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Improving Unsaturated Polyester Based Nanocomposites to Resistance Environmental Changes

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Abstract:

Ultraviolet radiation (UV) accelerated the degradation and cracking of polymers. Our work focused on delay the degradation rate of unsaturated polyester outdoor by loading Carbon black (CB) and carbon nanoparticles (CNP). We prepared composites and nanocomposites from modified unsaturated polyester (UPEG) as a matrix with different wt.%. of Carbon black (5%, 10%, 20%, and 30%CB) and carbon nanoparticles (0.1%,0.2%,0.3%,0.4%, and 0.5%CNP). X-ray diffraction and a High-resolution Transmission electron microscope investigated the morphology and surface of nanohybrid materials, showed the significant homogeneity and good dispersion of CNP into the UPEG matrix. Fourier transforms infrared detected the change of structure (UPEG) when compared with the neat resin. QUV accelerated weathering tester investigated the effect of wt. percentage and types (micro or nano) of filler in the degradation process of the modified unsaturated polyester resin. Mechanical properties (tensile strength and Hardness shore D) were done before and after the exposure of the sample to UV degradation. Hardness was improved with CNP than CB filler even at high content of 30% CB. The UPEG/CNP had high stability and their rate of degradation was more slowly than in net resin, also when it comparison with UPEG/CB hybrids. The thermal stability of UPEG/ CNP was enhanced compared to that of unfilled UPEG and determined by Thermal gravimetric analysis.

Keywords: Thermal aging, UV stabilizer, nanocomposites, unsaturated polyester, carbon nanoparticles, and environmental changes

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1. Introduction

Ultraviolet (UV) light produces free radicals in the polymer from the chemical bonds, and these free radicals generate color change, separation, and degraded physical properties by breaking chemical bonds.

As a good way of photochemical conversion into polymeric materials, the spectral irradiance of the practical polychromatic light source would be widely thoughtout, particularly in the case of yellowing when it is the product of photodegradation and yellowing after chromophores have been photobleached. It is normal to observe this phenomenon. The degradation process will be mitigated while UV stabilizer was added as additives to the samples. If a polymer material is to be applied outdoors, a UV stabilizer must be functional for the polymeric material to block or decrease photochemical reactions. This is now an established area that is now being spun out into durable commercial applications; it is a critical feature of the overall deployment of goods used in both indoor and outdoor applications where there may be adverse effects of sunlight and humidity. The most common source of polymer composite dissatisfaction when exposed to the natural environment is ultraviolet (UV) rays from sunlight [1].

Theextremely viscous liquid polymers[2], are unsaturated polyester resins within a broad range of polymer resins. In this type of the polymer, consequent crosslinking is likely to make them hard because of the presence of unsaturation [3]. It is also possible to produce a wide variety of thermoset products with a wide range of mechanical and chemical properties by combining the polymer with different reinforcements, fillers and curing with free-radical initiators [4, 5].

Due to their cost-effectiveness and greater performance than other resin forms, unsaturated polyester resins find diverse applications. However, the introduction of these resins to be used as a structural material is constrained by some shortcomings. Such drawbacks include low fire retardant properties, deterioration of UV radiation exposure, and diffusiveness of moisture. In order to address these drawbacks, some additives have been used, such as aluminum trihydroxide (ATH) and carbon black. By preserving successful fire retardant properties, ATH works, and carbon black provides the UV resistance composite. The main flame retardant agent modes have been reported [6].

Notwithstanding the way that unsaturated polyesters are had extraordinary consideration and applied extensively, genuinely of studies have been accessible on their long haul enduring/photochemical conduct [7-15].

UV radiation is disposed of by Aliphatic Aromatic Polyesters. In the aromatic domain, benzene rings have been introduced to prevent UV degradation by absorbing UV energy and serving as a buffer against energy sinks. On the other hand, in the ester bonds, carbonyl groups captivate UV radiation energy and cause chain splitting [16]. Long frequencies (around 300 nm) photolysis and photooxidation of movies, uncrosslinked and crosslinked utilizing styrene as well as methyl methacrylate (MMA) were examined and photochemical changes were broke down through FTIR and UV-Vis spectroscopy[17-20]. Anyway, the main discoloration was analyzed concerning appearance angles. Be that as it may, concerning appearance viewpoints, the main staining was considered. Practically all maleate bunches isomerize into fumarate bunches in the planning of unsaturated polyester gum dependent on maleic anhydride, isophthalic corrosive, and propanediol by means of polycondensation. The key engrossing chromophores are the excess fumaric two fold bonds (focus contingent upon styrene content and crosslinking settings) and isophthalic bunches [17-20]. Yellowing is noticed and attributed to the recombination of extremists happening in the polyester chain and without oxygen. The presence of oxygen impacts the possibility of the essential reaction things subject for yellowing. The looking at non-crosslinked materials don't yellow in the insufficiency of oxygen and in actuality, close to no inside seeing oxygen. The support of polystyrene a solicitation in the reestablished sap is the explanation behind yellowing and MMA crosslinking generally diminishes photo staining.

Carbon filler have been fused in different kinds of the grid which incorporate thermoplastics, for example, polypropylene [21,22], poly vinyl alcohol [23], polyaniline[24,25], and thermosets as polystyrene[26,27], polyesters[28], epoxies[29,30], and acrylic acid, methyl methacrylate (MMA)[31],

In this study, we prepare composites and nanocomposites based on unsaturated polyester. fillers are carbon black, and carbon nanoparticles. Polyester was modified by added an excess of ethylene glycol to become more flexible material. The loading of carbon black and carbon nanoparticles was done due to the increase of UV weathering stability.

2. Materials and Methods

2.1. Materials

Carbon Black Nanoparticles (CPN), Aldrich Co., synthesized by laser decomposition, with average particle size of 30 nm and purity 99wt%. Carbon Black, El-Nasr Pharmaceutical Co. of Chemicals, 96%, Mw 60.05). Ethylene Glycol, El-Nasr Pharmaceutical Co. of Chemicals, Methyl Ethyl Ketone Peroxide (MEKP), Fluka Chemika, Cobalt Octuate, El-Nasr Pharmaceutical Chemicals Co.

2.2.Preparation of modified Unsaturated Polyester (UPEG)

In 100 ml beaker 20 gm unsaturated polyester prepolymer and 3 gm (15%) of ethylene glycol were sonicated at 30 °C for 30 min. the new resin was poured in Petri dish then we added 0.5% of MEKP (Methyl ethyl keton peroxide) as curing agent and cobalt octoate as initiator at room temperature to produce UPEG film.

2.3. Preparation of Unsaturated Polyester/ Composites (CB/UPEG)

A series of modified unsaturated polyester as matrix and Carbon Black as reinforcement (UPEG/ CB) composites was prepared by sonicatore with the following molar ratio 5, 10, 20, and 30 % wt. in 100ml beaker 10 gm unsaturated polyester (UP), 1.5 gm (15%) of ethylene glycol (EG) and 0.5 (5%) gm of CB was sonicated at 30 ^{0}C for 30 min. the composite resin was poured in petri dish then we added 0.5% of MEKP (Methyl ethyl ketone peroxide) as curing agent and cobalt octuate as initiator at room temperature to introduce UPEG/CB composites.

2.4. Preparation of Unsaturated Polyester/ Nanocomposites (CNP/UPEG)

Another series of the UPEG/Carbon nanoparticles (CNP) nanocomposites were prepared by sonicatore with the following molar ratio 0 .1, 0. 2, 0. 3, 0. 4 and 0. 5 % wt by the same maner.

2.5.Characterization

GPC Perkin Elmer 200 instrument. The HPLC grade Tetrahydrofuran(THF) was rummage as a portable stage at a stream pace of 1.0 ml/min. Fourier-Transform Infrared Analysis (FTIR) worked in the transmission mode, in the wavenumber scope of 4000-400 cm^{-1} by association with KBr plate powder on a Mattson 1000, arrangement LC usable, Issue I (0791) spectrophotometer. X-beam diffraction examples of various structures have been examined utilizing an advanced PAN logical diffractometer, Xpert PRO model. A thermo gravimetric analyzer (TGA) was utilized to look at rot conduct and warm steadiness of the restored nanocomposites utilizing an indicator type: Shimadzu TGA-50H. Stander analyzer weight was around 8-10 mg and the investigation was accomplished at a warming pace of 10°C/min from 25 to 600 °C for nanocomposites tests under nitrogen air. Ductile tests were performed by the ASTM D412-80 test strategy and were done utilizing an Instron testing machine (Model H10KS from Hounsfield Co., England) at 25°C and the crosshead speed was 5 mm/min. Three examples of UPEG definition were tried. The enduring contraption utilized for this work was a QUV cyclic UV enduring gadget (120 V, 60-Hz model made by the Q-Panel Company, USA). This gadget utilizes eight fluorescent UVA 340 lights (UV range 365-295 nm). The 152.4 _ 304.8 mm SMC test boards were uncovered in the QUV bureau for a sum of 320 h. the cycle suggested in ASTM G154 (American Society for Testing and Materials).

3. Results and Discussion

3.1. Structure Analysis

Gel Permeation Chromatography (GPC), The number normal (Mn) of polyester tar test is 1824, weight normal (Mw) is 5432 and polydispersity (Mw/Mn) is 2.98. Gel saturation chromatography of polyester pitch. Unsaturated polyester tar for assertion to distinction applications unsaturated polyester gum for talent applications[32].

3.2. FTIR analysis

Figure 1 shows the FTIR Analysis of UPEG, 5 % CB/UPEG, and 10% CB/UPEG. the peaks that appear at 1286 cm^{-1} for CH2 winding, 1379 cm^{-1} for CH3 balanced bowing, 1600 cm-1 for ester ring extending, 1728 cm^{-1} for CO extending vibrations for range. The groups in the reach 2900–3100 cm^{-1} relate to expanding vibrations of CH group, for example, CH_2 and CH_3.The 3421 cm^{-1}band may be restricted to expanding the vibration of OH meetings, as confirmed from the spectrum. For 10% carbon black (CB) content in the composites, the spectra, the extending vibration of the OH group is transferred to a lower wavenumber 3408cm^{-1} It can very well be recommended from this result that hydrogen bond formation can occur between UPEG and carbon black (CB) particles. Figure 2. Show UPEG and 0.5 %CNP/UPEG the noticed peak of carbonyl (C=O) extending band of UPEG at 1708 cm^{-1} has been moved to a higher recurrence of 1724 cm^{-1} for UPEG/CNP. This might be shown to ester bond arrangement (C-O-C of UPEG with the pre-owned nanofiller Two peaks showing up at 1450 and 1380 cm^{-1} for neat UPEG has been moved to higher shift of 1455, 1395 cm^{-1} for UPEG/CNP. This might be given the bond formation between the loading nanofillers and UPEG [33].

3.3. Morphlogy of nanocomposites materials (CNP/UPEG).

3.3.1. XRD Analysis

Figure 3. shows the XRD profiles of UPEG, 0.1CNP/ UPEG, 0.2CNP/ UPEG, and 0.5CNP/ UPEG. The UPEG contain a sharp peak at the scattering angle of 2θ = 20.23 with lattice spacing was 3.18 Å. A new peak appeared at 2θ = 25.02, 25.21 and 25.71 with lattice spacing 3.56 Å, 3.72 Å & 3.55 Å. This expansion in the lattice borderline might be ascribed to the intercalation of nanofillers into the network, giving a cross section expression in UPEG gems. From these outcomes, it tends to be resulting that the nanofillers are appropriated well in the resin lattice, prompting an expansion in the interfacial control among filler and framework, which is reliable with the recently revealed result for carbon black enhanced the resin [34]. Additionally, a slight abatement in summit width and an expansion in peak power for the nanocomposites were likewise noticed.

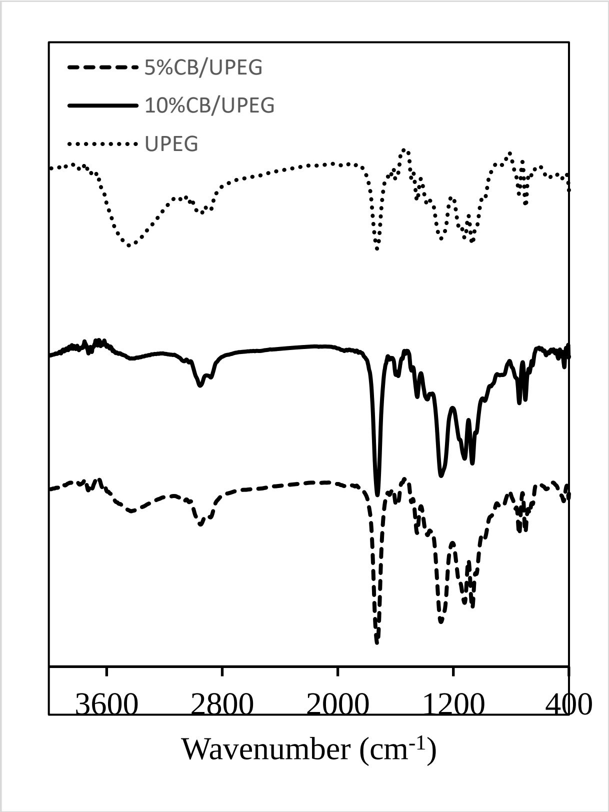

Fig (1): FTIR of UPEG, 5 %CB/UPEG & 10 %CB/UPEG

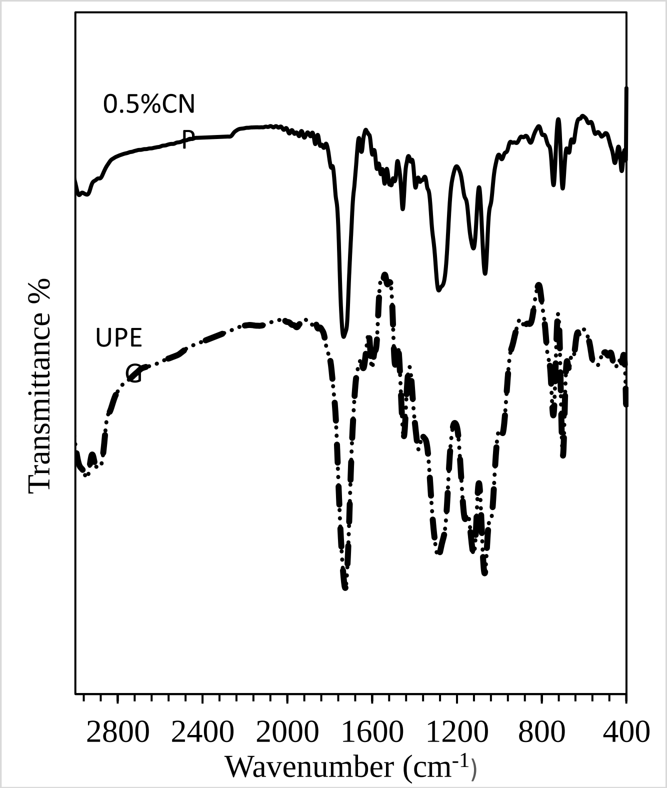

Fig (2): FTIR of UPEG & 0.5 %CNP/UPEG

3.3.2. TEM photograph

Figure 4. shows micrographs of carbon nanoparticles black (CNP) itself and 3%CNP/UPEG. The good distribution of sphrical shape of carbon nanoparicles in unstaured polyster matrix.also the hemogeinty of two types of matrial with each other which lead to enhance the properties of nanohybrid.

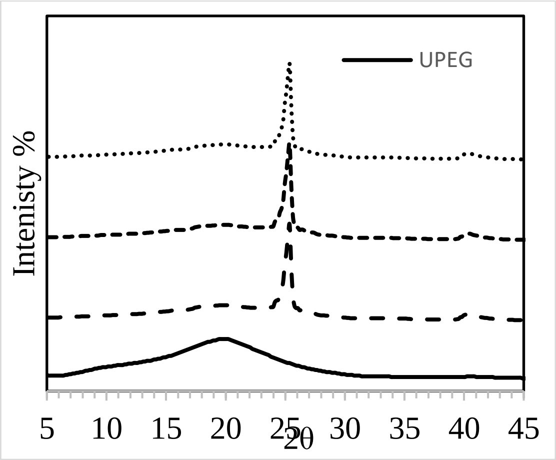

Fig (3):. XRD of UPEG, 0.1 %CNP/UPEG, 0.2%CNP/UPEG & 0.5%CNP/UPEG

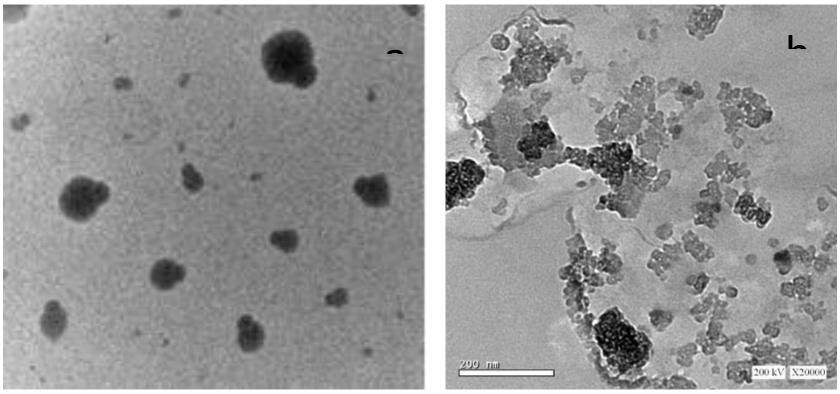

Fig (4): TEM of a) carbon black nanoparticles (CNP), b) 0.3%CNP/UPEG

3.4. Thermal properties

Figure 5 shows the TGA thermograms of different UPEG/CB samples. The weight loss appears to begin about 210°C, and the loss trend appears to be different for different samples. Clearly, weight loss is slowed as the temperature rises in response to the increase in CB material. The initiation of decomposition shifts to higher temperatures as the CB content rises. Consequently, As a result, the composites' thermal stability improves significantly. The stabilization effect of composites due to CB can be influenced by a number of chemical/physical processes. The reaction of free radicals from the resin matrix with CB is one of these mechanisms. The CB surface acts as a barrier to the adsorption of volatile degraded components. As a result, the molecular mobility of the resin molecules surrounding CB is reduced. The TGA of thermal degradation of UPEG takes place in four stages for UPEG/CNP samples, with the start of weight loss occurring at about 303 °C. Figure 6, TGA of UPEG/CNP nanocomposites shows that the decomposition of the UPEG/CNP composites occurred at 318 °C, which is different from the UPEG. This may be due to cross-linked resin composites' decomposition activity. The dissociation of C–C chain bonds and the release of styrene at the dissociation site have been attributed to the degradation of cross-linked resin [34,35]. Thermal properties were improved when CNP filler was used at a concentration of 0.5 percent. This is thought to be due to bond forming or the barrier effect of rigid CNPs, which prevent the cross-linked chain segments in UPEG/CNP composites from moving thermally [33].

3.5. Mechanical Properties

Figure 7 & 8 shows the hardness test type Shore (D), the hardness of unsaturated polyester (UPEG/CB) composites increments with CB content, the CB associated with the UPEG network acts like physical crosslinking centers and along these lines limits the advancement of UPEG chains. The improvement in the modulus and hardness may be achieved by the strong participation between the unsaturated polyester changed organization and CB, which prompts extraordinary dissipating of CB in the will disperse of CB may influence the network structure, in this way increase both the modulus and hardness [34]. Figure 8. shows UPEG/CNP the hardness regards increase with growing weight paces of the two fillers up to 30% and the hardness had shown up at its most outrageous assessment of 60 and 56 at 0.5%wt CNP and 30% independently.

3.6. UV resistance of carbon nanoparticles and carbon black filled samples

All exposed UPEG/CNP samples came back to their original weights after the accelerated weathering testing (Table 1). There was no weight loss in the UPEG/CNP samples. In contrast, samples of carbon black decreased in weight by approximately 0.57% (Table 1). There was some weight loss of the carbon black and carbon nanoparticles during the accelerated weathering test, however this weight loss negligible with the weight loss of the neat resins (UPEG). No visual signs of UV exposure appeared on the 30% samples No significant warpage was noticed on any of the samples tested. Accelerated weathering test results are summarized in Table1.according to the change in weight loss, carbon black and carbon nanoparticles were all around scattered at the grid of composites and nanocomposites and framed a hindrance to examine the impact of carbon stacking on the UV stability of the polymer partial class. The tensile modulus and elongation at break have been estimated in table 2, the effect of UV exposure with the carbon filler content, on Young's Modulus behavior. The results show an irrelevant decrease in the tensile modulus of the nanocomposites and composite on the foreword to UV radiation. The reduction in modulus is more at higher UV introduction times [6]. Another insight that can be made is that the rate decreased in the tensile modulus at higher loadings of carbon black is likewise less. The diminishing in modulus can be seen as the breaking of nuclear bonds on introduction to UV radiation. This security breakage makes free progressives that participate in the chain reaction. More unremarkable chains outlined to make the polymer weak. Moreover, introduction to UV causes heat which is extra liable for the corruption of a composite. By advantage of carbon and carbon nanoscale demolished the UV radiation obstructing the photo-oxidation by its surface substance properties. Table 2. Shows the rate reducing of strength of the nanocomposite test on the foreword to UV appeared differently in relation to the base model with no UV exposure. For similar UV outline conditions, for models with 0.4 % CNP added substance, the tensile strength reduced by 60 and 46 MPa, independently on when UV presentation. As seen from table 2, on an illustration of 0.5% CNP and UPEG, the strength improved by 45% on UV when introduced exclusively. As needs are, it will in general be seen that at higher loadings of carbon nanoparticles, the extension in tensile module.

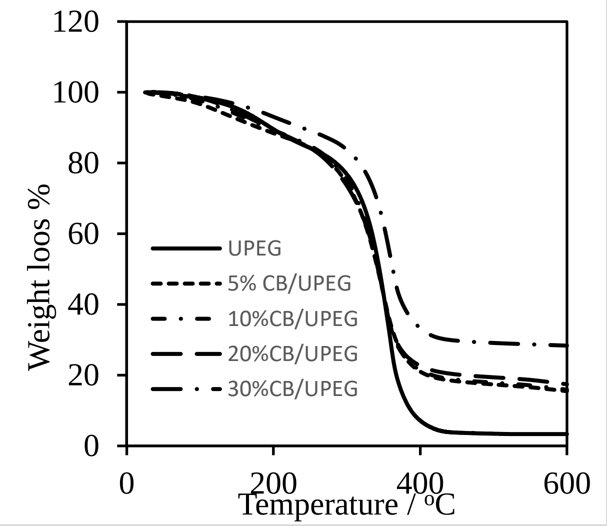

Fig (5): TGA of UPEG/CB composites

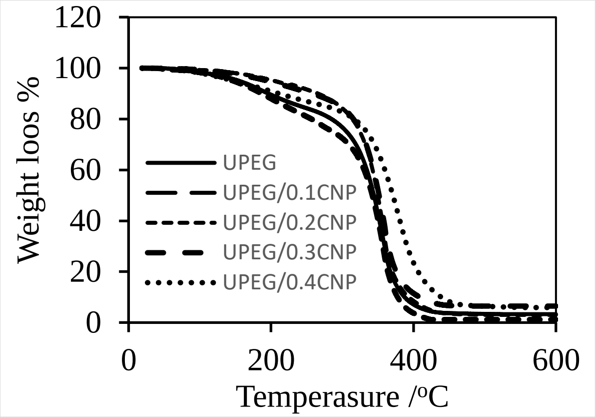

Fig (6): TGA of UPEG/CNP nanocomposites

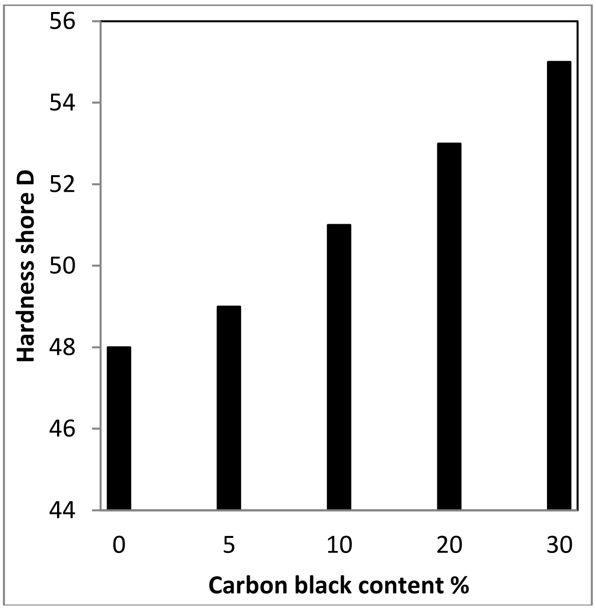

Fig (7): Hardness value Shore (D) of CB/UPEG samples

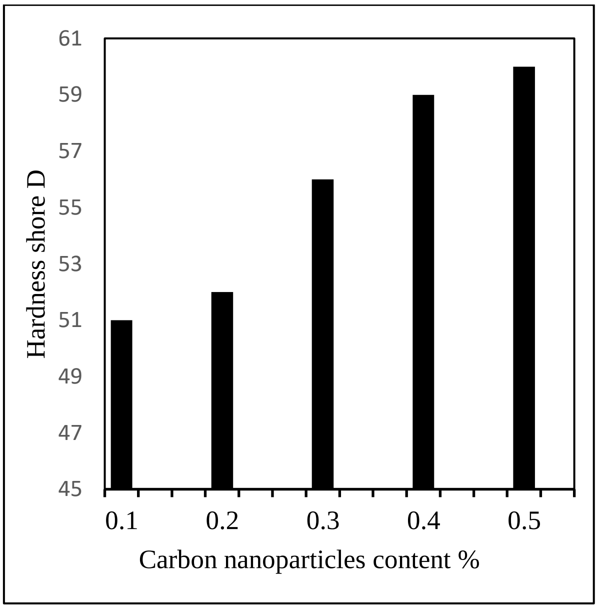

Fig (8): Hardness value Shore (D) of CNP/UPEG samples

Table (1): Initial weight, final weight, and weight change for samples exposed in a QUV weathering test for 320 hrs.

panel	Intial wt.(g)	Finial wt (g)	Change in wt.(g)
UPEG	5.541	5.140	0.401
5%CB/ UPEG	5.341	5.331	0.01
10%CB/ UPEG	5.567	5.531	0.036
20%CB/ UPEG	5.791	5.781	0.01
30%CB/ UPEG	5.612	5.612	00
0.1CNP/ UPEG	3.561	3.553	0.098
0.2CNP/ UPEG	3.437	3.433	0.004
0.3CNP/ UPEG	3.871	3.870	0.001
0.4CNP/ UPEG	3.523	3.523	00
0.5CNP/ UPEG	3.961	3.961	00

Table (2): Mechanical properties of tensile strength and elongation at break changes before and after the samples exposed in a UV weathering accelerator test for 320 hrs

panel	Before UV exposure		After UV exposure	
	Tensile strength (Mpa)	Elongation at break (%)	Tensile strength (Mpa)	Elongationat break (%)
UPEG	50	2.9	40	1.8
5%CB /UPEG	53	2.4	44	2
10%CB /UPEG	56	2.1	41	1.9
20%CB/ UPEG	56.6	1.7	39	1.2
30%CB /UPEG	57	1.2	34	1.1
0.1CNP /UPEG	52	2.7	51	2.6
0.2CNP /UPEG	55	2.5	52	2.3
0.3CNP/ UPEG	57	2.4	54	2.2
0.4CNP /UPEG	59	2.1	56	2
0.5CNP /UPEG	60	1.9	58	1.6

4. Conclusions

- Modified unsaturated polyester (UPEG) by adding 15% of ethylene glycol of the pristine polyester was synthesized.
- The modified unsaturated polyester (UPEG) has molecular weight higher than the neat resin.
- The homogeneity of carbon black enhanced the characterization of composites.
- The good dispersion of carbon nanoparticles has great effect for most properties of the nanocomposites.
- The nanofillers act as a reinforcement of the mechanical properties (tensile modulus and hardness) of modified unsaturated polyester (CNP/UPEG) more than the other.
- TGA illustrate the effect of CB& CNP % to enhance thermal and char yield of matrix.
- Carbon nanoparticles are the heights value of fillers when comparison with CB filler.
- UV stability has the optimum value at 0.5%CNP. Also, it acts as thermal aging of UPEG resin.
- The protection of UPEG film against UV radiation is increasing with increased the fillers contents.

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