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Mechanical Properties of UV Irradiated Bio Polymer Thin Films Doped With Titanium Dioxide

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Abstract. This study reports on the effect of UV-light on the mechanical properties of bio polymer thin films (BPF) doped with 10 % Titanium Dioxide (TiO_2). Bio monomer was mixed with 4, 4'-methylenebis (phenylisocyanate) (MDI) to produce neat BPF and TiO_2 was added to form BPF doped with 10 % TiO_2. The film samples were irradiated in UV Accelerated Weatherometer at 50 °C with different exposure time. Universal Testing Machine was used to measure the tensile strength and the fracture surfaces of the tensile specimens were observed by Scanning Electron Microscopy (SEM). The maximum tensile strength of UV irradiated neat BPF is lower than BPF doped with 10 % TiO2 of 3.5 MPa and 4.2 MPa respectively. Stress of neat BPF was decreased from 3.7 MPa to 3.2 MPa after 144 hours of UV exposure at 50 °C while BPF doped with 10 % TiO_2 decrease from 4.7 to 3.6 MPa. The Modulus Young of neat BPF is lower than BPF doped with 10 % TiO_2 which are 0.32 GPa and 0.33 GPa respectively. The cumulative strain percentage irradiated neat BPF is lower than BPF doped with 10 % TiO_2 with 98.7 % and 113.7 % respectively. Unexposed UV light of neat BPF and BPF doped with 10 % TiO_2 were observed by SEM shows smooth fracture and brittle fracture respectively. Neat BPF and BPF doped with 10 % TiO_2 exposed to UV light show higher ductility property as compared to unexposed BPF. The higher the exposure time of BPF to UV light, revealed systematic increment of tensile strength due to increased crosslink between isocyanate and hydroxyl group.

Introduction

Thin films has attracted much attention in the investigation of mechanical properties due to their widespread application in various industries, including sensors, microelectronics, paint, data storage, and MEMS device. To future enhance thin film performance, it is necessary to measure the mechanical properties of thin films and relate them to the structure and chemistry of the film [1]. The most interest mechanical properties including the elastic modulus, ultimate tensile strength, yield strength, and failure strain were used for various applications [1, 2, 3]. The application of bio polymer thin film like coating use to protect item, improve appearance and also to use as electrical insulation. Polymer additive as filler or stabilizer is added into polymer to improve mechanical properties and as UV protection.

The solar UV level dramatically accelerates the deterioration processes in polymers at high temperature. It is the synergistic effect of high temperature and solar UV radiation that is responsible for the rapid degradation of the polyethylene films under these conditions. Weathering is a degradation process and as such is temperature dependent, i.e. it will occur more rapidly at higher temperatures. The general rule is that for every 10 °C increase in temperature the reaction rate will double. Tropical areas therefore suffer not only from an increase in UV exposure but also

faster reaction rates because of the increased temperatures. Humidity also affects the degradation processes; most weathering processes are considerably slower in hot dry climates than in hot wet climates i.e. it will occur more rapidly at higher temperatures [4].

Tensile strength is the most often specified property of plastic materials used to indicate the inherent strength of the material. Tensile strength is dependent on the molecular structure and the orientation of the polymers within a particular sample, as well as any fillers or reinforcements that may be compounded into the polymer [5].

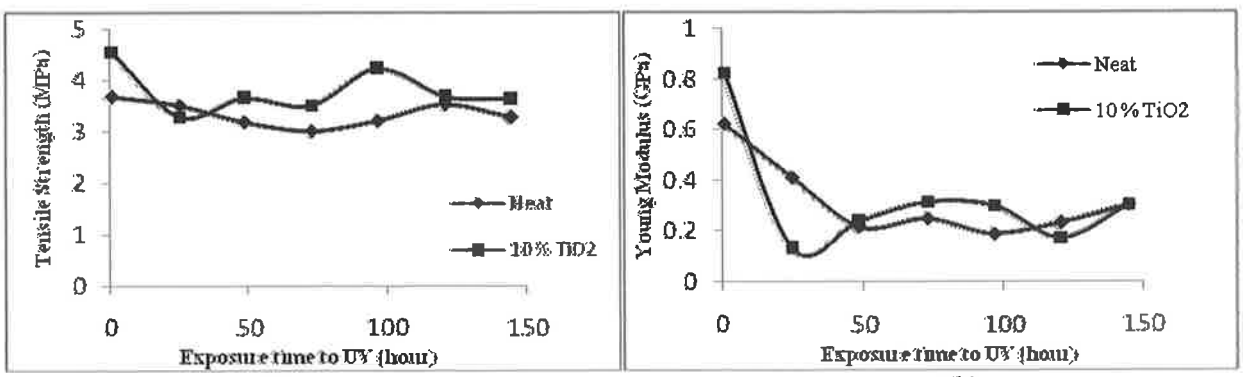
Titanium dioxide used to prevent the breaking and cracking operates as active material [6]. Rutile grade of titanium dioxide has a more compact crystal lattice, higher weathering resistance and higher light fastness than in case of anatase [7]. Salem [8] and Najat [9] studied the mechanical properties of UV-irradiated low-density polyethylene with carbon black and titanium dioxide and ferum and titanium dioxide respectively.

Methodology

Bio polymer thin film was prepared from renewable resources of waste cooking oil and mixed with 4,4'-methylen-bis-(phenylisocyanate), MDI and 10 % TiO_2 (wt by wt ratio of bio monomer) using mechanical stirrer and cast into a container [10-14]. The film was leave to cure at ambient temperature for at least 6 hours. Micrometer was used to measure the thickness of BPF samples at particular point ranging from 110 μm to 250 μm. The cure thin film samples of 130 x 25 mm were cut and put in the UV accelerated weathering tester (Haida International Equipment Ltd.) at temperature, T = 50 °C for different exposure time. The UV-irradiation of the samples was carried out using an array of UV fluorescent lamps emitting light in the region from 280 to 320 nm with a tail extending to 400 nm. Tensile strength, elongation at break and strain at break were measured by Universal Testing Machine (LLOYD Instruments) with load range; 20N, cross head speed; 500 mm min^{-1}, gauge length; 100 mm and efficiency within ±1%. Five samples were tested for each experiment and the average value has been reported. The tensile strength for the films was obtained and the results were compared with unexposed bio polymer thin film. SEM was used to examine the fracture surfaces of tensile specimens. The structure of specimen was coated with conducting material to allow electrons to flow through the specimen. Electron beam is applied to the image point on the fracture surfaces of examined specimens.

Results and Discussion

This experiment was conducted according to ASTM D4329 [15] and EN ISO 4892-3 [16] and also ASTM D882 [17].



(a) (b)

Fig 1: (a) Tensile strength (MPa) and (b) Young Modulus (GPa) of unexposed and exposed UV light (hour) for neat BPF and BPF doped with 10 % TiO_2

Fig 1 presents the tensile strength (MPa) and Young Modulus (GPa) as a function of exposure time to UV (hour) for neat and BPF doped with 10 % TiO_2. The result shows unexposed neat has lower tensile strength while 10 % TiO_2 of BPF has higher tensile strength of 3.5 MPa and 4.2 MPa respectively. The tensile strength decreases after 24 hour of UV exposure for neat BPF.

Meanwhile tensile strength of BPF doped with 10 % TiO_2 increases after 48 hours of UV exposure and remains increasing in systematic way after 72 hours until 96 hours. The tensile strength slightly decreases at 120 to 144 hours. The decrement of the tensile strength at 36 hours exposure for both neat and 10 % TiO_2 of BPF show the crosslinking interaction of TiO_2 in the polymeric structure is at the initial stage. Results show tensilized films of BPF doped with 10 % TiO_2 tend to have higher strength and moduli than neat BPF with average value of 3.8 MPa and 0.33 GPa and 3.5 MPa and 0.32 GPa respectively. This is due to the UV degradation, which causes a breakdown of chemical bonds, resulting in embitterment and also increased cross linking and chain scission, which lead to shrinking and crack. Thus neat BPF shows rapid loss of tensile strength but the addition of TiO_2 can improve its performance. This result is in good agreement with result obtained by Salem and Najat [8, 9].

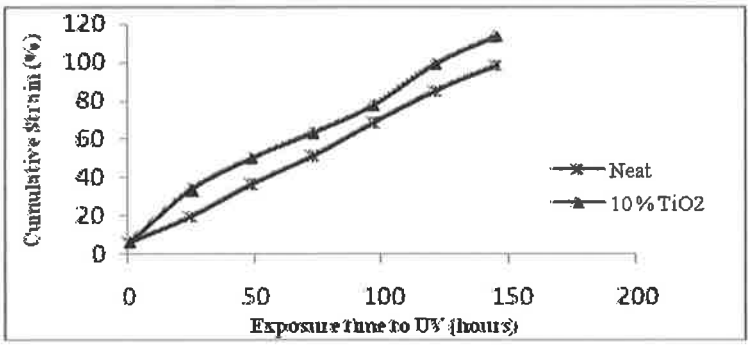


Fig 2: Cumulative strain (%) of exposure time to UV for neat BPF and BPF doped with 10 % TiO_2

Fig 2 shows cumulative strain (%) upon UV exposure time for BPF. The cumulative percentage strain for BPF doped with 10 % TiO_2 is higher than neat BPF with 113.7 % and 98.7 % upon 144 hours exposure at 50 °C respectively. The longer the UV exposure times the higher the cumulative strain percentage for both BPF. The mechanical tests reveal that both elongation at break and yield stress decreases with the ageing. This result is similar as other researcher where at UV exposure of shorter time; (until 24 hours) the tensile strength thermoplastic polyurethane (TPU), the mechanical properties were dramatically affected [18].

The observed facts can be ascribed to the physical degradation of the polymer (oxidation, chains scissions, etc.). The changes of mechanical properties during UV-exposure were essentially caused by chain scission reactions. The same results were found when studying the mechanical behaviour of polyurethane elastomers during different weathering tests. They have found that the elongation, the elastic modulus and the ultimate tensile strength decreased with the increase of the weathering time [19].

Fig 3A (a) and B (c) shows the tensile fracture surface of unexposed BPF while A (b) and B (d) after exposed to UV. SEM morphological of BPF had a smooth fracture where brittle fracture is observed. Brittle fracture is a mode of fracture characterized rapid crack propagation. This type of fracture have glassy smooth surface, flat, bright, shiny and having minimum plastic deformation as well as percentages of fracture with little yielding before the sample breaks.

Meanwhile, referring to Fig A (b) and B (d) the fracture surface shows higher ductility property as compared to unexposed BPF. This is maybe due to the hydrogen bonding interactions between the hard segments (-NHCO-O-) with the soft segment of OH group. The active participant of OH groups with isocyanate through was lead to the creation of more stress points (red circle). Thus, the maximum load is needed to bring to failure is lower for BPF after exposed to UV but the BPF doped with 10 % TiO_2 shows less brittle fracture with higher cumulative strain percentage as shows in Fig 2.

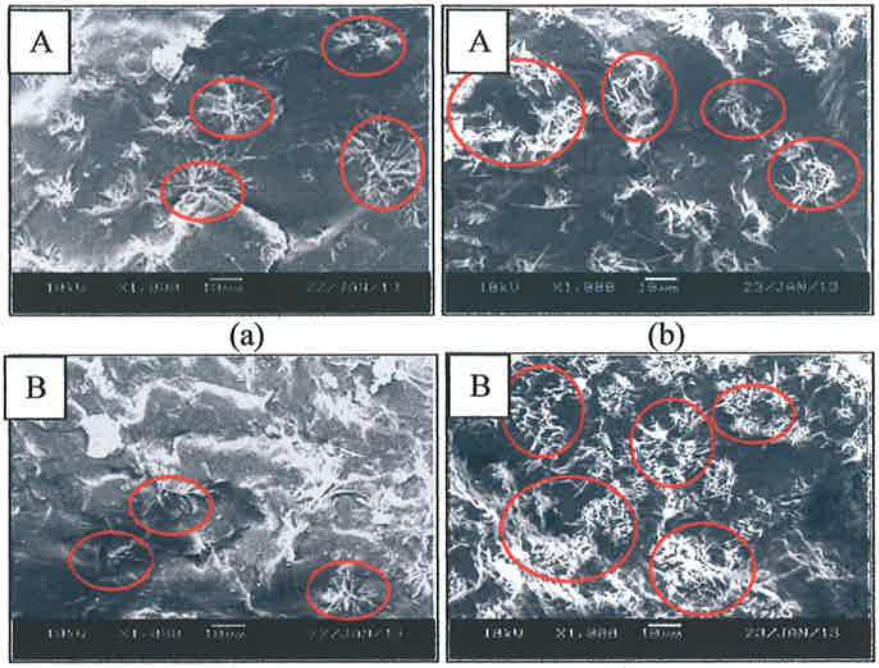


Fig 3: Morphology fracture surface at 1000x magnification of A (a) neat BPF unexposed to UV and A(b) neat BPF exposed to UV light; and B (c) BPF doped with 10 % TiO_2 unexposed to UV light and B (d) BPF doped with 10 % TiO_2 exposed to UV light, with the red circle indicated stress points

This study is a new process, particle-bonding technology, to produce bio polymer composites from agricultural commodities. In this technology, matrix-polymer complexes are formed by the interaction of micrometer-scale matrix material with particulate filler. This spontaneous process make use of the unique characteristic behavior of bio monomer adsorb to the surface of hydrophilic particles when the toluene content of solvent mixture increases. After that, van der Waals force between matrix-polymer complex particles induces the formation of even larger agglomerates. Removal of solvents from agglomerates yields the final product. Bio polymer thin film composites thus formed shows a broad range of strengths depending on the hardness of the starting raw material used as a matrix material. Incorporation of TiO_2 turns the composite into a semi-conductive polymer composite. It is also shown that TiO_2 can be used as low-cost substitute for UV stabilizer, colourant and plasticizer.

Conclusions

This paper presents the mechanical properties of UV irradiated bio polymer thin films doped with 10 % TiO_2. The mechanical properties of neat BPF and BPF doped with 10 % TiO_2 were strongly influenced by UV-light upon artificial weathering exposure. The longer time of the UV exposure was revealed the systematic increment of tensile strength of neat and doped BPF with 10 % TiO_2.

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