (Shore-D)	Abrasion Loss (mg)	Flexural Strength (Mpa)	Tensile Strength (Mpa)	Elongation at break (%)
Before Heat aging						
1	92/8/0	52.0	32.1	12.58	17.06	471.70
2	92/8/1	54.1	24.0	16.56	18.65	438.73
3	92/8/2	54.8	14.0	19.46	20.87	426.67
4	**92/8/3**	**55.6**	**10.0**	**21.68**	**21.90**	**415.08**
5	92/8/4	56.8	04.0	18.01	17.92	423.60
After Heat aging						
1_1	92/8/0	58	25.3	13.51	19.81	230.08
2_2	92/8/1	59.13	26.0	18.02	20.15	278.16
3_3	92/8/2	60.28	27.10	18.75	21.89	257.43
4_4	92/8/3	61.32	29.33	21.17	22.21	243.19
5_5	92/8/4	61.63	30.04	15.27	18.68	267.64

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical performance results of TPU/EPDM blends are tabulated in Table 1, which clearly shows the variation in mechanical performance with and without heat aging at different loading of EPDM content. This table also shows that addition of EPDM rubber content to TPU decreases the hardness due to soft nature of EPDM rubber by means of increasing the soft segment in thermoplastic polyurethane. Addition of EPDM also reduces the abrasion loss of TPU blend with increase in EPDM loading in blend .Tensile strength and flexural strength decreases with increase in EPDM loading but elongation% increases .On ageing the blend samples, increase in tensile and flexural strength is observed due to crosslinking effect. On ageing the blend samples, increase in hardness and decrease in abrasion resistance is observed. Addition of MMT nanoclay from 1 to 4 Phr in TPU/EPDM blends with different formulation of the materials shows in Table 2. There is an increase in hardness is found due to the presence of hard clay nano particles. Abrasion resistance reduced due to chipping of the lumps with nano MMT, which did not have good bonding with TPU. Addition of MMT increased the tensile strength as compared to unfilled TPU/EPDM blend with different formulation of the materials Elongation % for nano loaded TPU/EPDM blend was not affected much as compared to blend without nano MMTclay in Table 2 .

Increase in tensile and flexural strength was observed for all nano loaded blends as compared to pure TPU/EPDM blends. Maximum value was found for 92/8/3 formulation in MMT nanocomposite. Increases the loading of MMT nanoclay increased both the tensile and flexural strength but decreased the elongation at break. The nanocomposite shows the significantly increase on hardness, tensile strength but also shows the visible fall down in elongation at break, which indicates the good heat resistance The adding of surface modified MMT clay enhance the aging properties significantly with the increase of tensile strength and hardness because of improved interfacial bonding between polymer matrix and clay.

CONCLUSION

The incorporation of modified MMT nanoclay shows the prominent effect on the mechanical performance of thermoplastic polyurethane/EPDM rubber blend after heat aging. Tensile strength and elongation at break of TPU/EPDM blend increases and this trend carry on with an increase in clay content. The result indicates the increase in hardness, tensile strength and decrease in abrasion and elongation at break. The nanocomposite shows the significantly increase on hardness, tensile strength but also shows the visible fall down in elongation at break, which indicates the significantly very good heat resistance as unaged nanocomposite material because the bonding density of nanocomposite increases after heat aging. The adding of surface modified MMT clay enhances the aging properties significantly. In this study abrasion loss and elongation at break gradually decreases with the increase of tensile strength and hardness because of improved interfacial bonding between polymer matrix and clay. The essence of this approach is that hydraulic seals and gaskets of this material having high heat resistance with appropriate mechanical performance.

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