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The effect of chitosan on the physico-mechanical and antimicrobial properties of gamma-irradiated ethylene propylene diene monomer/fumed silica nanocomposites

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Abstract

The goal of this research is to evaluate the recovered chitosan from locally discarded shrimp shells for usage as a biofiller for ethylene propylene diene monomer (EPDM) rubber in green chemistry industries. The utilization of two distinct fillers are expected to improve the qualities of industrial applications while lowering the cost. A laboratory two-roll mill, was used to prepare the rubber nanocomposites by incorporating nano fumed silica and chitosan as biomaterials into the EPDM rubber matrix. The mechanical and morphology characteristics of the produced EPDM rubber were investigated. The rubber nanocomposites were exposed to gamma irradiation doses ranging from 20 to 150 kGy. The tensile strength (TS) of the EPDM/chitosan/fumed silica vulcanizate increased when the chitosan concentration was raised up to 5 phr, but the elongation at break was reduced. However, the use of fumed silica as binary filler with chitosan improved the mechanical performance and thermal stability. The influence of gamma irradiation on the mechanical properties was also explored. The antimicrobial activity of the EPDM nanocomposites agaist Gram-positive (S. aureus) and Gram-negative (E. coli) bacteria was investigated in terms of the zone of inhibition. The results indicated that the nanocomposites irradiated to 100 kGy and containing 10 phr fumed silica and 5 phr chitosan exhibited the highest mechanical, thermal, and antibacterial characteristics and might be used in a variety of applications such as packaging material and surface application/coating based for different devices

Keywords: Gamma radiation; Chitosan; Mechanical properties, Thermal properties, Morphology

Introduction

Ethylene propylene diene terpolymer (EPDM) is a member of unsaturated polyolefins so it can be widely used in industry where EPDM rubber has excellent outdoor properties such as excellent thermal resistance, weathering, oxidation, ozone, and aging resistance. Additionally, it has been widely used in different applications such as automotive weather-stripping and seals, radiator hoses, thermal, and electrical insulations. EPDM rubber has low density, large Mooney viscosity, and strong filling ability [1, 2]. It can be filled with a large amount of rubber filler to alleviate the pressure brought by rubber products to rubber manufacturers. Filling EPDM rubber products with a large amount of filler can increase product volume, reduce production costs and improve the performance of EPDM vulcanizate [3, 4]. In actual production, commonly used reinforcing fillers for EPDM rubber products include carbon black, white carbon black, various inorganic fillers, short fibers, and waste EPDM vulcanizate. For some specific applications several types of fillers were used in vulcanized rubber technology [5-12]. Natural fibres such as sisal [13, 14], banana fibre [15, 16], wood [17, 18], bagasse [19, 20], and chitosan [21, 22] are being employed as reinforcements for thermosetting and thermoplastic polymer composites [19,20] Which might help to reduce pollution [21]. The incorporation of natural fibres in polymer composites improves certain qualities such as high strength, simplicity of processing, and reduced density [22, 23]. Chitosan has several uses, including medicinal and antimicrobial applications, and chitin nano-whiskers generated from crab shells were utilised to strengthen a natural rubber matrix [24-26]. The utilization of chitosan and chitin as antimicrobials may reduce the quantity of synthetic

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food preservatives now used [27, 28]. Chitosan, the world's second natural biopolymer after cellulose, is composed of organic components. Chitosan is a linear biopolymer and a modified polysaccharide. The applications of chitosan are usually contingent upon the degree of deacetylation (DD) and molecular weight (MW) of the polysaccharide [29].Chitosan is mostly derived from shrimp shells [30, 31]. Because nano-fillers have a high specific surface area/volume ratio, even at low loading, the interaction between polymer and nano-fillers can be enhanced. [30, 31]. Because of their inexpensive cost, nano-fillers are a superior solution for ensuring that the original characteristics of the polymer are not compromised by overloading [32, 33]. Fumed silica additions to rubber nanocomposites increase mechanical characteristics, thermal stability, and biodegradability [34, 35]. The introduction of two distinct fillers can improve the end product qualities of vulcanised rubber. Radiation crosslinking provides benefits over traditional chemical crosslinking methods for rubber because it is quicker, more adaptable, produces crosslinking that is consistent, uses less energy, and is ultimately waste-free by nature [36]. It is widely known that radiation exposure improves the mechanical and structural characteristics of crosslinking type polymers. The purity of the processed goods may be maintained because no catalyst or additives are needed. **M. M. Magida et al [37]** Prepared Blends of chitosan/natural rubber latex with different ratios of CS and irradiated by gamma radiation to different doses (10, 25, 50, and 100 kGy). Properties of various blended films of unirradiated and gamma irradiated CS/ NRL blends such as water absorption, thermogravimetric analysis (TGA), FT-IR, mechanical properties, and scanning electron microscopy (SEM) were investigated. It was established that the mechanical property was enriched with the addition of CS into natural rubber. In this study, chitosan was isolated from locally discarded shrimp shells and utilized as a biofiller for EPDM rubber. The effect of binary fillers such as fumed silica and chitosan on the physical and mechanical properties, thermal properties, and morphological assessments of composites was explored. The effect of different gamma radiation doses on elongation and tensile strength was also studied. To establish the applicability of the suggested formulation in the food, health, and medical industries, the bactericidal activity of all composites was tested using the zone of inhibition technique against both gram-negative bacteria (Escherichia coli) and gram-positive bacteria (S. aureus).

Experimental and methods

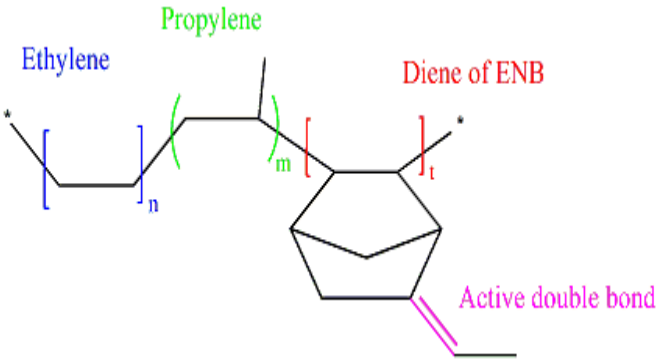
Materials

EPDM (Dutral® TER 4049) with (60%) ethylene content was supplied from Versalis, Italy. The fumed silica (surface area 360-440 m2/g) was supplied by WACKER Chemie AG Co., Germany. The particle size of 28 nm was measured by Abdel Aziz et al [38] using TEM as shown in Fig.1, Merck, Germany, provided The trimethylolpropane trimethacrylate (TMPTM) crosslinking agent was provided by Merck, Germany. Wingstay L antioxidant was made available by the ELIOKEM Company in the United States. Stearic acid, zinc oxide, sodium hydroxide, and acetic acid were supplied by El-Nasr Pharmaceutical and Chemicals Co., Egypt. All of the components were used exactly as they were.

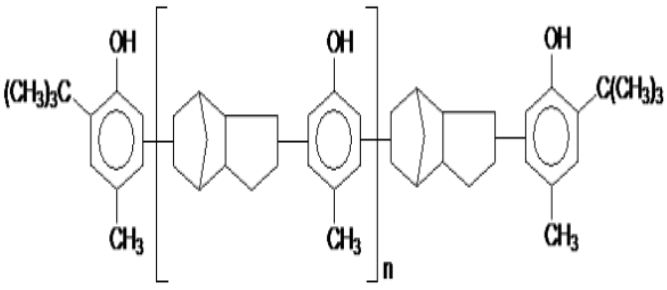
The chemical structure of the rubber nanocomposite ingredients

As shown below, EPDM terpolymer rubber has a chemical structure that has repeating units based on the three monomers ethylene, propylene, and diene. The diene has an active double bond, which is crosslinked when it is extracted.

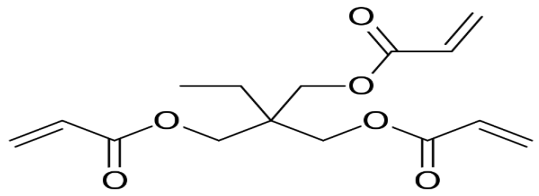
EPDM



Wingstay L antioxidant;

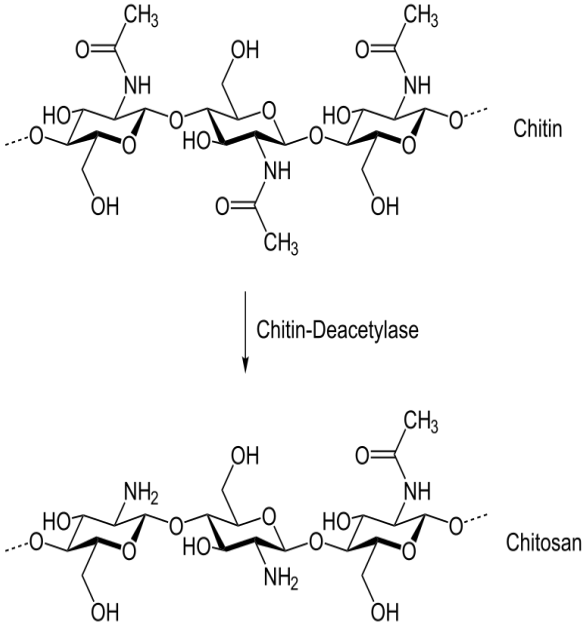


Trimethylolpropane trimethacrylate (TMPTM) crosslinking agent;



Extraction of chitosan [39, 40]

A local enterprise provided the shrimp shells (El-Obour, Cairo). The shrimp shells were scraped, rinsed and then were dried and crushed. To extract pure chitin from powdered shells, deproteinization and decalcification were utilized. The deproteinization procedure was then completed by using a 10% NaOH solution (material/liquor) ratio of 1:5 (w/v) at room temperature for 24 hours. Following that, water was used to wash the shells, and aqueous acetic acid (60%) was used to neutralize the alkali-treated shells. Chitosan was produced by treating previously separated chitin with 50% sodium hydroxide for 90 minutes. The solid-to-alkaline solution ratio was 1:10 (w/v). The purified samples were extensively cleaned with double distilled water until they reached a pH of neutral. The samples were then dried at room temperature. The chemical reaction is represented in Schema 1. The prepared chitosan is a 79 kDa molecular weight, and the viscosity was determined by 0.05–0.15% chitosan dissolved in 0.5 mol/l acetic acid and 0.2 mol/1 sodium acetate solutions using an Oswald viscometer [41, 42]. FT-IR was used to establish the characterization of the generated chitosan.



Schema.1. Deacetylation of chitin forming chitosan

The formulations composition and the recipes

Table 1 lists different prepared formulations of EPDM composites. Except for the chitosan level, all of the components in these formulations remain constant. The mixing was done with a two-roll rubber mill type M 150.

Preparation of composites

The samples were pressed at a pressure of 16 MPa and 180°C for 10 min using a Carver hot press type M 154.

Irradiation technique

Cobalt-60 gamma ray unit at dose rate1 kGy/h, was utilized to irradiate the nanocomposites in the presence of air at irradiation doses 20, 50, 70, 100, and 150 kGy.

Mechanical measurements

The sheets were cut into dumbbell-shaped specimens with a working distance width of 4 mm and a thickness of roughly 2 mm. Tensile strength and elongation at the beak of the nanocomposites were measured at 50 mm/min using the Hung-Ta tensile testing equipment Model HT-9112 (Taiwan).

Scanning electron microscopy (SEM)

The morphology of the nanocomposites was investigated using a JEOL JSM 5400 high-resolution microscope (Shimadzu Co., Japan)

Thermogravimetric analysis (TGA)

Thermal characteristics were evaluated using a Shimadzu (Japan) TG- 50 at a heating rate of 10°C/min and up to 600 °C under nitrogen gas with a flow rate of 20 mL/min. Encapsulated in aluminum pans, the sample weights were around 4 mg.

Evaluation of the bacterial resistance of the composites with different concentration of chitosan

The antimicrobial properties were measured by evaluating the bacterial resistance of the composites with varying concentrations of chitosan against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria. A sterile swab of cotton was used to spread bacteria suspension across the top of nutrient agar plates. Small (1 cm^2) portions of the examined samples were carefully put on the agar surface. The plates were left at 37°C for 24 hours. The inhibitory zone's diameter was assessed [43].

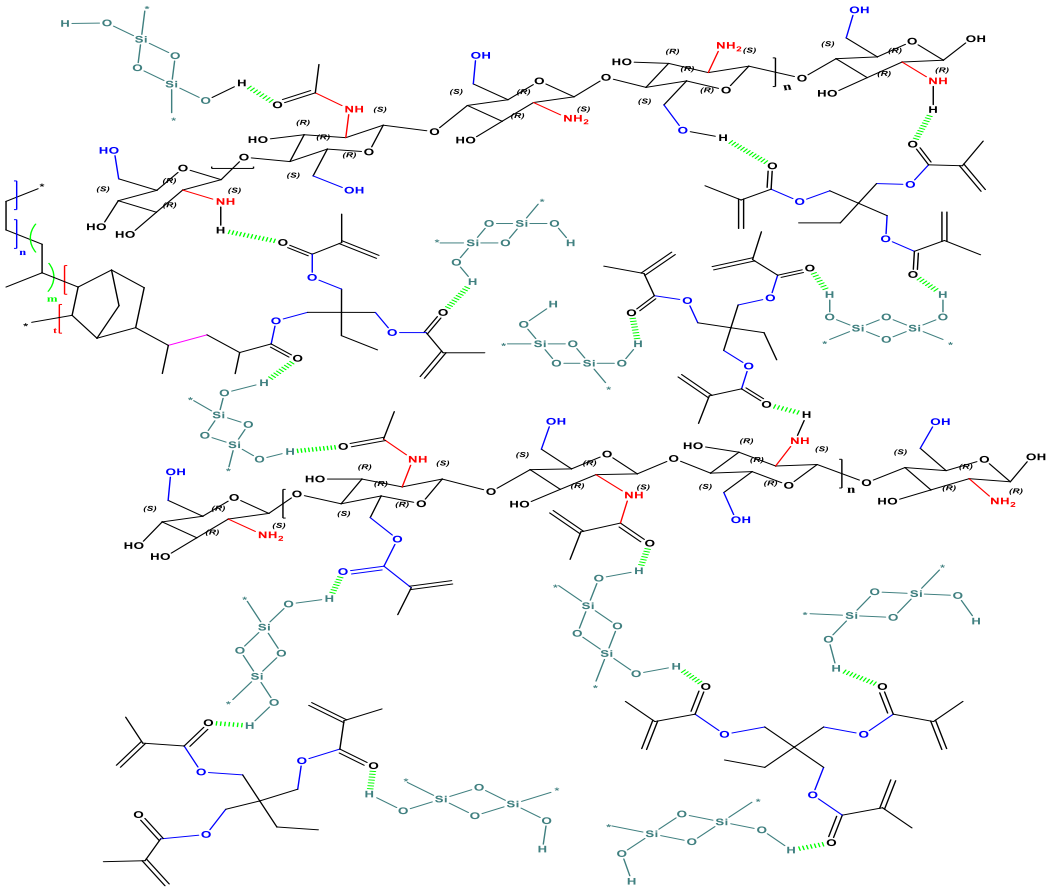
Results and discussion

The FT-IR spectra of the isolated chitosan are shown in Figure 2. The FTIR spectra showed that chitosan displays the typical absorption bands seen around 1620 cm^{-1} (bending vibration of N-H of R-NH_2) and the peaks due to C-H stretching vibrations are observed at 2923.16 and 2858 cm^{-1} and bending vibrations at 1423.72 and 1375 cm^{-1}. The peak for N-H stretching vibration of NH_2 group is shown at 3422.41 cm^{-1}. While confirming the full diacylation of

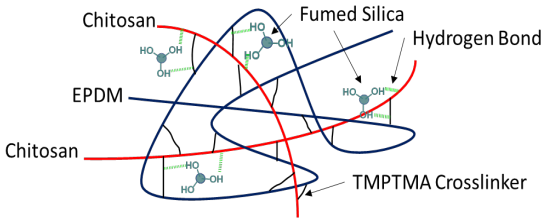
chitin forming chitosan is by the absence of the peaks at 1674.1 cm^{-1} and in the areas around of 3085.9 and 3265.3 cm^{-1} which all correspond to the stretching vibration of C=O and N-H in ($NHCOCH_3$), respectively [44-45].

Mechanical Properties

The association between the tensile strength (TS) of the samples and the γ- irradiation dosage is depicted in Figure 3. According to the graph, adding fumed silica simply enhances the TS; however, inserting chitosan up to 5 phr into EPDM rubber enhances the tensile strength and higher contents marginally decreases the TS values. Tensile strength was improved at low concentrations of 2, 5 phr loading chitosan due to excellent dispersion of chitosan particles through the EPDM rubber chain matrix and good interaction between them [35]. While the TS decreased with increasing chitosan content (10 phr), this might be owing to the agglomeration of long chitosan molecules preventing the dispersion of chitosan and fumed silica in the composite phases. The lack of a well-dispersed phase in composites leads to facile fracture propagation and, as a consequence, poor TS. This tested data was confirmed with the results of some scientific researchers [35, 46-48]. In addition, the TS levels over all composites increased with increasing irradiation dosage, up to 100 kGy, and thereafter declined. When EPDM is exposed to gamma radiation, both degradation processes and polymer chain cross-linking occur at varying speeds [49, 50]. Because polymer breakdown is more prevalent at higher irradiation doses, the tensile value decreases [51]. The possible proposed chemical reactions mechanism between rubber, silica, and chitosan are presented in schemes 2, 3. Figure 4 depicts the relationship between the elongation at break (E %) and irradiation dosage. E% values for composites are expected to decrease as radiation exposure increases due to higher crosslinking density. On EPDM vulcanizate, adding fumed silica and increasing chitosan loading decreased elongation at break. The elongation at break was decreased according to increasing chitin loading on EPDM vulcanizate. The decrease in elongation at break is due to the over load of chitin that reduce and restrict the EPDM chains mobility and consequently reduce the flexibility of chains.



Schema 2: Schematic diagram of the proposed overall chemical reaction possibilities of EPDM/chitosan/fumed silica blend coupled with TMPTMA



Schema 3: The proposed overall crosslinking of EPDM/chitosan/fumed silica blend coupled with TMPTMA

Scanning electron microscopy (SEM)

Figure 5 (a-e) shows the morphology of the EPDM composites gamma irradiated to a dose of 100 kGy using a scanning electron microscopy. Figure 4 (a) shows a smooth and continuous surface for the EPDM composite in the absence of fumed silica and chitosan. Figure 4(b) demonstrates that the fumed silica was dispersed evenly throughout the rubber matrix as a white particles. Figure 4 (C, d) also shows that fumed silica and chitosan were found on the whole interfacial surface, indicating that these reinforcing fillers were dispersed evenly throughout the rubber matrix. Because of their smaller size, the fumed silica nanoparticles are uniform on the surface of the composite than the chitosan. Figure 4(e) also shows that increasing the quantity of chitosan (10 phr) in EPDM causes some clumping and the lowest dispersion.

Thermal Properties

The TGA technique was utilized to measure the thermal properties of the irradiated composites at 100 kGy. The TGA curves and data for these composites were shown in Figure 6 and Table 2. It can be seen that the nanocomposites containing silica has a higher thermal decomposition temperature, indicating an improvement in thermal stability, in which the T_{onset}, T_{50}%, and the **temperatures of the maximum rate of thermal decomposition reaction** (T_{max}) values are greater than those of the blank. Silica is a very hygroscopic material and contained various amounts of free and bond moisture [51,52]. Hence, the earlier commencement of degradation and relatively higher weight loss at the early stage of heating of the samples containing fumed silica is due to the vaporization of the moisture content. A possible reason for the increase in the onset temperature is that fumed silica is an inorganic material with high thermal stability and great barrier properties, which can prevent heat from transmitting quickly and thus limit the continuous decomposition of the nanocomposites. Furthermore, the inclusion of chitosan increased the thermal stability of the composites [35]. These may be attributed to increasing the stiffness of the rubber matrix

Antibacterial activity of EPDM nanocomposites

Table 3 and figure 7 demonstrate the antibacterial activities of the EPDM nanocomposites against Gram-positive and Gram-negative bacteria when evaluating the antibacterial activity for its use as antibacterial. By increasing the content of chitosan, the inhibition zones of the EPDM composites films against Gram-positive and Gram-negative bacteria were enhanced. This result could be attributed to chitosan's antibacterial impact as an antimicrobial agent. Chitosan can interact with the bacterial surface or core, where it penetrates the cell and demonstrates significant bactericidal action. However, the EPDM film containing chitosan had poorer antibacterial efficacy against E. coli than S. aureus. The film's antibacterial action is mostly determined by the cell wall structure of Gram-positive and Gram-negative bacteria. The presence of EPDM film containing chitosan immediately connects with the outer cell wall of Gram-positive bacteria, which has many holes that allow chitosan to easily penetrate the cells, triggering leaking of intracellular contents and cell death. However, in Gram-negative bacteria, chitosan initially connects with the bacterial outer cell membrane, which includes lipoprotein, lipopolysaccharide, and phospholipids, which may inhibit chitosan adhesion.

Conclusion

Using a laboratory two-roll mill, the rubber compounds were formed by incorporating chitosan as a biomaterial and fumed silica into an ethylene propylene diene monomer (EPDM) rubber matrix. Chitosan was derived from leftover shrimp shells. The mechanical characteristics and morphology of rubber nanocomposites were assessed.

The influence of gamma irradiation dosage on the values of the TS for all compositions increased at 100 kGy and then after subsequently declined. Whereas the values of elongation at break (E%) for all the EPDM compositions was found to decrease as the irradiation dosage increased. The composite comprising 10 phr fumed silica and 5 phr chitosan has the greatest TS, while the addition of chitosan marginally lowered the TS while increasing the elongation throughout all applied irradiation doses evaluated. Composites exposed to 100 kGy radiation have the finest thermal and mechanical performance. It can be concluded that EPDM/ 10 phr fumed silica and 5 phr chitosan composites irradiated to 100 kGy have strong thermal, mechanical, and antimicrobial activity capabilities and so have possibility for industrial applications due to their good thermal, mechanical, and antimicrobial activity. EPDM formulations are now used to manufacture goods such as O-rings, gaskets, and hoses. This research suggests that EPDM composite formulations are providing new

properties, which lead to using the composite in advanced applications such as packaging material and surface application/coating based for different devices

Conflict of Interest: The authors declare that they have no conflict of interest

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Abbreviation:

EPDM: ethylene propylene diene monomer

Phr : part per hundred parts of rubber

TMPTM: trimethylolpropane trimethacrylate

TS: tensile strength

E%: Elongation at break

Tonset: the temperature, at which the sample begins to decompose,

$T_{50\%}$: the temperature at which the materials' weight loss is 50%,

T_{max}: the temperature at which the rate of weight loss is maximum.

NCRRT: National Center for Radiation Research and Technology

EAEA: Egyptian Atomic Energy Authority