



Enhancing the Physical, Mechanical, Oxygen Permeability and Photodegradation Properties of Styrene-acrylonitrile (SAN), Butadiene Rubber (BR) Composite by Silica Nanoparticles

Nooredin Goudarzian¹, Soheil Samiei², Fatemeh Safari¹, Seyyed Mojtaba Mousavi^{3*}, Seyyed Alireza Hashemi⁴, Sargol Mazraedoost⁵

¹Department of Applied Chemistry, Shiraz Branch, Islamic Azad University, Shiraz, Iran

²Department of Applied Polymer, Shiraz Branch, Islamic Azad University, Darab, Iran

³Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan

⁴Department of Mechanical Engineering, Center for Nanofibers and Nanotechnology, National University of Singapore,

⁵Pharmaceutical Sciences Research Center, Shiraz University of Medical Sciences, Shiraz, Iran. 71348-14336

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Abstract

Polymer-nanosilica composite was prepared using Silica nanoparticles as reinforcing fillers in Styrene-acrylonitrile (SAN). Copolymer Styrene-acrylonitrile (SAN) is such warm, soft clear resins that because of having suitable Physical and mechanical properties, have excellent resistance against chemical also low solvent and cost toward another copolymer styrene that caused to be in a category of much used of them. The effect of increasing nano-silica loadings on the mechanical properties of BR nanocomposites was also studied. Its defect is its fragility that, with its alloying with Butadiene Rubber, prevents its fragility. Basically, with adding inorganic Nano bits, changed strength and modulus of elasticity of plastics while increasing Nano bits decrease the strength of the hit. In this study, copolymer Styrene-acrylonitrile considered as a matrix and for increasing mechanical qualities used Nano bits silica diacid. Results of automated tests (XRD), (TGA), (HDT), and (SEM) were a sign of improvement of mechanical and thermal qualities. Nowadays, due to using lots of plastics in various industries, this probability exists that destroyed whit being exposed to direct solar radiation. So light destroyed plastics is very important. In this project whit using Oxoperoxidant blend prepared with the ability of light destruction, so that after one and three months, results show to destroy its lights.

Keyword: Permeability, Oxoperoxidant, Styrene-acrylonitrile, Degradation

1 Introduction

In the last decade, polymer nano-composites have drawn significant interest from both industry & academia because they often exhibit remarkable improvements in material properties at an excellent level with very low nanofiller loading when compared to pristine polymer or conventional composites. Polymer nanocomposites are a particular class of polymer composites, a type of reinforced polymer having a two-phase material with the reinforcing phase having at least one dimension in the 10-9 m (nm) scale. It constitutes a new class of material having nano-scale dispersion, typically 1-100 nm, of the filler phase in a given matrix. The outstanding reinforcement of nano-composites is primarily attributed to the large interfacial area per unit volume or weight of the dispersed phase (e.g., 750 m²/g). Silica is an abundant compound over the earth employed mainly in industries to produce silica gels, colloidal silica, fumed silica, and so on (1). The nano-sized silica particles are unusual because they are applied in emerging areas like medicine and drug delivery etc. Silica nanoparticles have been used in the industry to reinforce the elastomers as a rheological solute (2-5). Silica nanocomposites have been attracting some scientific interest as well due to the

advantage of the low cost of production and in the high-performance features. Studies on nano-silica dispersions in polymer matrices like poly(methyl methacrylate) (6-8), polyethylene (9), and poly (ethylene oxide- 600) (10), were reported. Studies were reported on polymer nanocomposites based on silica and polymers like poly (vinyl alcohol) (11), poly (vinyl pyrrolidone), and chitosan. The mechanical and thermal properties of polymer nanocomposites were found to be enhanced compared to the pristine polymers. Acrylonitrile-Butadiene Rubber (NBR), is a synthetic Rubber, the most widely used rubber in automobiles components such as fuel hoses, gaskets, rollers, and other products in which oil resistance is required along with heat resistance properties (12-14). Rubbers are reinforced with fillers to improve their performance by incorporating materials of conventional fillers such as carbon blacks, silica, clay, talc and calcium carbonate, etc. In recent trends, Rubber Nanocomposites made out of nanofillers were found to exhibit remarkable property enhancements compared to conventional micro composites (15-18). Polymer nanocomposites with layered silicates which are made using typical fillers, (19-21) and carbon nanotubes had attracted significant interest in the improvement of

Corresponding author: Seyyed Mojtaba Mousavi, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taiwan. E-mail: kempo.smm@gmail.com.

structural properties and the development of new materials having different functional properties (22-25). Sadhu and Bhowmick reported the effect of acrylonitrile content on the mechanical, dynamic mechanical, and rheological properties of the nanocomposite. The Role of an Organic modifier used with montmorillonite on the formation of nanocomposite in the melt compounding process has been studied by Kim and White. Rajkumar et al. studied the effect of liquid NBR as dispersion media for dispersing nano graphite in the NBR matrix, and consequently, polymer nanocomposites were found to improve its thermal stability (26-31). In the current studies, Styrene-acrylonitrile (SAN), Butadiene Rubber (BR), was used as dispersion media to disperse the nano-silica in a polymer matrix using conventional mixing techniques. SAN -Nanosilica based Nanocomposites were prepared using BR as dispersion media and conventional mixing processes. The effect of Nanosilica on mechanical and thermal and photodegradation properties of polymer nanocomposites was studied. The dispersion of the silica nanoparticle in the polymer matrix was studied using scanning electron microscopy [SEM] combined with FTIR. The effect of an increase in nano-silica loadings on the physical properties like tensile strength, modulus, and Elongation at the break, retention properties after air aging were studied, and momentous changes were found in the properties of SAN/ (BR) polymer nanocomposite (32-37).

2 Materials and Methods

Butadiene Rubber (BR JSR -230), Styrene-acrylonitrile (SAN), Nano-silica powder obtained from Nanoshell USA, Styrene acrylonitrile (SAN), (SAN w1540) was supplied by Iran Petro Chemical Co., Ltd. (Iran), [MFR =50 g/10 min (200 °C /21.6 Kg), Density = 1.04 g/cm³]. Styrene/Butadiene/Styrene (SBS) was supplied by Amole Plastic Co, Ltd. Iran. Casein is a commercial material; it was brought from local suppliers and used as received, nano-silica used in this study is commercially available as fine amorphous, nonporous and typically spherical particles, white color, specific gravity 1.12, p the size of nano-silica particles was determined by solving them in an ethylene glycol solvent. The size of the nanoparticles is determined to be 61.5 nm. Figure 1 depicts the diagram of the nanoparticle size (PSA) of the nanoparticles.

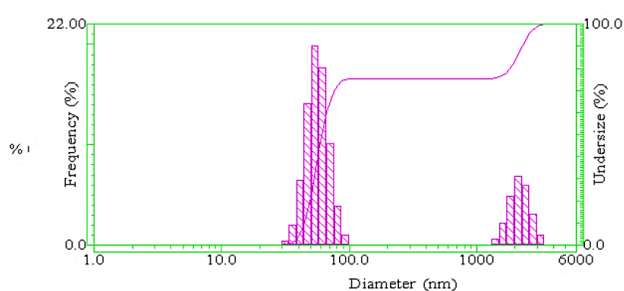


Figure 1: It depicts the diagram of nanoparticle size (PSA) of the nanoparticles

In the first step, the combination of Styrene Acrylonitrile (SAN) and Butadiene Rubber /nano SiO_2 and using the Oxoperoxidant blend was manually mixed to prepare samples. The materials mentioned above percentages combination mixed in a bag by hand to compare the effect of SAN and BR over impact and flexibility of the SAN, and because the materials were new and fully packed was delivered from the manufacturing factory, there was no need to dewatering and gas removing. Adding nano SiO_2 and using Oxoperoxidant blend into SAN, BR combination. To evaluate the biodegradation of

composites, Oxoperoxidant mixture, and nano-particles with different amounts were inserted into the SAN-BR sample, and the samples were prepared. Weight percentages combinations of the prepared samples are presented, as shown in Table 1.

The test specimens, i.e., dumbbell specimens, punched out from the compression molded sheet using Die Cas per ASTM D 412 and utilized for determining physicommechanical properties at the cross-head rate of 500 mm per minute using a universal testing machine (UTM, Zwick 1445). The aging studies were carried out. Evaluate the physical and mechanical properties of all samples with the following conditions for tensile and impact testing standards for injection (see fig. 2).

3 Results and Discussion

3.1 Mechanical properties test results

3.1.1 Investigating the effect of SAN/BR/nano SiO_2 /oxo/on mechanical properties

The mechanical properties of the films depend on intermolecular forces of their polymeric manufacturer chains, the nature of the polymer, fillers, and process conditions. The mechanical properties of pure SAN/BR and SAN/BR/nano SiO_2 /oxo suspension are shown. Moreover, in Figures 3 and 5, these results were compared with each other. As can be seen in Figure 5, with the presence of SAN with coupler agent BR, the tensile strength of sample B has increased in comparison with sample A. Generally, SAN/BR are non-polar polymer and polar copolymer respectively. Their mixture in any weight percentage can cause the formation of two-phase morphology. This phenomenon indicates that the SAN/BR are immiscible. However, with an increase in tensile strength, it seems that BR caused an increase incompatibility between two phases and strengthened the joint surface interactions. By an increase in the interface, the stress transfer to the minor stage SAN/BR/nano SiO_2 /oxo occurred more convenient during the process and caused its uniform distribution in the context of a matrix. On the other hand, very high BR adhesion can act as a crosslinking agent. Therefore, by applying external tension, concentrated stress on the BR can cause stress loss, and avoid the creation of stress concentration areas on holes and cracks. Also, as can be seen in Figure 5, elongation in sample B has decreased poorly, which is due to the high adhesion force of BR and its strong interaction with SAN. It seems that this strong interaction and surface adhesion did not let the polymer chains move and caused a decrease in elongation. Moreover, as can be seen in Figure 5, the amount of Tensile strength and elongation of samples has decreased in comparison with sample 3% nano SiO_2 that is due to the nature of BR that has less modulus than SAN.

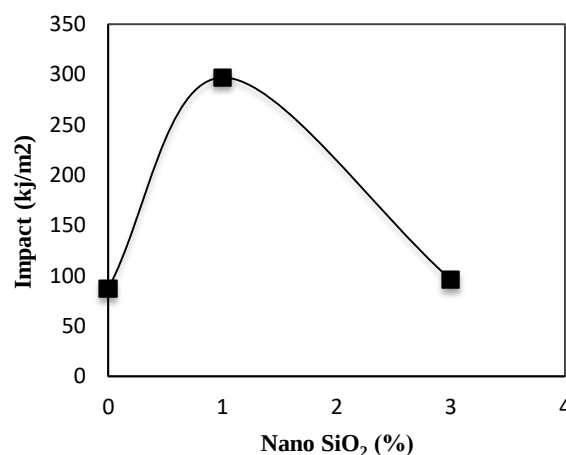


Figure 3: Diagram of the impact index of samples containing different weight percentage nano SiO_2 %

Table 1: Formulation for preparation of SAN/BR – Nano-composites

Sample	SAN (%)	BR (%)	N (%)	OXO (%)
SAN/BR	95	5	-	-
SAN/BR(A)	90	10	-	-
SAN/BR(B)	80	20	-	-
SAN/BR(C)	70	30	-	-
SAN/BR(D)	60	40	-	-
SAN/BR 0% N(E)	79	20	1	-
(F)/N 20% SAN/BR	77	20	3	-
OXO0.5(G)/ SAN/BR	79.6	19.9	-	0.5
OXO1(H)/ SAN/BR	79.2	19.8	-	1
OXO2(L)/ SAN/BR	78.4	19.6	-	2

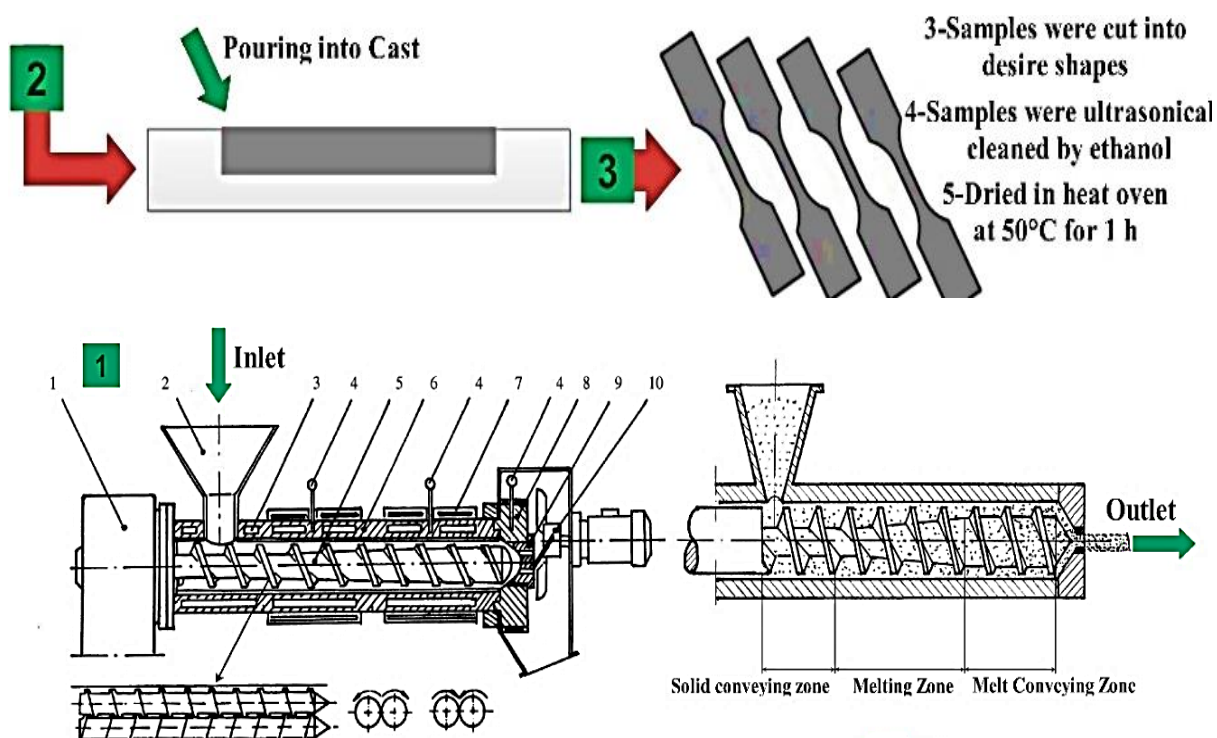


Figure 2: Steps of the manufacturing method, also in step 1, numbers 1-10 shows 1-engine, 2-feeder, 3-cooling jacket, 4-thermocouple, 5-screw

Table 2: Terms of molding injection, molding blends injection

Samples	Process Temperature (°C)	Mold Temperature (°C)	Pressure injection (Mpa)	Rate Injection ($\frac{mm}{s}$)
SAN/BR	180-220	40	25-35	15
N/SAN/BR	180-230	50	30-40	15
OXO/N/SAN/BR	180-220	40	25-35	15

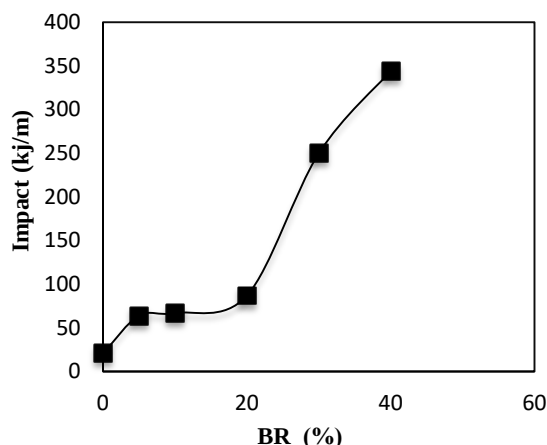


Figure 4: Diagram of the impact index of samples containing different weight percentage BR%

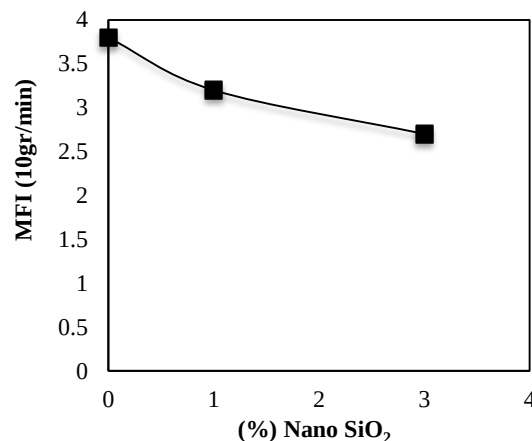


Figure 7: Diagram of the melt flow index of samples containing different weight percentage nano SiO₂

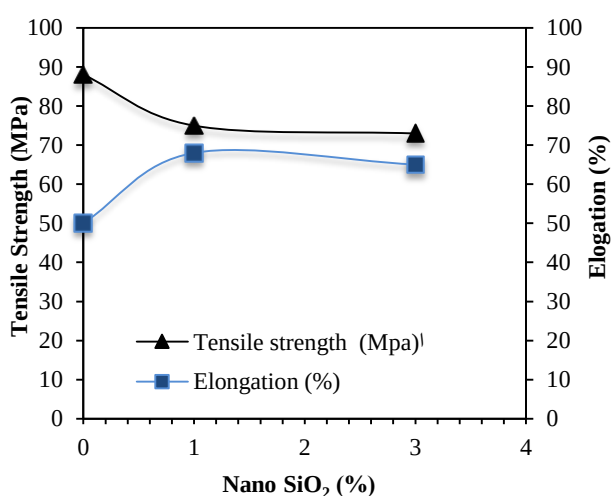


Figure 5: Diagram of the Tensile strength and elongation index of samples containing different weight percentage nano SiO₂

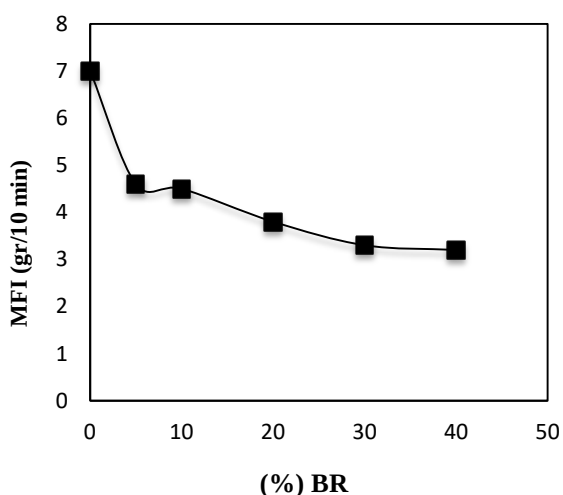


Figure 6: Diagram of the melt flow index of samples containing different weight percentage Nano BR

By observing the obtained results form (see fig 6 and7) diagram it can be concluded that by rising SAN/BR/nano SiO₂/oxo percentage the amount of Hank elastomeric materials in the sample increases and consequently, the fluency decreases and the viscosity also increases thus resulting, melt flow index reduces.

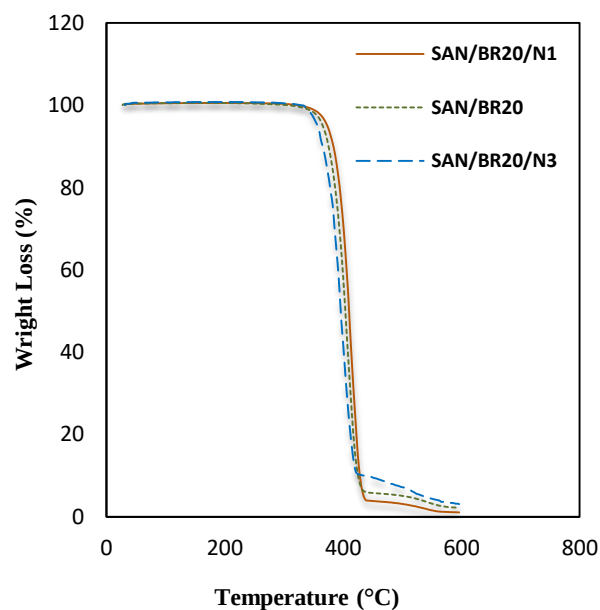


Figure 8: Diagram of Thermal Stability of Blend by TGA

3.2 Thermogravimetric analysis (TGA)

Shimadzu TGA-50 performed TGA test under flowing nitrogen (20 ml/min) atmosphere by 10 °C/min temperature growth rate. 6mg of each sample was placed in a platinum pan, and the change in weight vs. temperature was measured. The above figure shows the results of samples' thermal stability containing various percentage combinations of elastomer polyolefin. Thermal resistance with 1,3% nanoparticles of weight increase of SAN/BR/nano SiO₂/oxo matrix has increased that was due to the formation of the network in the SAN/BR matrix. By the further increase in the percentage of nano SiO₂/oxo in combination, the degradation is shifted to lower temperatures that are due to reduction of percentage combination of SAN/BR in other words, the decreasing in percentage composition of C-N functional group and, by increasing Acrylonitrile group, alloy's thermal resistance rises. Also, according to the diagram can be seen that thermal

degradation of SiO_2 nano-particles and cheese powder starts at about 220°C and thermal resistance of SiO_2 nano-particles, cheese powder, and OXO are lower than SAN/BR matrix alloy, thus by increasing their percentages, thermal destruction occurs faster (see Fig 8).

3.3 Heat temperature results test (HDT)

Nanoparticle silica, the thermal stability matrix, is a polymer that illustrates in Figure (9), increased the matrix polymer of the crystallinity network, strengthen is because of HDT Increased, postponed has been lattice crystal crumble Completely.

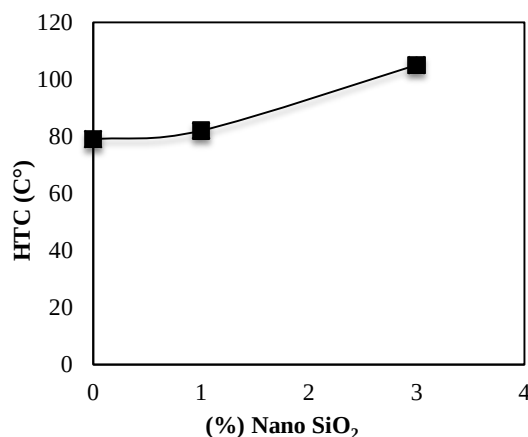


Figure 9: heat temperature results for samples

3.4 X-Ray Diffraction (XRD) test results

Figure 10 shows the XRD results of pure SiO_2 and sample. As can be seen, the related peak to the closest 30B in 2θ is 81.3° , which shows that the distance between the layers of SiO_2 nanoparticle is about 34.18° . But this peak in the sample with polymeric context has vanished that is due to foliating of NC layers. As mentioned in the mechanical test sections, presence of OXO as a compatible agent and on the other hand presence of SAN/BR/nano SiO_2 /oxo can lead to better dispersion of nano SiO_2 , because OXO polar chains have better compatibility with nano-size particles [61.5nm]. Due to applied shear force during the process, it has penetrated the nano SiO_2 layers and has turned these layers apart. By an increase in distance of silicate layers in nanoparticles, the dispersion quality of nanofillers will increase, and their interaction with the polymeric substrate will be improved. Also, XRD results justified the mechanical properties.

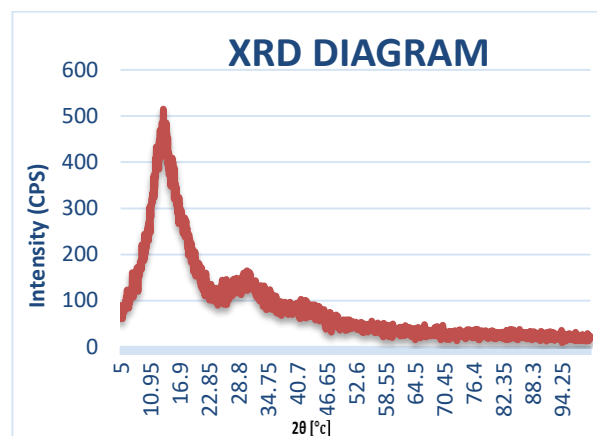


Figure 10: X-Ray Diffraction (XRD) test

3.5 Oxygen permeability tests results

Results of samples' oxygen permeability can be seen in Table 3. In Fig. 11 the effects of oxygen permeability for samples were compared. As can be seen, with the presence in sample D, the amount of oxygen permeability in comparison with sample E was increased. As mentioned in the steam permeability section, it seems that aggregation nano SiO_2 in the polymer context can lead to the creation of gaps in the polymer context. Thus, gas molecules have the opportunity to pass. The results of the mechanical properties section justified this possibility.

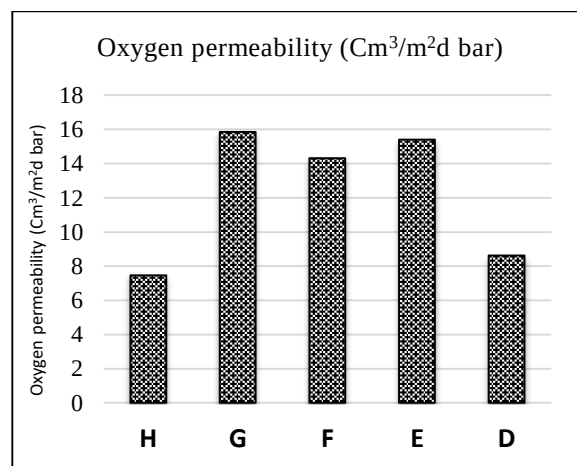


Figure 11: Amount of oxygen permeability for the samples

Table 3: Effects of oxygen permeability

Sample code	Relative humidity (%)	Temperature (°C)	Oxygen permeability (Cm ³ /m ² d bar)
D	24	23	8.63
E	24	23	15.4
F	24	23	14.32
G	24	23	15.86
H	24	23	7.46

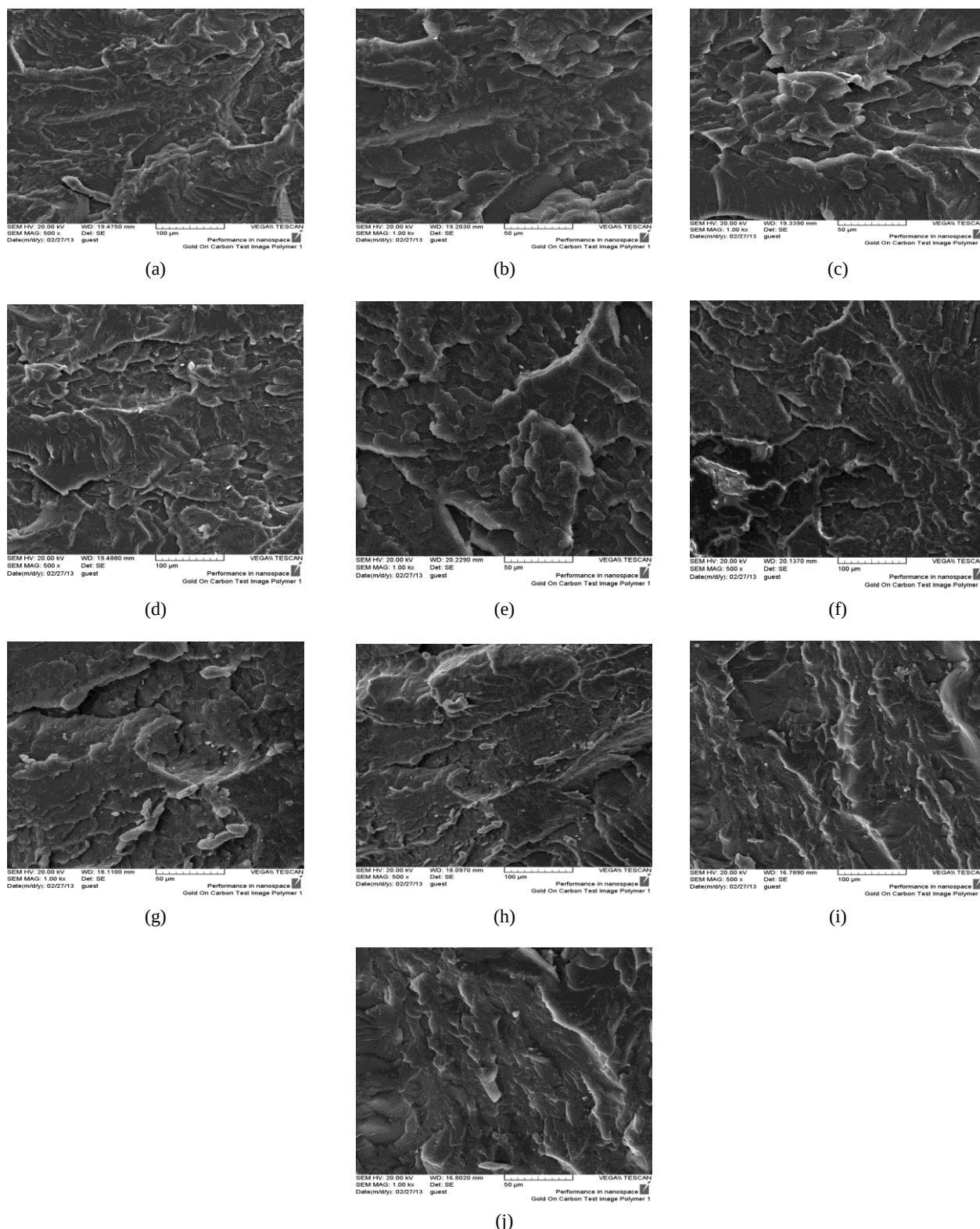


Figure 12: Microscopic images of samples containing different weight percentage of (a,b), (c,d), (e,f), (g,h), (i,j)

Also, the presence of nano SiO_2 in the sample F formulation can lead to an increase in oxygen permeability of this sample in comparison with sample E. On the other hand, the presence of nano SiO_2 and oxo in sample G, increasing the oxygen permeability of this sample in comparison with samples. In fact, according to what has been observed, each one of nano SiO_2 and oxo can lead to an increase in oxygen permeability. Also, the simultaneous effect of these two factors can be

directed to a significant increase in the amount of oxygen permeability. Also, the same situation has been observed for steam permeability. Also, as mentioned in the steam permeability section and by citing to the XRD and SEM results, these results justified the distribution of fillers between the layers and foliation of nanoparticles. It seems that the placement of the silicate sheets with high surface to volume ratio between the polymer chains has increased the oxygen

passage route distance in the film. Thus these silicate sheets acted as oxygen blockers in the context of a matrix. Also, the highest oxygen blocking is related to the nanocomposite film. Therefore, the order of oxygen permeability for different samples is as follows.

3.6 Scanning Electron Microscopy (SEM)

The electron microscope was used to capture from the surface of the samples (a,b),(c,d),(e,f),(g,h),(i,j) SAN/BR composite that extracted from the soil to investigate surface and microstructure of alloys containing various weight percentages of the samples weight percent of oxo before degradation, one and three months afterward. The below figures present the waste, and polymer phases rupture due to chain separation increasing in oxo and SiO_2 nano-particles percentages. In general, with the departure of oxo and SiO_2 nano-particles from the polymer matrix, the polymer chains are disjointed. This phenomenon is due to the termination of a link between the materials and the polymer. On one side, the interactions of the polar functional groups of whey protein and SiO_2 nano-particles on the other side Non-polar and aliphatic groups is destructed by separation of molecules. The ruin of these interactions leads to polymer chains rupture, chain length reduction, and also, the molecular weight that with increasing the percentage of SiO_2 nano-particles and oxo, this reduction has more significant results. The SEM images approved biodegradation of these alloys after one and three months. The rupturing of polymeric phases due to ruptured chains with holes formed in the polymer observed. Finally, composites showed appropriate degradation about mechanical and thermal properties, and flow-ability can be used in full applications such as home appliances and packaging industries (see fig 12).

3.7 Microscopic images (SEM) photodegradation study

The typical synthetic polymer that can be attacked includes SAN and BR whit oxo, where tertiary carbon bonds in their chain structures are the centers of attack. Ultraviolet rays interact with these bonds to form free radicals, which then react further with oxygen in the atmosphere, creating carbonyl groups in the main chain. The showing surfaces of products may then discolor and crack, and in extreme cases, complete product disintegration can occur. Oxidation tends to start at tertiary carbon atoms because the free radicals formed here are more stable and longer-lasting, making them more susceptible to attack by oxygen. The carbonyl group can be further oxidized to break the chain, this weakens the material by lowering its molecular weight, and cracks start to grow in the regions affected. Biodegradable SAN/BR can be biologically degraded by photo UV to give lower molecular weight molecules. This research aims to understand and find a relationship between photooxidative degradation and yellowing of SAN/BR/nano SiO_2 /oxo copolymer. Furthermore, find a simple method for following the degradation. By changing the microstructure of SAN/BR/nano, SiO_2 /oxo copolymer UV oxidation can induce photooxidative degradation of the copolymer. The butadiene phase is the main responsible phase that causes the photo-oxidative degradation in SAN/BR/nano SiO_2 /oxo copolymer degradation. Photo-oxidative degradation of SAN/BR/nano SiO_2 /oxo copolymer begins, like all polymers, at the surface, which is directly subjected to UV light. The surface of the SAN/BR/nano SiO_2 /oxo copolymer, however, shows more damage when compared to the interior part and other polymers. Photo-oxidative degradation of SAN/BR/nano SiO_2 /oxo copolymer leads to color development (degradation) on the surface of the UV aged samples. Surface degradation is one of the measures of the extent of photo-oxidative degradation. This means that as the

UV irradiation time and energy of UV light increase, yellowness at the surface of SAN/BR/nano SiO_2 /oxo copolymer samples becomes more. **SEM Analysis.** The surface identification and distribution of SAN/BR/nano SiO_2 /oxo 0.5% and 2 % nanocomposites, and 30 and 90 days (day) after the photodegradation was carried out by SEM analysis (see fig 13 to 16).

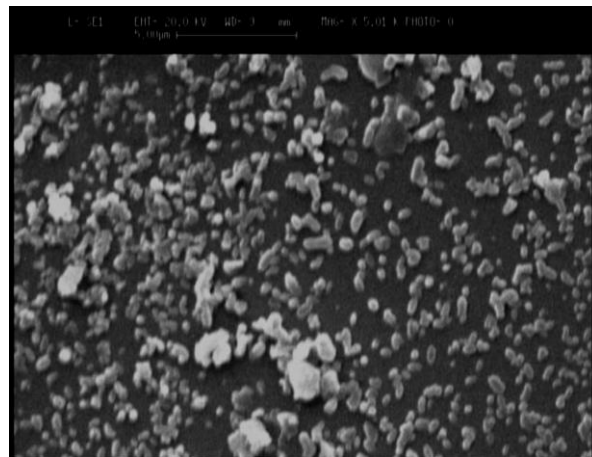


Figure 13: SEM test of sample 0.5% oxo the 30 days' time (day) after the photodegradation

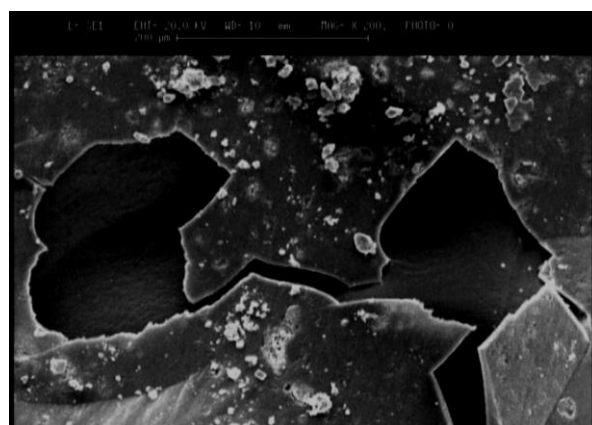


Figure 14: SEM test of sample 2% oxo the 30 days' time (day) after the photodegradation

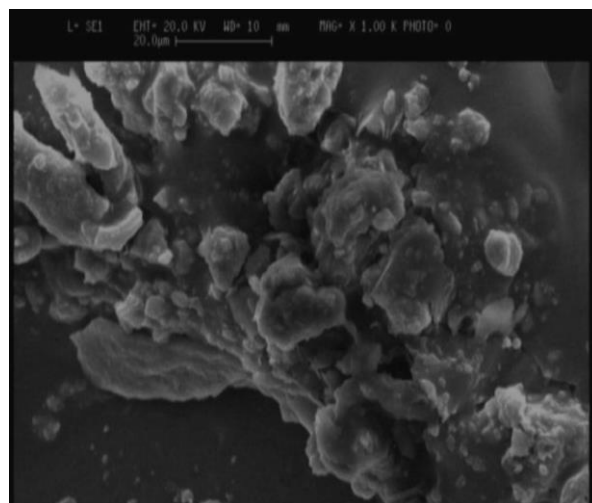


Figure 15: SEM test of sample 0.5% oxo the 90 days' time (day) after the photodegradation

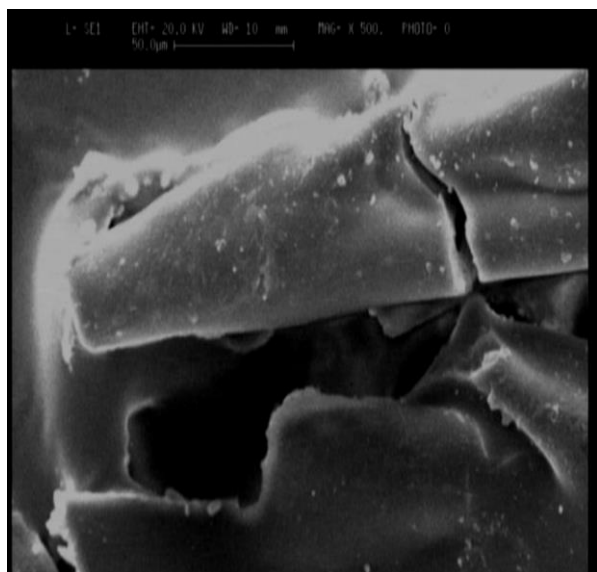


Figure 16: SEM test of sample 2% oxo the 90 days' time (day) after the photodegradation

4 Conclusion

In this paper, Preparation of the Oxoperoxidant and physical, mechanical, and oxygen permeability, photodegradation of nanocomposite using the SAN/BR/nano SiO₂/oxo was studied. The results cleared that water adsorption increased in the presence of SiO₂ nanoparticles. Besides, to study the photodegradation of nanocomposite samples under the soil, XRD and SEM were used. Their results revealed that the existence of the hydroxyl group increased the degradation of the sample.

Additionally, adding the Oxoperoxidant to samples had a positive effect on its degradation. The effect of the addition of Nano-silica fillers in SAN/BR Nanocomposites using liquid nano SiO₂ and oxo dispersion media using conventional mixing techniques was investigated. The addition of Nano-silica increases the thermal resistance of polymer nanocomposites. Improvement in and physical, mechanical properties were found at higher loading of Nanofillers. Also, the simultaneous effect of these two factors can be led to a significant increase in the amount of oxygen permeability. Besides, the same situation has been observed for steam permeability.

Ethical issue

Authors are aware of and comply with best practices in publication ethics, specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution to data collection, data analyses, and manuscript writing.

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