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Influence of Nanofibrillated Cellulose on Mechanical and Thermal Properties of Polyester Composites

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Abstract

This study reports the effects of bio-based CNF (nano fibrillated cellulose) fillers on the properties of PE (Polyester) composites. In the study, the PE was mixed with CNF) in the ratios of 0.5, 1, and 1.5 % using Methyl Ethyl Ketone Peroxide (MEKP) and Cobalt octoate (CoOc) as initiator and catalyst, respectively. For characterization, chemical and thermal analyses were carried out with FT-IR and TGA. Mechanical properties were investigated with Universal Testing Machine, and morphological properties were investigated with SEM. In consequence, minor altered vibrations were observed in FT-IR while thermal stability decreased. The compressive strength of composites was lower than that of the neat PE composite whereas tensile strength increased. Mostly homogenous dispersion was also seen in the composites. This study reveals that CNF fillers are able to applicate in PE resin which used in the pipeline sector.

Keywords: Polyester, CNF, mechanical properties, thermal properties

1. Introduction

Recently, industries have begun to allow new projects related to the green material based composites which reveals high strength at a small specific weight as well as can be tailored for certain aims [1].

Fillers (silica, basalt, aramid, carbon fibers) are important in the composite production since used as a reinforcing agents. However, those materials are not well welcomed due to environmental concerns since mostly obtained from synthetic ways. Therefore, green material based filler for composite fabrication have attracted recently.

Although a number of green material are found in the environment, the most encountered green material is nanocellulose [2-5]. Nanocellulose which consisted of β-1,4 anhydroglucose monomer units revealed superior mechanical properties and biodegradability. And those are abbreviated as nano fibrillated cellulose (CNF), nano crystalline cellulose (CNC) and bacterial cellulose (BC) after isolating from vegetables or synthesizing from bacteria via with different process [6,7]. Of these types, CNF has gained more interest since reveals a higher aspect ratio, and gerater interfacial adhesion. Thus, they are used in 3D bioprinting, membrane, medicine, polymer and electronic film [8].

The other important player in the composite production is resin. There are a variety of resins used in the composite industry. Unsaturated polyesters (UPs) which consisted of phthalic acid, maleic anhydride (C=C double bond), styrene (curing agent), toluene (solvent), and ethylene glycol (viscosity modifier), are the most widely used types since having cost-effective, ease of use, and superior mechanical properties. Thus, UP is preferred much more in the applications such as adhesives, automotive components, boat hulls, aircraft and appliance components.
Recently, pooling the polyester with biodegradable green material is of great interest. Therefore, several studies have been conducted to give detailed information on this aspect [9]. First study was carried out by Chirayil et al. that they produced CNF based PE composites to reveal their mechanical properties. They observed that CNF enabled higher tensile strength due to the fact that transferred the stress to the CNF effectively [10].

In another study, rheological parameters were investigated in detail by the same group that CNF's shear thinning behaviour was not initially changed during interaction whereas it was converted to Newtonian behaviour in the high shear. Also, lower gelation time was determined after CNF. This circumstance reveals that the CNF enabled faster cure-accelerating ability by carrying out early network formation [11]. In other study, Ansari et al. [12] conducted study to investigate CNF based PE composite's mechanical and thermal properties. The produced composites, at the high concentration, gave higher glass transition temperature, modulus, ductility as well as fracture toughness. Also, the study revealed that CNF based PE composites, having 40 wt %, was able to be produced with high thermal and mechanical properties [12]. Lavorati et al. [13] joined the trend and produced polyester composites having CNF. They observed that CNF enabled higher dynamic-mechanical properties as well as thermal stability whereas water absorption was not influenced significantly [13].

In the present study, CNF-PE composites were prepared with different CNF ratios (0.5 wt. %, 1 wt. % and 1.5 wt.%) via compression molding method. Afterterward, chemical, thermal, mechanical and morphological properties of the produced CNF-PE composites were investigated.

2. Materials and Methods

2.1 Materials

In the present study, the orthophtalic acid resin (PE) (1.12 g/cm^3. 66% solid content, Polipol 3562-SR, Turkey) . methyl ethyl keton peroxide (MEKP) (ER 59, Akperox. Turkey) and cobalt octaoate (CoOc) (RC88, Akkobalt, Turkey) was chosen as matrix, initiator and catalyst, respectively. The used CNF were prepared and produced with the method which explained before studies by applying enzymatic hydrolysis and high-pressure homogenizing (M-110Y, Microfluidics Corp., USA) [14].

2.2 Design of The Experiments

In the present study, CNF based polyester composites were fabricated via compression molding method with different ratios 0.5 wt. %, 1 wt. % and 1.5 wt.% in certain conditions (those are abbreviated as a PE-0,5 CNF, PE-1 CNF and PE-1,5 CNF). Afterward, chemical, thermal, morphological and mechanical properties were investigated with Fourier Transform Infrared Spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscope (SEM), and Universal testing machine (UTM), respectively.

2.3 Composite Fabrication

Composite fabrication was carried out in three stages. In the first stage, orthophtalic resin and CNF were mixed and sonicated in the ultrasonic homogenizer (1 min at 35 KHz) (Bandelin, RK 100 H, Germany) to gain the homogeneity. In the second stage, MEKP, and CoOc were poured on the PE resin found in the beaker with micropipette (volume ratio of 100:1:1). Then, the former mixture was stirred in the magnetic stirrer (30 sec. at 300 rpm). The mixture was moved to the ultraturrex disperser to improve homogeneity and mixed again (30 sec. min at 800 rpm) (Heidolph, Hei TORQUE 100, Germany) before reaching resin's gelling time. Finally (as last stage), the prepared resin mixtures were moulded in the glass molds (25cm*45cm*10mm) to form CNF based PE composites and kept according to ISO 291 (4 h, 20±2˚C and one week, at 80 °C). Pre-mold, release agent (Poliya, Polivaks SV-6, Turkey) were applied to the molds. Afterward, the produced composites were cut in laser cutting device for mechanical analysis with controlled levelling. Experimental demonstration was given in Figure 1.

Figure 1. Experimental demonstration.

a: Interaction of PE resin, initiator and catalyst
b: Addition of CNF filler
c: Preparation of dog-bone shaped specimen
d: Analysis of tensile strength
e : Analysis of compressive strength

2.4 Composite Preparation

Chemical interaction carried out between CNF and PE was given in Figure 2.

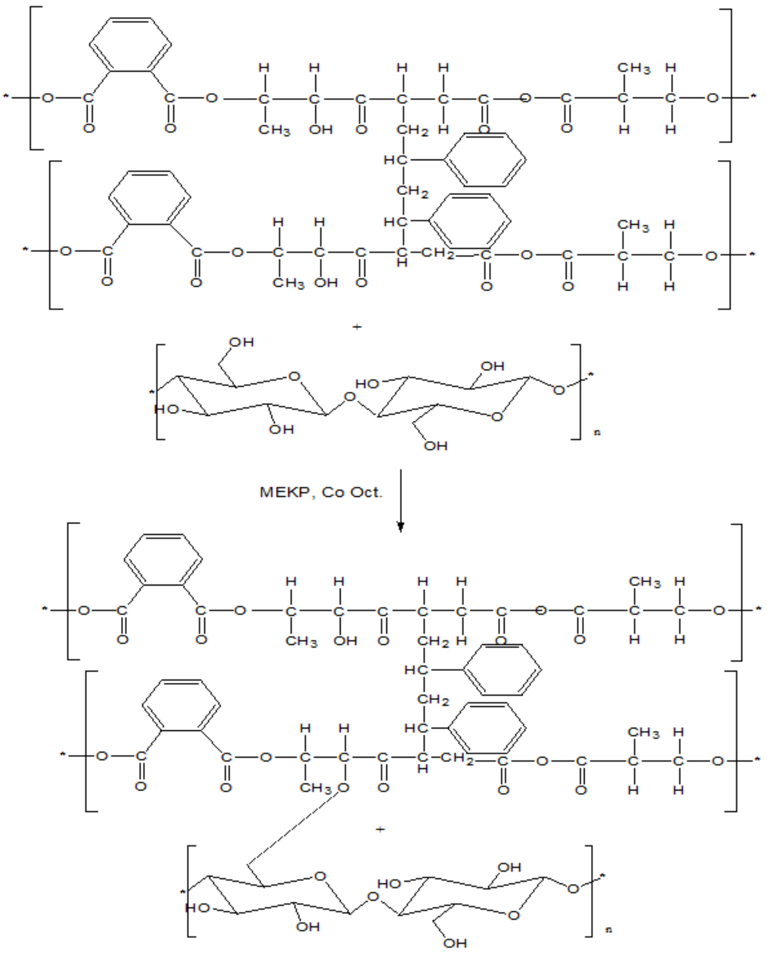

Figure 2. Chemical interaction between CNF and PE.

2.5 Chemical Analysis

The FTIR device (IR Prestige-21, Shimadzu, Japan) with attenuated total reflectance (ATR) attachment was used to investigate chemical interaction carried out between CNF and PE (4000-600 cm^{-1}, 20 scans, resolution of 4 cm^{-1}).

2.6 Thermogravimetric Analysis (TGA)

For TGA, composites were placed into Pt pan as 5-10 mg following dried overnight. Afterward temperature was applied to composites from room temperature to 800 °C (heating rate of 10 °C/min, N_2 atm) (DTG 60, Shimadzu, Japan).

2.7 SEM

For determination of the morphology, the specimens were placed with tweezers onto a substrate with carbon tape and then coated with a thin layer of Au/Pd for taking surface and cross-section pictures at SEM (FEI, Quanta 250, Netherland).

2.8 Mechanical analysis

For determination of the mechanical properties, tensile strength and compressive strength were applied to specimens in the universal testing machine (100 kN, BESMAK, Turkey). Tensile strength was performed until tensile failure occurred (cross-head speed of 5 mm/min, 25°C). Compressive test was carried out (loading speed of 41 MPa/min, 25°C) according to ASTM C 579-01[15].

3. Results and Discussion

3.1 Chemical Characterization

The FTIR spectra of the composites was given in Figure 3.

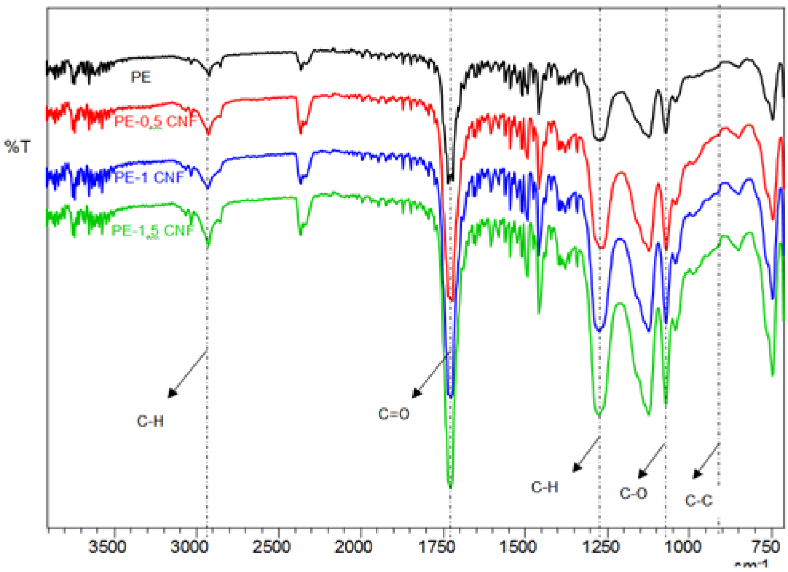

Figure 3. FTIR spectra of PE, PE+0,5 CNF, PE+1 CNF, PE+1,5 CNF.

The most observed vibrations sourced from methylene stretching were seen at 2920 cm^{-1} (asymmetric) and 2910 cm^{-1} (symmetric) for all composites. C=O asymmetric vibration, which has only maleic anhydrite, and C-O symmetric vibration was seen at 1727 cm^{-1} and 1118 cm^{-1}, respectively. The considerable vibration in relation to the CNF were observed between 1000 cm^{-1} and 1200 cm^{-1}. Those vibrations is attributed to C-O-C vibrations in the cellulose intra-molecular and inter-molecular structure. The vibration at 1160 cm^{-1} for CNF is due to C_1-O-C_5 that give an insight about asymmetric bridge stretching. The C_1-O-C_4 vibration which give insight about the glycosidic main structural deformation were seen at 1029 cm^{-1} [16].

3.2 Thermal Characterization

TGA and DTG (derivative of TGA) analysis were carried out and the obtained thermograms were given in Figure 4.

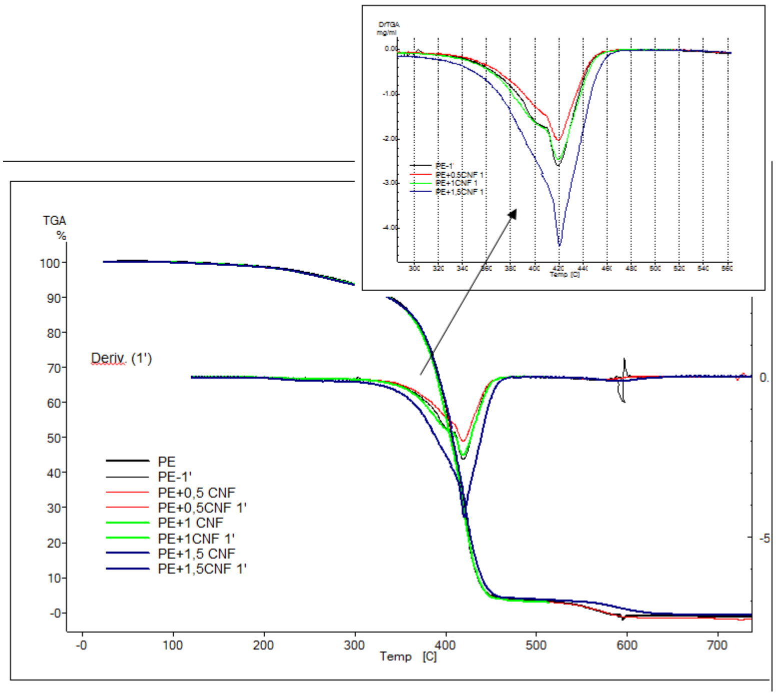

Figure 4. Thermogravimetric analysis test results.

All composites revealed similar thermal degradation trend. Mass loss of composites was investigated in the two regions: 25˚C-200˚C and 200˚C-480˚C to elucidate the degradation and thermal stability properties. The first region (25˚C-200˚C) gives an insight about low molecular weight as well as humidity whereas second region (200˚C-480˚C) give an insight about main structure degradation. It was observed that there was no considerable alteration among thermograms of the composites. When checked the derivative giving more detailed insight about thermal stability, two thermal degradations were seen for each composites with different degradation temperature. Those revealed that thermal stability improved with the CNF and the higher value was seen in the PE+1.5 CNF as 420.93 ˚C whereas lower value was seen in the PE as 419.26 ˚C. Shimazaki et al. conducted a study revealing the CNF effect favorably on PE's thermal stability. They claimed that organic fillers posed higher thermal stability [17]. In the present study, similar results were obtained as they found. This circumstance can be explained that the CNF fillers enabled chain mobility within the composite and this caused higher thermal stability [18].

3.3 Mechanical Properties

Tensile strength results of the composites were given in Figure 5.

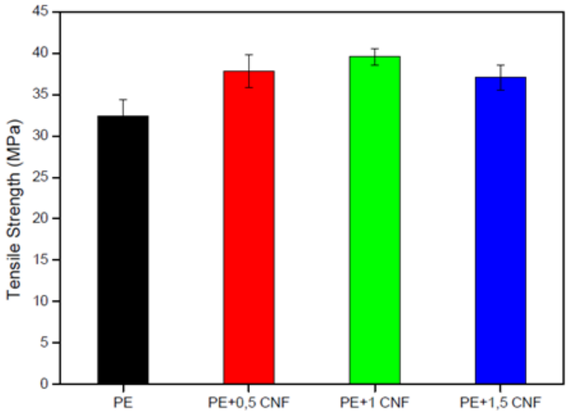

Figure 5. Tensile Strength values of the PE, PE+0.5 CNF, PE+1 CNF, PE+1.5 CNF.

Figure 5 reveals that tensile strength value of the PE+0.5CNF composite has 37.82 MPa, PE+1CNF has 39.6 MPa value, and PE+1.5CNF 37.7 MPa whereas the neat PE has 32.4 MPa. It was also observed that PE+0.5 CNF and PE+1.5 CNF values had close values to each other and the highest increment was seen in the PE+1CNF with 22%. Overall, with incorporation of the CNF, tensile strength of the composites increased. This circumstance could be ascribed to the CNF 3D network structure as well as high aspect ratio. Because, this structure is enabled greater stress transfer for sticking the matrix particles to the filler surfaces. However, it was observed that the highest value was not seen in the PE+1.5 CNF. This circumstance may be ascribed in entanglement of CNF in the PE matrix. Therefore, it can be said that the most suitable CNF filler ratio in the PE matrix for forming CNF based PE is the 1% CNF.

Compressive strength is of important parameters for evaluating mechanical property of the composites. The obtained values were given in Figure 6.

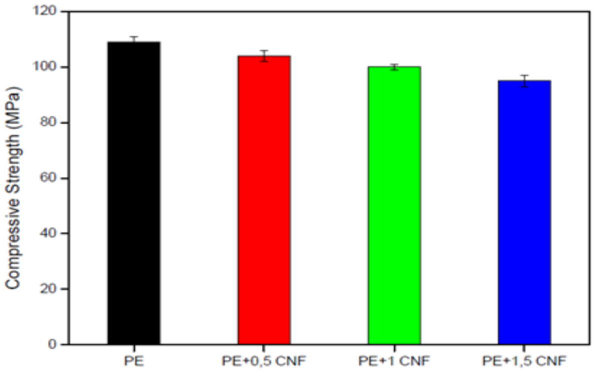

Figure 6. Compressive strength mean values of the PE, PE+0.5 CNF, PE+1 CNF, PE+1.5 CNF.

When Figure 6 was examined, the compressive strength value of the composites lowered with CNF and the progressively lower value was obtained. And, the lowest value was seen in the PE+1.5CNF composite with decreasing of 16 %. These results were as expected since PE resin which gained thermoset qualification has high elastic modulus and enabled the higher compressive strength values whereas bio-based CNF fibers caused lower. This is probably ascribed to the low density of CNF and the low hardness that can not carry the higher load. This circumstance was also explained by the buckling effect and weak interface by Sari et al. They studied the compressive strength of the fiber based PE composites and they observed lower compressive strength value as the fibers content increased. This is ascribed to the weak interface bonds between fibers and PE as well as the increased damage of the fibers sourced from buckling of the composites.

3.4 Morphological Characterization

The obtained SEM pictures were given in Figure 7 as surface and cross-section to reveal morphological alterations.

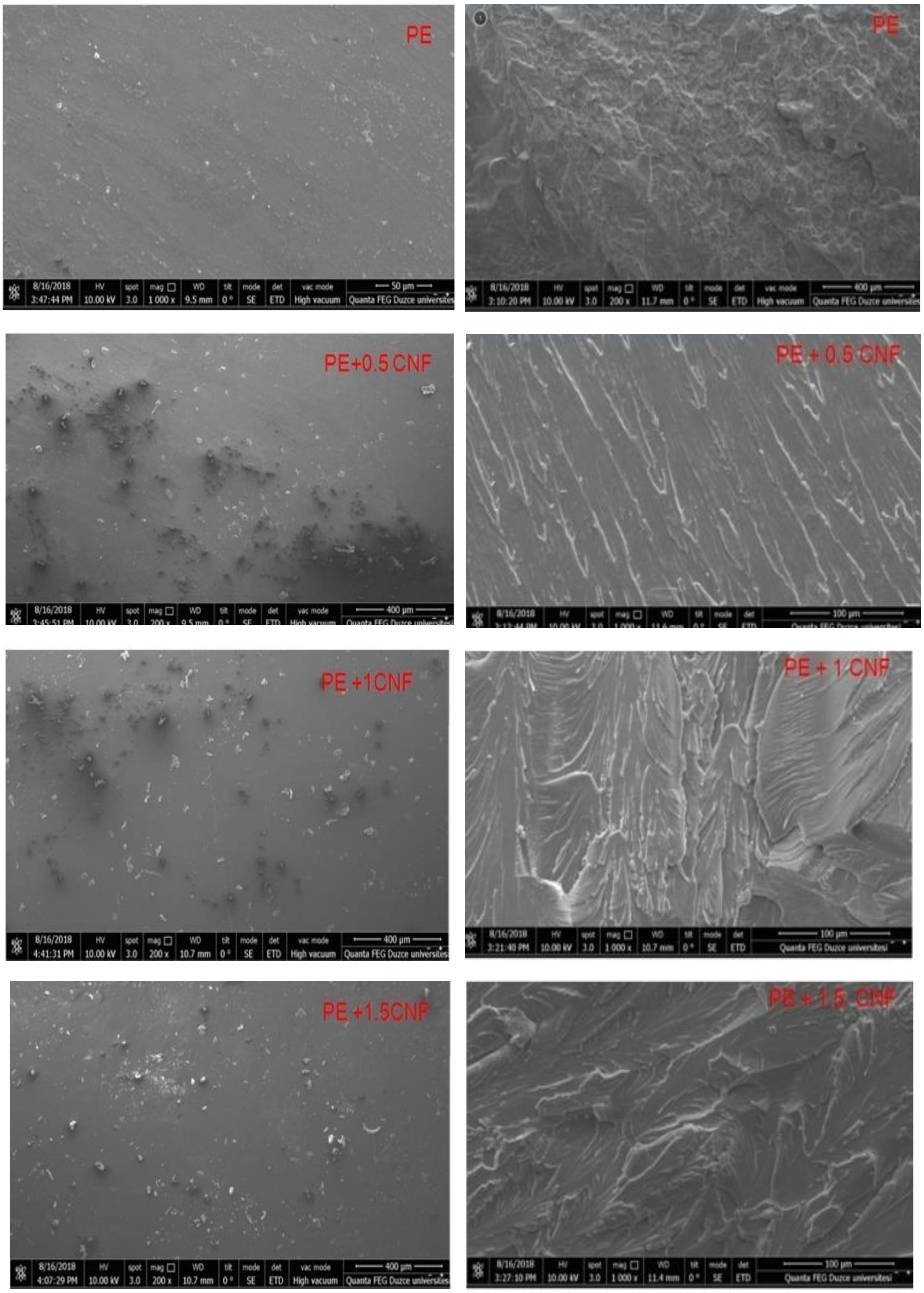

Figure 7. SEM pictures of the PE, PE+0.5 CNF, PE+1 CNF, and PE+1.5 CNF (Pictures were given as surfaces and cross section, respectively)

SEM surface images reveal that all of the CNF mostly dispersed homogeneously in the PE resin matrix. However, some minor agglomerations were observed in the PE-CNF composites that this agglomeration was increased progresively with CNF content. This phenomena reveal that there is no uniform distribution of CNF filler which resulted from overlapping of CNF filler. However, there has not been considerable cracking and void in the structures.

In the cross-sections images, a layered morphology having a different orientation can be discerned. Besides, any signs related to CNF agglomeration were not observed. In addition, no individual CNF fibrils were also seen.

The images reveals the local plastic deformation was carried out in the composites. Therefore, it can be said that CNF filler's having low hardness can not carry to higher load. However, some cracking carried out since eluding the CNF from the surface of the matrix towards to sliding side following increasing load.

4. Conclusion

This study reports the effects of bio based CNF fillers on the chemical, thermal, mechanical, and morphological properties of PE composites. Considerable conclusions from the present study are as follows:

1. The neat PE and its composites with CNF were successfully produced in the presence of initiator and catalyst.
2. The CNF filler caused the minor chemical shifts in obtained PE composites.
3. CNF based composites showed higher thermo-stability.
4. The CNF was not dispersed homogenously and some regional agglomeration was observed.
5. The CNF filler enabled higher tensile strength over the neat PE due to the fact able to stress transfer.
6. The CNF filler caused lower compressive strength over the neat PE due to low hardness as well as the buckling effect.

This study reveals the applicability of CNF filler as reinforcing for higher tensile strength value in the PE polymer composites. Therefore, it can be said that this type of fiber is able to apply in the production of the PE based pipe which has glass reinforced plastic (GRP) industry.

Author's Contributions

The Authors contributed to the study as follows,

Bayram Poyraz: Investigation, Writing- Original draft preparation, Methodology, Formal analysis
Şevki Eren: Investigation, Methodology, Formal analysis.
Serkan Subaşı: Methodology and Preparation
Ayhan Tozluoğlu: Methodology and Preparation

Ethics

There are no ethical issues after the publication of this manuscript.

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