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The Potential of Tempo-Oxidized Cellulose Nanofibers to Replace Ethylene-Propylene-Diene Monomer Rubber

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***Abstract*—**In recent years, petroleum-based polymers began to be limited due to effects on human and environmental point of view in many countries. Thus, organic-based biodegradable materials have attracted much interest in the composite industry because of environmental concerns. As a result of this, it has been asked that inorganic and petroleum-based materials should be reduced and altered with biodegradable materials. In this point, in this study, it is aimed to investigate the potential of use of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl)-mediated oxidation nano-fibrillated cellulose instead of EPDM (ethylene-propylene-diene monomer) rubber, which is a petroleum-based material. Thus, the exchange of petroleum-based EPDM rubber with organic based cellulose nanofibers, which are environmentally friendly (green) and biodegradable, will be realized. The effect of tempo-oxidized cellulose nanofibers (TCNF) instead of EPDM rubber was analyzed by rheological, mechanical, chemical, thermal and aging analyses. The aged surfaces were visually scrutinized and surface morphological changes were examined via scanning electron microscopy (SEM). The results obtained showed that TEMPO oxidation nano-fibrillated cellulose can be used at an amount of 1.0 and 2.2 phr resulting the values stay within tolerance according to customer standard and without any chemical degradation, crack, colour change or staining.

***Keywords*—**EPDM, cellulose, green materials, nanofibrillated cellulose, TCNF, tempo-oxidized nanofiber.

I. Introduction

COMPOSITE materials are formed by combining at least two different materials in macro dimensions. The purpose of the composite production is to add new features to the materials, which are not suitable for themselves or for each other, in order to give the properties which are suitable for their usage areas [1]. In recent years, researchers began to carry out lots of studies in order to develop new high performance composites in different application areas [2], [3]. If at least one of the combined materials is in nanometer (10^{-9} m) size, the material is called as nanocomposite [4] and these materials are widely used in polymer industry such as automotive, packaging, electronic devices, household appliances and all kinds of flame resistant products [5].

One of the most used polymers in sealings, roofing parts, cables and barriers is EPDM. EPDM is a synthetic polymer which is formed by ethylene (45%-80%), propylene (20%-40%) and unsaturated diene (1%-12%) monomers. It is much preferred due to its high mechanical property, UV-resistance, ozone stability and water-proof structure [6], [7].

Many composites have been prepared with combination of polymer types with EPDM in order to develop mechanical, rheological, chemical and morphological properties [8]. In researches the most used polymers in combination of EPDM are polypropylene (PP) [9], [10], butadiene (BR), polyethylene, maleic anhydride (MA), natural rubber (NR), polyamide-12 and polystyrene (PS) [11]-[15].

Polymeric composites are filled with organic or inorganic additives to improve mechanical and molding cycled properties [16]. However, these inorganic polymers were determined as harmful for health and environment whereupon they started to be limited as well as petroleum-based polymers in many countries. Therefore, organic-based biodegradable fillers, especially cellulose began to attract attention in the composite industry recently [17]. Cellulose, the most abundant polymer on Earth, can be characterized as a high molecular weight linear homopolymer composed of D-anhydroglucopyranose units (AGU) which are linked together by β-(1 --> 4)-glycosidic bonds. It is renewable, abundant, biocompatible, sustainable and has unique mechanical properties. By mechanical or chemical processes, cellulose can be converted into materials having superior properties than cellulose, such as cellulose nanofibers (CNF) or cellulose nanocrystals (CNC) [18], [19]. Different chemical methods are applied in order to lower the energy consumption during the production of nanocellulose such as acid hydrolysis, enzyme interaction or TEMPO [20]-[22]. The TEMPO method is a practical one because unwanted chemical media is not necessary and uniformly dispersion is possible with widths of 3-4 nm and high aspect ratios (> 50) [18].

There are so many researches on CNF with TEMPO oxidation. Jose et al. studied - the morphological properties [23]. In other study, Cobut et al. investigated cellulose nanocomposites produced by filling TEMPO treated wood fibers into the thermoplastic starch [24]. Then, Melone et al. prepared ceramic aerogels from TEMPO oxidized cellulose and investigated characterization and photocatalytic properties of them [25]. In addition, Zheng et al. synthesized nanocomposite with polyvinyl alcohol (PVA) and TEMPO oxidized cellulose nanofibrils in order to investigate their absorbent properties [26]. It is aimed with this study to

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investigate the potential of usage of TCNF instead of EPDM rubber used in production of automotive sealing profiles.

II. Experimental Details

A. Materials and Procedures

EPDM which is used in this study was produced by Standard Profile with a formula given in Table I.

TABLE I
COMPOUNDING RECIPE OF EPDM RUBBER

	EPDM	Carbon Black+ White Filler	Process Oil	Activators	Sulphur	TCNF
EPDM	100	165	63	11	6.5	0
EPDM-C1	99	165	63	11	6.5	1
EPDM-C2	97.8	165	63	11	6.5	2.2

TCNF which is used instead of EPDM rubber in a certain amounts was supplied by Cellulose Lab.

Five plates for each material, totally 15 different plates were prepared by adding 0, 1.0 and 2.2 phr TCNF to EPDM compound instead of EPDM material (Table I).

The materials shown in Table I were mixed in Carter Bros 1.5 L lab-scale mixer with an internal temperature changes between 23 ± 2 °C and 100 °C. The compounds were mixed 5 min. with a constant speed of 47 rpm. After the mixtures had been passed through the ESER Machine branded lab-scale cylinder, EPDM plates were prepared by pressing the mixtures 7.5 min. at 180 °C with ESER Machine branded lab-scale compression press. After preparation mechanical, chemical and aging tests were carried out for each plate.

B. Fourier Transform Infrared Spectroscopy (FTIR) Analyze

FTIR analysis was carried out with Shimadzu IR Prestige-21 device in order to see chemical interaction by measuring the vibration frequencies of bonds in the EPDM compound plates.

C. Thermal Properties

TGA analysis was carried out to measure the mass changes of samples after heating the plates with a constant heating rate. Analysis was done with Shimadzu DTG 60 test machine in a dynamic nitrogen atmosphere of 75 ml/min with a heating rate of 20 °C/min and at a temperature rate between 0-550 °C.

D. Mechanical Properties

EPDM plates were analyzed mechanically in terms of tensile, tear, and elongation test. The tensile and elongation specimens were tested according to DIN 53504 standard while the tear specimens were tested according to DIN ISO 34-1 standard. Tests were realized at room temperature (23 ºC) with a cross-head speed of 200 mm min^{-1} using a universal testing machine. Five samples were tested for reliable results.

E. Rheological Properties

The rheological properties were analysed by viscosity, scorch and moving die rheometer (MDR) tests. Mooney viscosity tests were done at 1+4 min at 100 °C according to ASTM 1646 standard in order to investigate the flow, motion and shape-taking properties of the rubber during the time spent in the extruder. Similarly, scorch tests were carried out at 1+20 min at 121 °C according to ASTM 1646 standard to determine the properties of the rubber in the extruder. The MDR tests were performed for 2.5 min at 180 °C according to ASTM 1646 standard in order to measure and analyze the vulcanisation times of ts2 (scorch time) and t90 (the 90% optimum vulcanisation time of rubber). The rheological tests were carried out by using ALPHA Technologies MDR 2000 test machine.

F. Deformation Properties as Permanent Set

The permanent set tests were realized according to DBL 5571 standard. Test specimens were measured after aging 22 h + 2 h at 100 ºC with a gauge, Mitutoyo, and the deformation values were calculated by:

$$\text{Permanent set (\%)} = \frac{h_i - h_f}{h_i - h_0} \times 100 \quad (1)$$

where h_i is the height of the sample before thermal aging, h_f is the height of the sample after aging and h_0 is the compression distance. Three samples were specified to test for reliable result.

G. Artificial Weathering Test

An artificial weathering test was carried out for EPDM plates to simulate natural weathering conditions in laboratory because of the difficulties in natural weathering tests such as long-term time consuming and difficulties in reproducibility. Artificial weathering test simulated the weathering conditions of Kalahari region with the cycles consisted of UV (λ = 300 – 400 nm) radiation at 90 ºC at a relative humidity of 20% and 75 W/m² irradiance intensity. The plates were exposed 100 and 250h in an equipment (Atlas Ci4000) according to the PV3929 standard.

H. SEM Analysis

The surfaces of EPDM plates were characterized morphologically via FEI Quanta FEG 250 optical microscope after gold coating. The chemical contents of EPDM plates were analyzed in terms of EDX spectrum taken from SEM micrographs.

III. Results and Discussion

A. Chemical Characterization

The chemical characterization of the EPDM rubbers was investigated with FT-IR and results are given in Fig. 1.

Rubbers give complex spectroscopic analysis because of overlapping of asymmetric, symmetric and bending vibrations. The main chain in EPDM is asymmetric and symmetric stretching interactions at 2925 cm^{-1}, 2853 cm^{-1} and C-H bending vibrations at 1460 cm^{-1}, 1377 cm^{-1} that occurs due to CH_2 and CH_3 found in the ethylene, propylene and diene monomers of EPDM structure. C-H vibrations have the

greatest intensity in the structure because they are observed in process oil and TCNF, as well.

The spectrum of CS_2 group that reveals crosslinking C-S interactions is seen at ~2320 cm^{-1} and ~2180 cm^{-1}.

C-O-C intra- and inter-molecular vibrations of TCNF are seen between 1200 cm^{-1} and 1000 cm^{-1}. The C_1-O-C_4 glycosidic deformation (intra-molecular) between the glucose units is observed between 1100 cm^{-1} and 1000 cm^{-1} whereas C_1-O-C_5 asymmetric bridge stretching is seen between 1150 cm^{-1} and 1200 cm^{-1}. However, they are not observed clearly. Briefly, the graphs of EPDM, EPDM-C1 and EPDM-C2 are the same because the amount of TCNF is too low. Therefore, it can be said that TCNF does not cause a reaction that degrades the matrix structure.

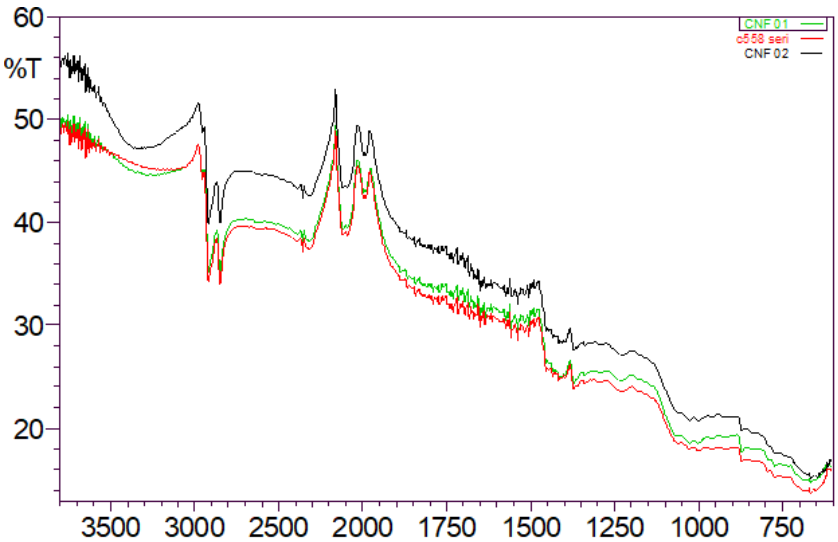

Fig. 1 FTIR spectra of the EPDM plates

B. Thermal Characterization

TGA analyses of TCNF based EPDM rubbers were carried out and obtained thermograms were given in Fig. 2. Firstly, process oil is degraded and removed from rubber. In the second region EPDM is degraded chemically and removed from structure. In the last region carbon black burned and mass loss occurred. After 600℃ only ash remained.

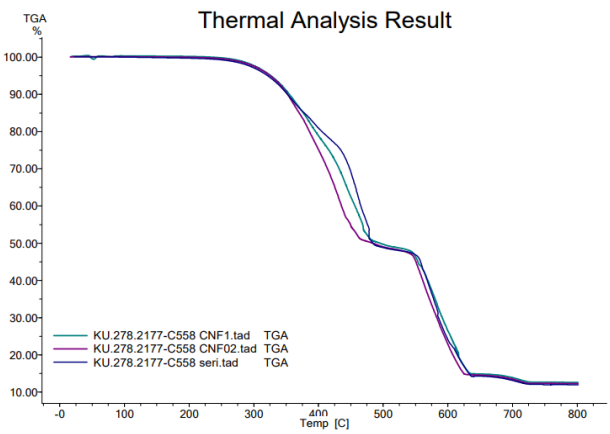

Fig. 2 Thermal Properties of TCNF based EPDM plates

As seen from thermal stability analysis, it can be seen that TGA graphs of EPDM, EPDM-C1 and EPDM-C2 are the same because of too low amount of TCNF. Therefore, it can be said that TCNF does not affect the thermal stability of EPDM plates.

C. Evaluation of Mechanical Properties

The effect of TEMPO oxidized nano-fibrillated cellulose on the mechanical properties of the EPDM rubber (EPDM; EPDM-C1; EPDM-C2) plates was investigated in detailed. The obtained mechanical properties are given in Figs. 3-5, respectively.

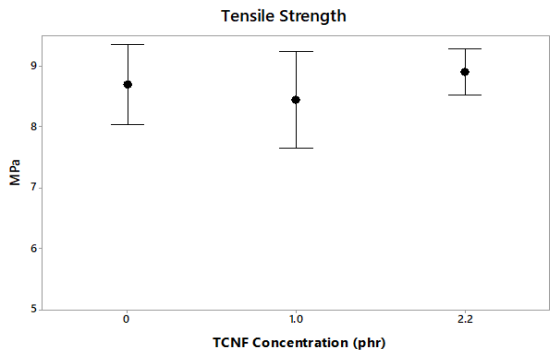

Fig. 3 Effect of TCNF on tensile strength of EPDM rubber

It can be seen from Figs. 3 and 4, tensile strength values do not change while tear strength values increase with adding TCNF. Besides, Fig. 5 shows that adding of TCNF causes decrease in elongation at break values (ε). It means that adding TCNF makes the rubber more rigid. This circumstance limited stretching of the rubbers and resulted in lower ductility.

According to customer specification, TL52345 standard, the mechanical properties of EPDM are within tolerances. As a result, TCNF can be used in these amounts instead of EPDM rubber. However, if the amount increases, the mechanical properties should be controlled whether within tolerance.

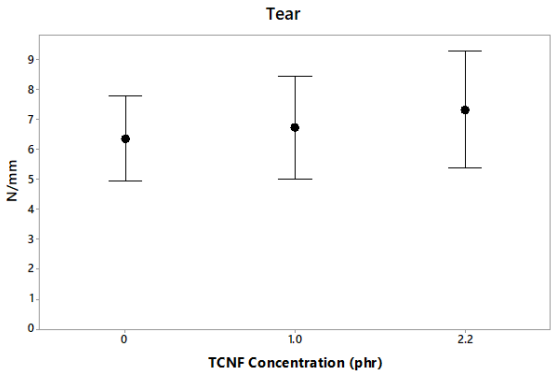

Fig. 4 Effect of TCNF on tear strength of EPDM rubber

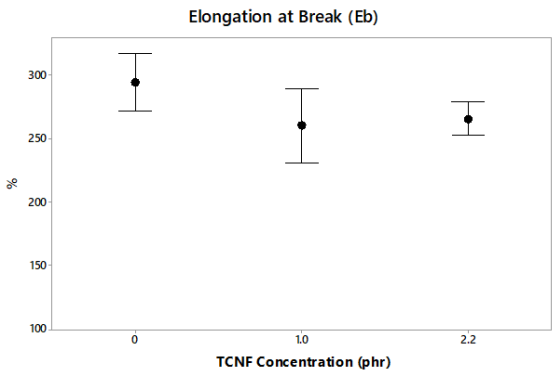

Fig. 5 Effect of TCNF on elongation of EPDM rubber

D.Evaluation of Rheological Properties

The effect of TCNF on the rheological properties is represented by the comparison of the Mooney viscosity, Mooney scorch and vulcanisation times as ts2 and t90 values of the EPDM plates (Figs. 6-8, respectively).

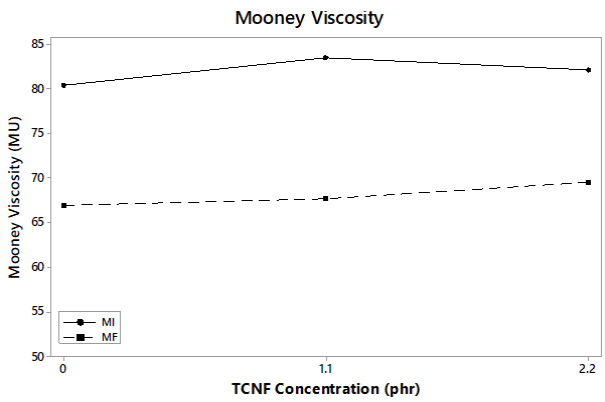

Fig. 6 Effect of TCNF on viscosity

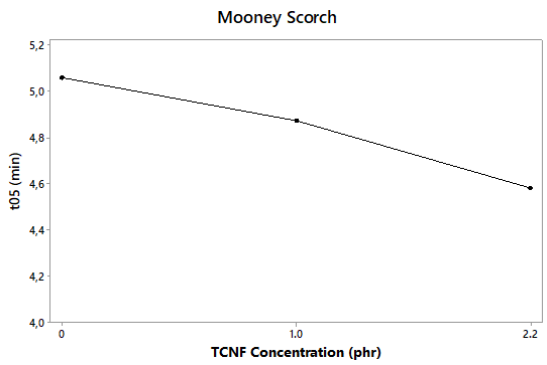

Fig. 7 Effect of TCNF on scorch

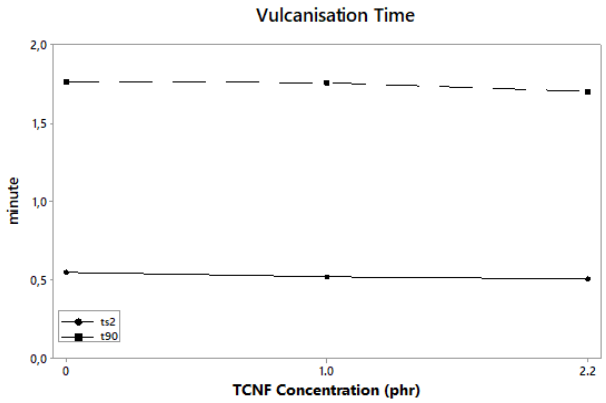

Fig. 8 Effect of TCNF on vulcanization times

The initial (MI) and final (MF) viscosity values are presented in Fig. 6 and it shows that adding TCNF caused a small but insignificant increase in the viscosity values.

As seen in Fig. 7 the plates prepared with added TCNF had lower scorch values than those of serial EPDM rubber. It can be concluded that usage of TCNF decreased the t05 values and caused earlier vulcanisation, thus providing faster production.

Fig. 8 shows that usage of TCNF has no effect on ts2 and t90 vulcanisation times. It means that EPDM rubber with TCNF can be vulcanised without any change on process conditions.

E. Evaluation of Deformation Properties as Permanent Set

Permanent set values on deformation properties is a significant property in the rubber industry. Permanent set values for the rubber are given in Fig. 9. It is detected from Fig. 9 that usage of TCNF has no effect on permanent deformation values.

F. Artificial Weathering Test

The EPDM plates were evaluated visually after aging in an artificial weathering environment for 250 h. The visual control results are presented in Fig. 10.

There are no cracks, color change or staining on the surfaces after 250 h aging. It can be said that TCNF can be used in these amounts instead of EPDM rubber.

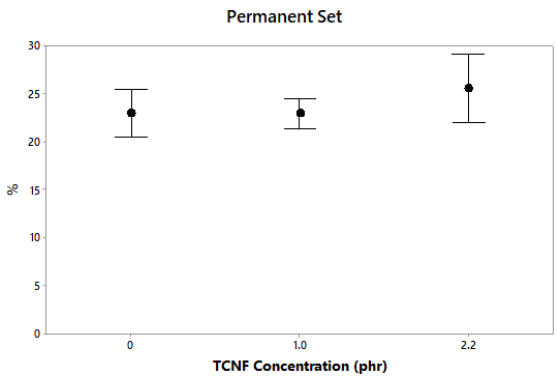

Fig. 9 Effect of TCNF on permanent set of EPDM rubber

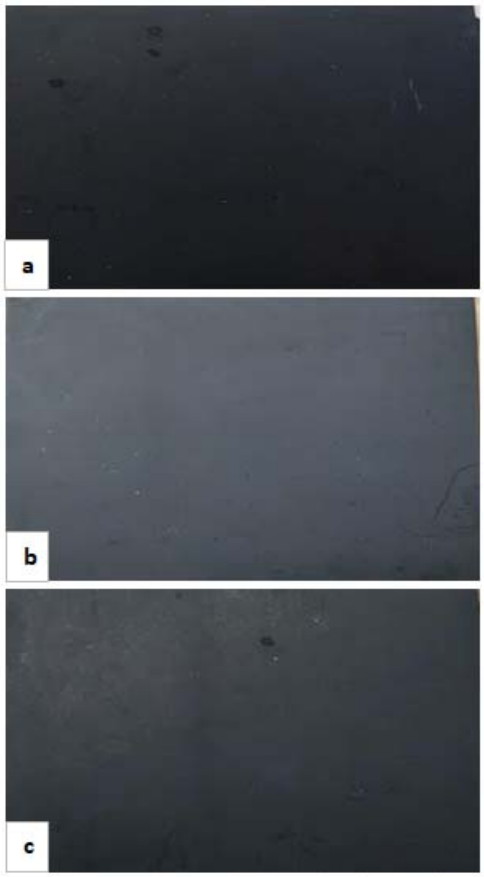

Fig. 10 Visual controls of (a) EPDM, (b) EPDM-C1, (c) EPDM-C2 after Kalahari weathering

G.SEM

The SEM pictures taken from EPDM plates prepared by addition TCNF are shown in Fig. 11. As seen from SEM images of EPDM plates, TCNF can be homogeneously dispersed in EPDM rubber and no considerable difference is observed with increasing amount of TCNF. Agglomeration, crack, individual fibrils as well as void are not seen from SEM photos. It means that TCNF does not chemically degrade in EPDM matrix.

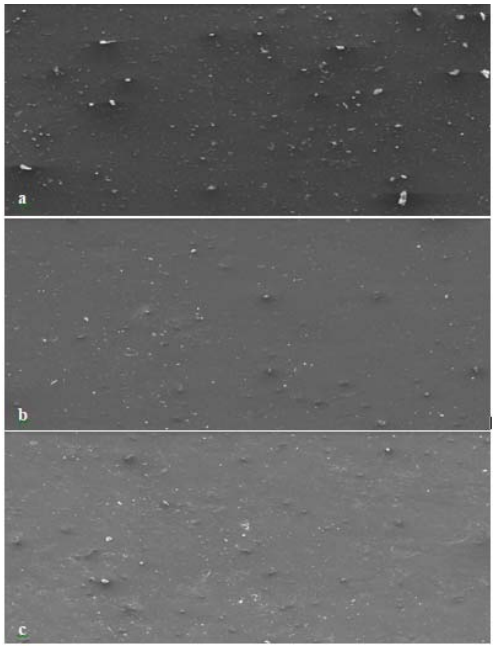

Fig. 11 Photographs of (a) EPDM plate SEM, (b) EPDM-C1 plate SEM, (c) EPDM-C2 plate SEM

IV. Conclusion

The effect of TCNF on rheological, mechanical, chemical, thermal and aging properties of EPDM rubber was investigated in detail. It is detected that TCNF makes EPDM more rigid regarding to tear strength and elongation at break values. However, it can be used instead of EPDM at an amount of 1.0 and 2.2 phr which are providing the values to stay within tolerance according to customer standard. The vulcanisation times do not change while scorch values decrease with increasing TCNF. It means that usage of TCNF causes earlier vulcanisation but it can be vulcanised without any change on process conditions. Regarding to aging and morphological analysis, TCNF does not cause crack, change colour or staining. It can be said that it does not occur chemical degradation in EPDM matrix.

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