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Mechanical, rheological and aging properties of nano-fibrillated cellulose/EPDM composites

Nano-fibrillenmiş selüloz / EPDM kompozitlerin mekanik, reolojik ve yaşlanma özellikleri

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Abstract

This work was aimed to develop green composite materials from nanocellulose / Ethylene Propylene Diene Monomer (EPDM) rubber. The obtained green composites were investigated in terms of chemical, thermal, mechanical, morphological, and aging properties. The results obtained in this work showed that the tensile strength and elasticity of the composites decreased with nanocellulose while permanent set values increased. Green composite materials have lower scorch values that means easier and faster vulcanization. Some cracks and staining were seen after 250h aging over 3 phr of nanocellulose whereas the surfaces were not degraded up to 100h weathering. All values are in the range of acceptable limits except for tear strength. Briefly, the study conducted reveals that nanocellulose can be used with EPDM until the concentration of 10.0 phr without any chemical degradation. Thus, sealing profiles used in automotive sector can be produced by nanocellulose/EPDM green composites instead of EPDM rubber. This can be an innovative technology in order to replace petroleum-based materials with bio-degradable materials.

Özet

Bu çalışmanın amacı nanoselüloz / Etilen Propilen Dien Monomer (EPDM) kauçuktan yeşil kompozit malzemeler geliştirmektir. Elde edilen yeşil kompozitler kimyasal, termal, mekanik, morfolojik ve yaşlanma özellikleri açısından incelenmiştir. Bu çalışmada elde edilen sonuçlar, nanoselülozun eklenmesi ile kompozitlerin çekme dayanımı ve elastikiyetleri azalırken, kalıcı deformasyon değerlerinin arttığını göstermektedir. Yeşil kompozit malzemeler daha düşük scorch değerlerine sahiptir, bu da daha kolay ve daha hızlı vulkanize olacakları anlamına gelir. EPDM plakaların yüzeyleri 100 saatlik yaşlanmaya kadar bozulmazken, 250 saat yaşlandırıldıktan sonra 3 phr üzerinde nanoselüloz eklenen plakaların yüzeyinde bazı çatlaklar ve lekelenmeler gözlenmiştir. Yırtılma mukavemeti dışında tüm değerler kabul edilebilir sınırlar aralığındadır. Kısaca yapılan çalışma, nanoselülozun herhangi bir kimyasal bozulma olmaksızın 10.0 phr konsantrasyonuna kadar EPDM ile kullanılabileceğini ortaya koymaktadır. Böylelikle otomotiv sektöründe kullanılan sızdırmazlık profilleri EPDM kauçuk yerine nanoselüloz / EPDM yeşil kompozitler ile üretilebilmektedir. Bu, petrol bazlı malzemeleri biyolojik olarak parçalanabilen malzemelerle değiştirmek için yenilikçi bir teknoloji olması açısından önemlidir.

INTRODUCTION

Today, composites are widely used in many industrial applications from automotive to electronic devices (Jayamol et al. 2004). Therefore, there are lots of studies in literature about obtaining new high performance composites in order to extent its application range (Ghosh et al. 2007).

One of the most used polymer types for using in automotive sealing profiles, building systems and electrical cables is ethylene propylene diene terpolymer (EPDM) which formed by a combination of ethylene (45%-80%), propylene (20%-40%) and unsaturated diene (1%-12%) monomers due to the fact that having high mechanical property, water-proof structure and excellent resistance to ozone, heat, UV and oxygen (Arayapranee and Rempel 2008, Obrecht et al. 2012).

A variety of EPDM based polymer blends has been prepared to obtain new polymer having improved characteristics. The first attempt related to EPDM based polymer blend was conducted by Allen (Allen 1972). After that, the most used polymer which incorporated in EPDM was polypropylen (PP) (Antunes et al. 2011, Wang et al. 2011). Butadiene (BR), polyetyhlene (PE), maleic

anhydride (MA), natural rubber (NR), polyamide-12 and polystyrene (PS) are another polymer used with EPDM along with the propylene (PP) (Jung et al. 2015, Stelescu et al. 2013, Lourenço and Felisberti 2006, Go and Ha 1996, Kim et al. 1996).

Another type in polymers has been carried out with fillers, divided two categories as organic and inorganic as additive; to increase prospective mechanical properties and improve molding cycled (Xanthos 2005). The property of matrix polymer could be affected depending on the type of filler. For example, melt viscosity could be significantly increased if filler polymer consisted of fibrous materials. Similarly, mold shrinkage and thermal expansion would be reduced when inorganic fillers were used. However, it was determined that those inorganic polymers are not compatible with the environment as structural. Therefore, usage of these materials as well as petroleum-based polymers starts to be worried about the damage of them that causes to humans and environment in many countries. For this reason, the interchangeability of these inorganic and petroleum-based materials with biodegradable materials has begun to be investigated. This has caused organic-based biodegradable fillers to attract great attention in the composite industry in recent years (Ashori 2008). Among the organic based biodegradable fibers, cellulose is the most researched one due to its renewability, abundant, sustainable, and unique mechanical properties. Especially, recently, the cellulose has been used by converting to nanofibrils such as nanofibrillated cellulose (CNF) and nanocrystalline cellulose (CNC), in order to improve mechanical properties with its increased surface area (Poyraz et al. 2019, Clarkson and Jeffrey 2018).

CNF has some advantages over CNC in terms of the long fiber structure, high tensile strength due to strength/weight ratio, transparence, safety for human consumption and easily functionalized (Ayrilmis and Ashori 2014). Thus, a number of studies have focused on new ligno-celulosic based polymer composites. Loos and Robinson carried out a study related to wood-vinyl monomer and its swelling properites (Loos and Robinson 1968). Then, Witt and Bosco investigated hardness and elasticity modulus of wood-plastic composites (Witt and Bosco 1973). In other study, Menezes et al. prepared new cellulose whiskers reinforced polyethylene nanocomposites (Menezes et al. 2009). They observed a significant improvement in terms of elongation at break. In addition; thermoset polymers, especially resins, has been used with CNF. Lavoratti et al. studied on composites of unsaturated polyester resin and CNF (Lavoratti et al. 2016). PE-CNF composites revealed higher thermal stability and the storage modulus compared to that neat CNF. However, their glass transition temperature (Tg) was not significantly affected. In addition, better dispersion was seen in the composites produced. In other study, the use of high residual lignin containing cellulose nanofibrils (LNFCs) has been explored for first time to reinforce epoxy resins by Sandeep et al (Sandeep et al. 2017). These novel composites showed much better mechanical properties than those reported in the literature with a similar loading amount of CNFs. Farhan et al. CNF based polyester produced to reinforce an unsaturated polyester matrix (UP) without the need of coupling agents or CNF surface modification (Farhan et al. 2015).

The CNF content significantly increased the glass transition temperature (Tg). 45% CNF by volume causes an increase 3 times in the modulus and tensile strength almost and 2 times in ductility and apparent fracture toughness.

However, limited study was carried out regarding EPDM in this area. Sarkhel and Choudhury studied dynamic mechanical and thermal properties of Polyethylene (PE)-EPDM based jute fiber composites (Sarkhel and Choudhury 2008). It is detected that if the amount of fiber material and compatibilizer increased, the mechanical parameters such as modulus, tensile and impact strength, and hardness also increased. The storage and loss module of the High density polyethylene (HDPE)-EPDM/jute fiber composites were higher than those of the Low density polyethylene (LDPE)-EPDM/jute fiber composites at any amount of fiber material and compatibilizer. Similarly, the strong relation between fiber and compatibilizer amounts and the relaxation process of polymer matrix can be seen from the damping efficiency. The thermo-oxidative

stability was increased for treated composites more than untreated composites.

Another study was conducted by Xu et al.2015. In that study, lignin was used as coupling agent in EPDM rubber. It can be detected from the mechanical test results and thermal analysis that using lignin as coupling agent improved the mechanical properties and thermal stability compared to the pure EPDM rubbers. Behind that it can be seen from SEM results the inter-phase cohesion can be occured between the lignin molecule and EPDM particles.

The aim of this study was to investigate the effect of nano-fibrillated cellulose (CNF) on mechanical, chemical, thermal, morphological and aging properties of EPDM rubber. There is no similar study reported with nanocellulose and EPDM in the literature. From this point of view, the present study will make extra contribution to the literature and industry.

MATERIAL AND METHODS

Material

Ethylene and propylene (EPM) is mostly used in many applications. 5-ethylidene-2-nonbornene (ENB) is added up to 10 wt. %, dcylopentadiene (DCPD) is added up to 5 wt. % and 5-vinylidene-2-nonbornene is added less than 1 wt.% to EPDM terpolymer. Activators and accelerators have been used with EPDM for production the rubber.

Ethylene-propylene-diene monomer (EPDM) was used in this study. EPDM is a synthetic amorphous elastomer with high mechanical properties, waterproof structure, high elasticity, high resistance to deformation, degredation, heat and ozone (Sibel et al. 2018). Nano fibrillated cellulose (CNF) which is a natural and biodegradable material with high mechanical and electrical properties is also used in certain amounts instead of EPDM. EPDM was produced by Standard Profile and formulation is given in Table 1. Compounding was done using rubber-grade chemicals. CNF is supplied by Cellulose Lab and is used as nanofibrillated cellulose instead of cellulose nano crystals (CNC) due to the fact high aspect ratio in the structure that could enable high mechanical properties.

After producing CNF based EPDM rubbers, chemical, thermal, mechanical, morphology and ageing properties investigated in detail.

Methods

Production of EPDM plates

A total of 25 different plates (five plates for each material) were prepared by adding 0, 1.0, 3.0, 5.0 and 10.0 phr nano-fibrillated cellulose (CNF) to EPDM compound instead of EPDM material (Table 1). The materials shown in Table 1 were mixed in Carter Bros 1.5L lab-scale mixer with an internal temperature changes between 23±2°C to 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 in order to carry out the analysis.

Table 1. Experimental Design of the Novel Green Composites

	EPDM (phr*)	Carbon Black+ White Filler (phr)	Process Oil (phr)	Activators (phr)	Sulphur (S) + Accelerators (phr)	CNF (phr)
EPDM	100	165	63	11	6,5	0
EPDM-C1	99	165	63	11	6,5	1
EPDM-C3	97	165	63	11	6,5	3
EPDM-C5	95	165	63	11	6,5	5
EPDM-C10	90	165	63	11	6,5	10

*phr: parts per hundred parts of rubber

Testing of EPDM plates

Fourier Transform Infrared Spectroscopy Analyze (FTIR)

Fourier transform infrared (FTIR) analysis was carried out to investigate chemical interaction by measuring the vibration frequencies of bonds in the complex matrix. For that purpose, the samples were placed in the diamond. The molecular vibration signals were in the range of 4000–600 cm^{-1}, and the resolution was 20 scans of 4 cm^{-1}. The IR spectra were taken via FT-IR with an attached ATR (attentuated total reflectance) device (Shimadzu IR Prestige-21, Shimadzu Corp.).

Thermal Properties

TGA (Thermogravimetric Analysis) was applied to the samples 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. The test was carried out via Shimadzu DTG 60 test machine. According to the TGA measurement principle, the changes in the mass of the sample were measured with scales after heating the plates with a heating program with a constant heating rate. The change in the mass was measured via temperature.

Mechanical Properties

The mechanical properties such as tensile and tear strength, elongation at break, and hardness values were measured. The specification of the tensile strength and elongation at break test was performed according to DIN 53504 and the tear strength test specification was realized according to DIN ISO 34-1. All tests should be performed at room temperature (23 °C). Tests were carried out by a universal machine called Zwick Roell Z010. The speed of machine should be 200 mm/min. The hardness (shore A) values of EPDM plates were measured by a hardness meter. The hardness test was performed according to DIN ISO 7619-1.

The rheological properties such as viscosity, scorch and moving die rheometer (MDR) values were measured according to the test specification ASTM 1646 with ALPHA MDR 2000 test machine. For the viscosity measurements, specimens were firstly pre-heated 1 min. and then specified 4 min. at 100 °C. Viscosity values showed the flow, movement and taking shape properties of rubber in extruder. Similarly, after 1 min. pre-heating scorch tests were identified by heating 20 samples 20 min. at 121 °C. Scorch values were controlled to determine the properties of rubber along the extruder. For MDR tests, specimens were heated 2.5 minutes at 180 °C without pre-heating. MDR values give the vulcanization times such as ts2 and t90. The starting time of vulcanization and 90% vulcanization time of rubber can be interpreted in advance with ts2 and t90 values. The mechanical and rheological values were controlled via five samples.

Deformation Properties as Permanent Set

The permanent deformation tests were realized by 2 hours of unpressed aging after 22 hours of pressing aging at 100 ºC as written in Daimler Automotive standard, DBL 5571. After aging the height of specimens were measured with a gauge called Mitutoyo, and calculated using the following equation:

$$Permanent\ Set\ (\%) = \frac{hi-hf}{hi-h0} \times 100 \quad (1)$$

where h_i is the sample height before aging, h_f is the sample height after aging and h_0 is the pressing distance. Three samples were used for permanent deformation tests.

Artificial Weathering Test

Natural weathering tests are long-term tests and caused time consuming. They are also difficult to reproduce. For this reason, artificial weathering tests were carried out with a machine called Atlas Ci4000. It is an equipment that stimulates natural weathering such as humidity, UV-radiation, temperature, etc. The samples were aged according to PV3929 standard, which stimulates the climate in Kalahari desert with 300-400 nm UV radiation at 75 W/m² intensity, 90 ºC temperature, 20% relative humidity. The aging durations were 100 and 250 hours.

Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the samples prepared by adding CNF material was characterized by SEM analysis which is taken with FEI Quanta FEG 250 optical microscope.

RESULTS AND DISCUSSION

Chemical Characterization

The FT-IR analysis results are given in Figure 1. Sulphur vulcanization of EPDM is visually performed in the presence of activators and accelerators such as sulfenamides, thiazole, dithicarbamates, thiurams, guanidins. The mechanism of sulphur vulcanization of EPDM is seen like that of polydiene elastomers. As a result of exposure to sulfur of unstable allylic H-atoms, alkyl sulfides are formed. While ENB unsaturation continues, allylic positions are activated. In the first step, the sulfur used as a vulcanization accelerator binds to the allylic positions with a sulfur bridge, causing crosslinking. Sulphur bridges are occured at C-3exo, C-3endo and C-9. With the formation of sulfidic species with 1 to 5 carbon atoms due to isomerism, 40% of the cross-linking is completed.

Rubbers are complex structure in terms of spectroscopic instrumental analysis due to the fact that a number of asymmetric, symmetric and bending vibrations overlapped each other. The main chain in EPDM sourced from C-H asymmetic, symmetic streching interactions and C-H bending vibrations at 2925 cm^{-1}, 2853 cm^{-1} and 1460 cm^{-1}, 1377 cm^{-1} owing to CH_2, CH_3 in the ethylene, propylene and diene monomers in the EPDM structure, respectively. Also, process oil and CNF are consisted C-H vibrations, as well. Therefore, those C-H vibrations had a greater intensity compared to other groups in the rest of structure. The spectra of CS_2 group revealing crosslinking C-S interaction seem mostly in ~2320 cm^{-1} and ~2180 cm^{-1} region. N=C=S (isothiocyanate) group can be seen in the 2072 cm^{-1} and 2048 cm^{-1} (Sanches et al. 2015).

C-O-C intra- and inter molecular vibrations related to CNF are seen in the wavelengths between 1200 cm^{-1} and 1000 cm^{-1} that is C_1-O-C_4 glycosidic deformation (intra moleculer) between the glucose units were observed at 1100 cm^{-1} - 1000 cm^{-1} whereas C_1-O-C_5 asymmetric bridge stretching are seen 1150 cm^{-1} - 1200 cm^{-1}. However, those vibrations are not observed as specifically due to probably overlapping. It was seen that interaction between EPDM and CNF did not caused unfavorably reaction that is degraded the matrix structure.

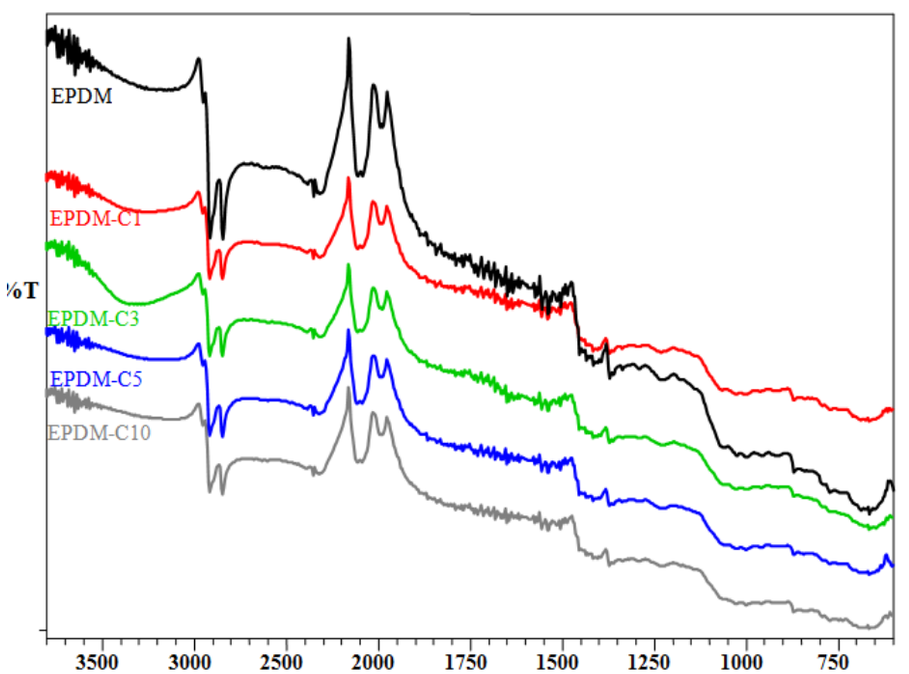

Figure 1. FTIR spectra of the EPDM, EPDM-C1, EPDM-C3, EPDM-C5, EPDM-C10

Thermal Characterization

TGA analyses of the nanocellulose reinforced EPDM rubbers were carried out and obtained thermograms were given in the Figure 2.

TGA thermograms were analyzed in three region that 300 °C-400 °C and 400°C-500 °C, 600 °C-700 °C and rest. In the first region, CNF degraded and removed from the rubber structure. Then, in the second region, EPDM was degraded chemically and removed from the structure. In the last region, mass loss sourcing from the carbon black degradation. After 600 C, zinc oxide and other activators are left in the structure. When thermal stability investigated, that value decreased with increasing CNF. The lowest thermal stability was seen in the EPDM-C10 rubber sample that contains highest CNF whereas the highest thermal stability was seen in the neat EPDM rubber for both in the first region and second region. This is probably due to CNF high aspect ratio that covers the gap between EPDM matrix and increased heat transfer. Therefore, CNF decreases the thermal stability of the rubbers.

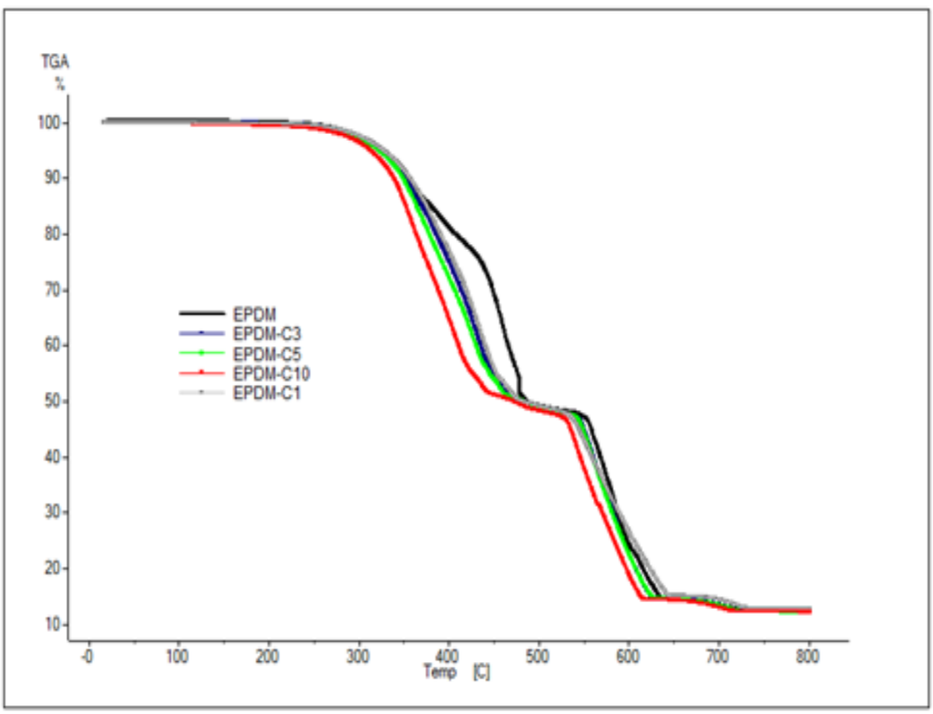

Figure 2. Thermal Properties of Nanocellulose Reinforced EPDM rubbers

Evaluation of Mechanical Properties

The effect of the nano-fibrillated cellulose (CNF) on the mechanical properties of the EPDM rubber (EPDM; EPDM-C1; EPDM-C3; EPDM-C5; EPDM-C10) plates were investigated in detail. The obtained tensile and tear strength values of those rubbers were given in the Figure 3. It can be seen from Figure 3, the tensile strength value decreased with the increasing amount of CNF. According to customer requirement standard, TL 52345, tensile strength should be the least 7 MPa. The results reveal that CNF can be used with EPDM until the concentration of 10.0 phr. After than that of amount, tensile strength decreased to the inacceptable value. This can be explained by saturation point.

A lot of studies have been carried out in the literature. Generally EPDM/thermoplastic polymers revealed higher TS value compared to filler reinforced polymers. Siriwardena investigated EPDM + Silica/ Rice Husk (RH) that tensile stress of EPDM+RH was 8.6 MPa. Arayaprance found as 13.5 MPa of EPDM+NR+Rice Husk Ash (Siriwerdana et al. 2001). In other study, Wang Jie et al. studied EPDM+SBR+ Hemp Hurd Powder and its tensile stress was 9.8 MPa. Those results are compatible with results that we obtained (Wang et al. 2010).

As of tear strength, tear strength revealed fluctuating value with the CNF. However, all the obtained values are acceptable limits as its acceptable value should be the least 4 N/mm with respect to customer requirement standard. Addition of 10.0 phr or more of CNF exceeds the saturation point causing difficulty in tearing (Maya and Sabut 2008; Ahmad and Luyt 2012).

Similarly, exceeding the saturation point may be caused an increase in both maximum/minimum torque results and crosslink density that is presented in Figure 6.

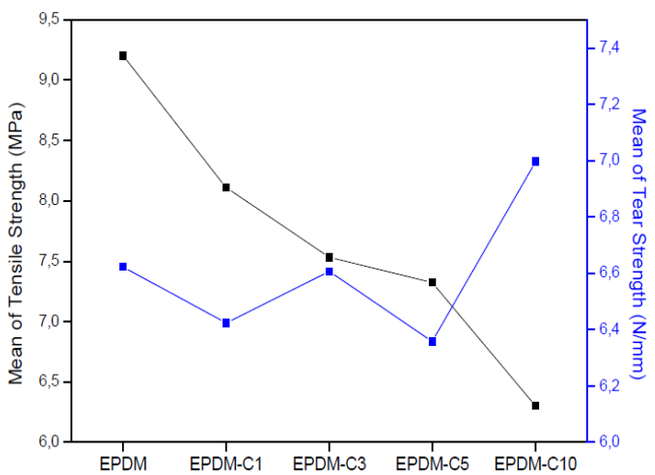

Figure 3. Effect of CNF on tensile strength and tear strength.

Elongations at break and hardness properties of EPDM rubber with CNF were investigated and the obtained results were given in the Figure 4. When checked the Figure 4, as carried out in the tensile strength, adding of up to 10.0 phr or more of CNF, caused decrease in the elongation at break value (ε). CNF loading increased, ε decreased since the obtained rubbers became more rigid which restricted polymer chain. Also this circumstance limited strecthing of the rubbers and resulted in lower ductility (Afrifah 2010). It means that the elasticity of EPDM rubbers decreased by adding CNF resulting.

Evaluation of Deformation Properties as Permanent Set

Permanent set values on deformation properties are a significant property in the rubber industry. Permanent set values for the rubber are given in the Figure 5. It is detected from Figure 5 that permanent deformation values increased by the addition of CNF. According to customer requirement standard, DBL 5571, permanent deformation should be min.35 %. It can be said that nano-fibrillated cellulose can be added until the amount of 10.0 phr instead of EPDM. However, when it is added 10.0 phr or more the permanent set exceeds the limit and reaches inacceptable value. Increasing in permanent set values means that EPDM plates lose their elasticity and deform easily.

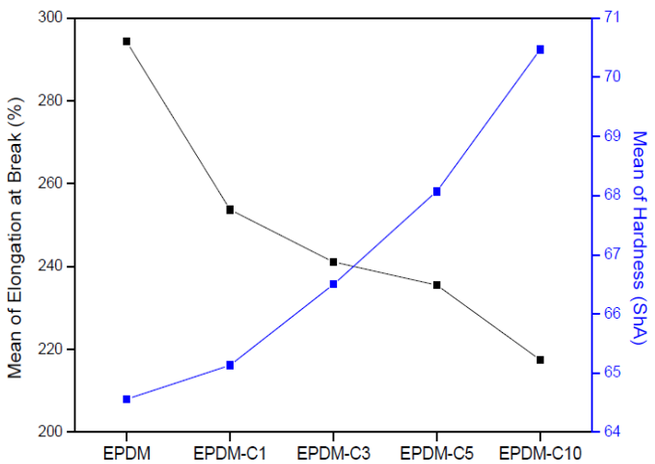

Figure 4. Effect of CNF on elongation at break and hardness of EPDM rubber.

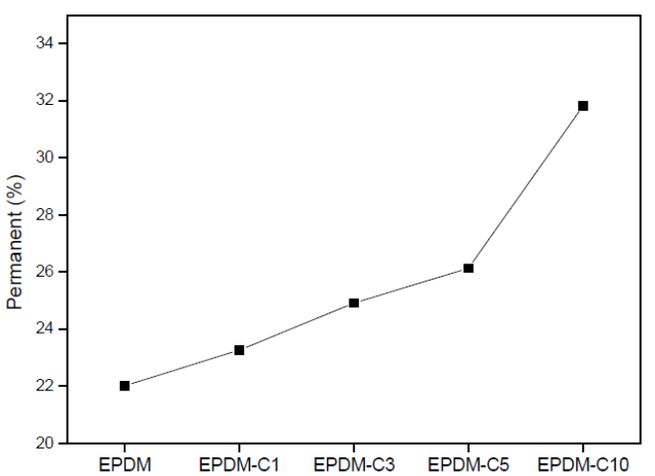

Figure 5. Effect of CNF on permanent set of EPDM rubber.

Evaluation of Rheological Properties

The effect of CNF instead of EPDM on rheological parameters are presented by the comparison of crosslinking-scorch time. The obtained results are presented in Figure 6 - 8, respectively.

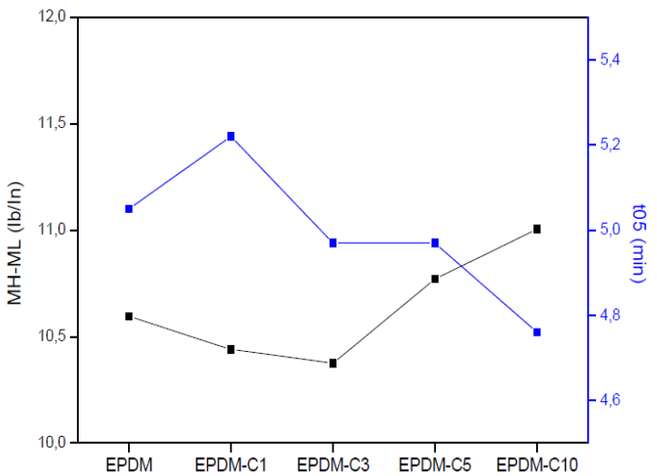

Figure 6. Effect of CNF on crosslink density and mooney scorch.

When checked the croslink density are prone to increase after 5 phr, whereas mooney scorch decreased. It can be said that CNF biopolymers having nanofibrils interacted with rubbers as cover the gap between CNF and rubber. For that purpose, croslinking density revealed the higher values compared to EPDM rubber.

The initial (MI) and the final (MF) viscosity values are presented as Mooney viscosity in Figure 7. Mooney viscosity value mostly increased with CNF. However, the increase is not considerable.

The vulcanisation times of EPDM plates are shown in Figure 8. As seen on Fig. 8, there is no considerable alteration in the rubbers with addition of CNF instead of EPDM. It means that no change in process conditions is required.

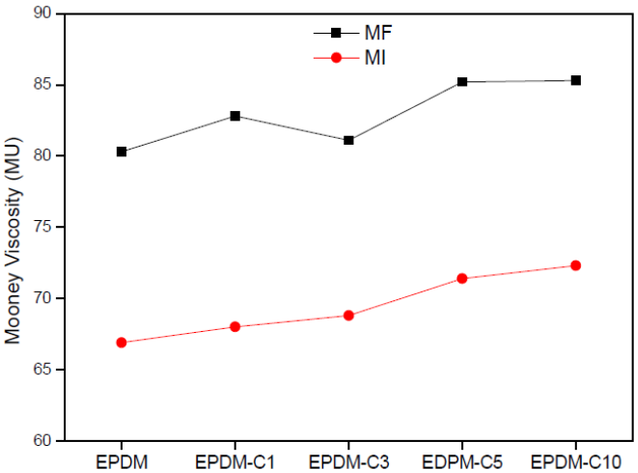

Figure 7. Effect of CNF on Mooney viscosity.

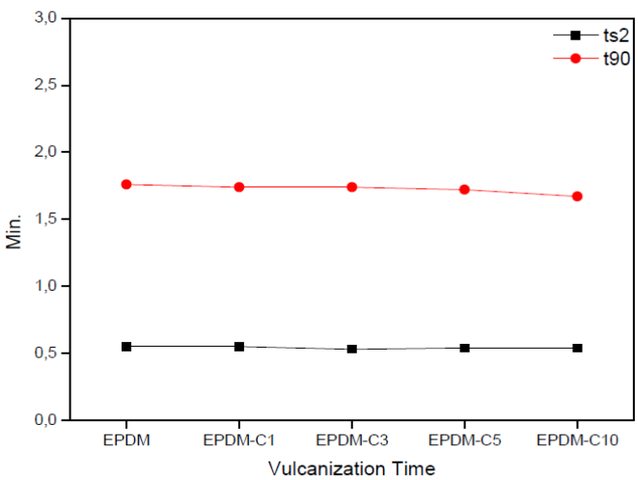

Figure 8. Effect of CNF on vulcanisation time

Artificial Weathering Test

The photos of EPDM plates surfaces were taken after aging 100 and 250 hours with Atlas Ci4000. The surface photos are presented in Figure 9. Although the surfaces were not degraded after 100h artificial Kalahari weathering, cracks and staining started to be occurred for 3th, 4th and 5th plates after 250h aging. It can be said that adding CNF instead of EPDM in an amount 3.0 phr caused minor cracks and color alterations on the surface of EPDM plates.

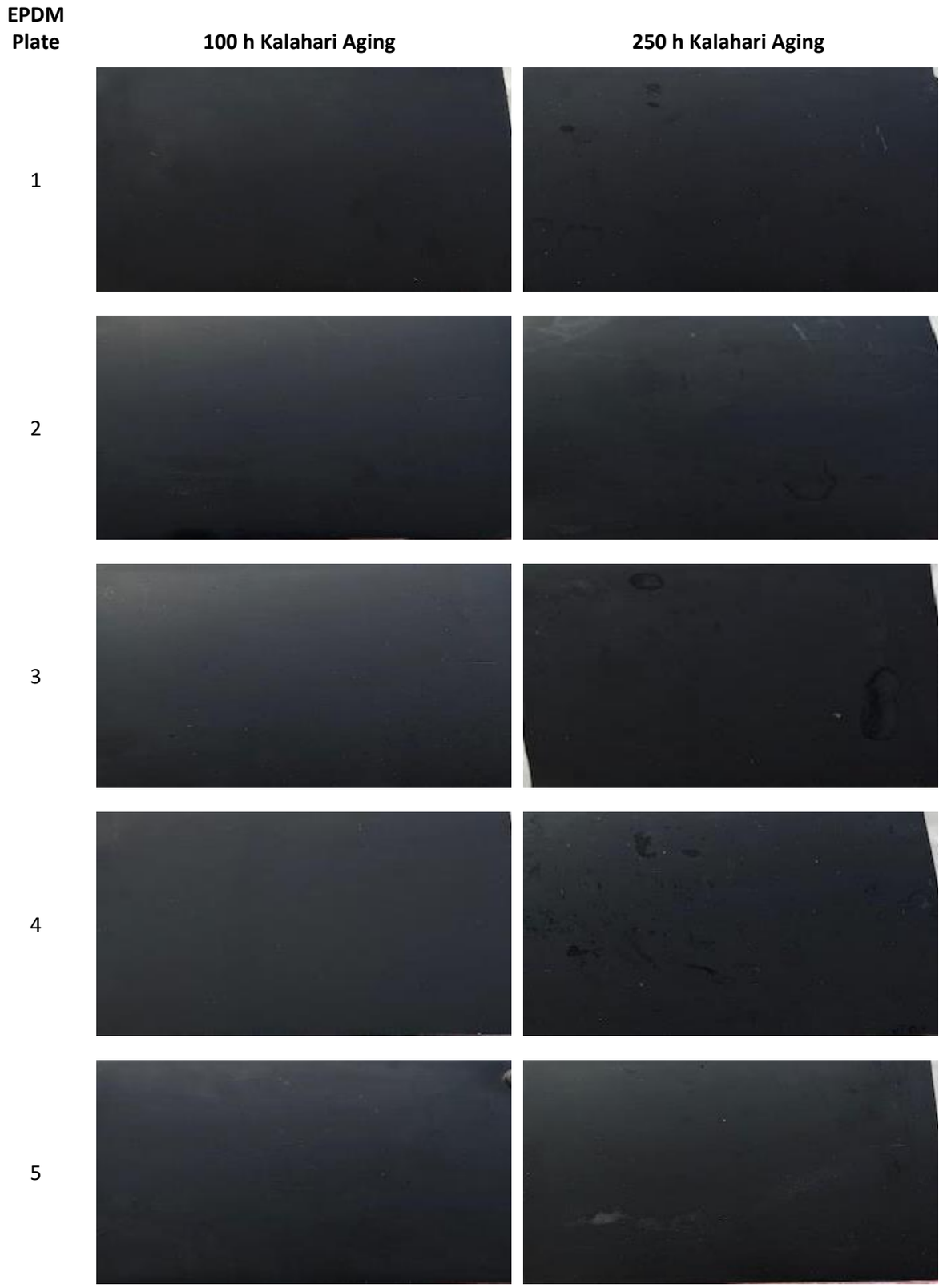

Figure 9. Visual control results of plates added 0, 1, 3, 5 and 10 phr CNF respectively after Kalahari weathering

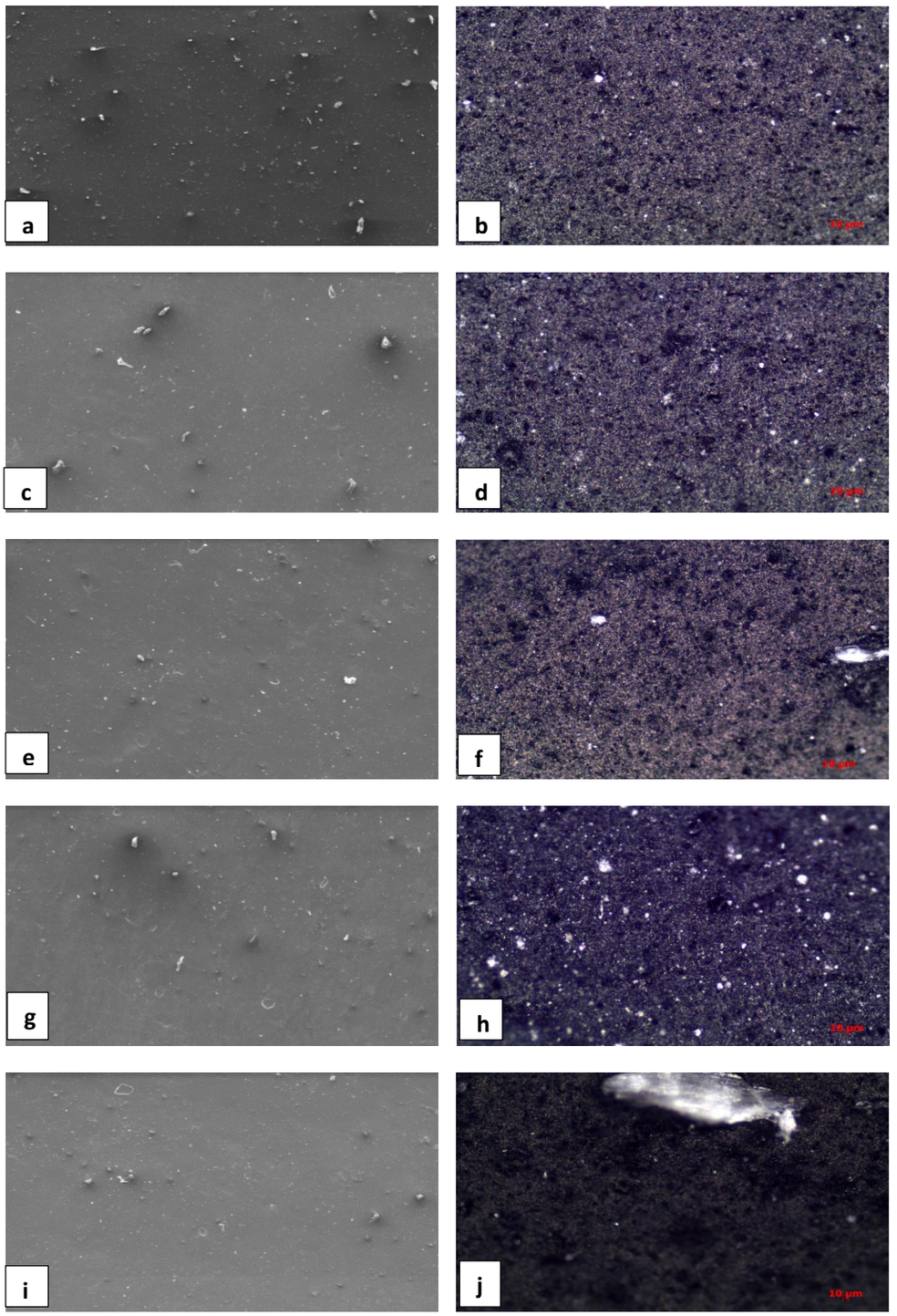

Figure 10. Photographs of (a) EPDM plate 1 SEM, (b) EPDM plate 1 micrograph, (c) EPDM plate 2 SEM, (d) EPDM plate 2 micrograph, (e) EPDM plate 3 SEM, (f) EPDM plate 3 micrograph, (g) EPDM plate 4 SEM, (h) EPDM plate 4 micrograph, (i) EPDM plate 5 SEM, (j) EPDM plate 5 micrograph

Scanning Electron Microscopy (SEM) Analysis

The SEM pictures taken from EPDM plates prepared by addition CNF are shown in Figure 10.

When investigated SEM images of the composites, CNF fillers mostly homogenously dispersed in the EPDM (Fig. 10 b;c;d;e). In addition, no considerable difference was observed although the CNF concentration increased in

the EPDM. Besides, in the images, serious agglomeration, crack, individual fibrils as well as void were not seen. It can be said that in the applied process conditions, CNF as chemically is not degraded in the EPDM matrix.

CONCLUSIONS

In recent years, automotive manufacturers have started research on the use of biodegradable materials in the interior and exterior parts of vehicles. Therefore, nanocellulose reinforced EPDM rubbers were succesfully fabricated as EPDM, EPDM-C1, EPDM-C2, EPDM-C3, EPDM-C4, and EPDM-C5. Then, as mechanical, chemical, thermal, morphological and aging, the obtained EPDM-CNF green composites were investigated detailed. It was seen that tensile strength, elasticity and elongation at break values in the CNF based EPDM rubbers decreased with the CNF, whereas permanent set values increased by the addition of nanocellulose. However, all the obtained values are in the range of acceptable limits. In the rheologic parameters, crosslink density is prone to increase whereas mooney scorch decreased. In the artificial Kalahari weathering test, some cracks and staining in the surfaces were seen after 250h aging over 3 phr of CNF while the surface of those rubbers were not degraded after 100h weathering. When SEM images of the composites are investigated, it can be seen that CNF fillers dispersed homogenously in the EPDM. No alteration is required in process conditions as vulcanisation time has not been changed. Overall, it was concluded that the CNF can be blended with the EPDM matrix up to 10 phr. Nanocellulose/EPDM green composites can be used in the production of sealing profiles. By further studies, sealing profiles used in all vehicles can be a green material.

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