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Improving The Thermal And Mechanical Properties Of Reinforced Polybutadiene Rubber Composite Using Nano-Sized TiO₂

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Abstract

Polybutadiene rubber (PBR) is the most elastic rubber formed from butadiene polymer. PBR finds wide application in the production of sportswear, golf balls, automobile components, shoe heels. PBR low glass transition temperature allows it to have excellent abrasion resistance (leading to longer tread life), excellent flexibility, and low rolling resistance. In order to improve wet traction, tread compositions often include natural rubber or styrene-butadiene rubber. This study aims to examine the effect of nano titanium dioxide (TiO_2) on the mechanical, thermal properties of polybutadiene rubber (PBR) which was used as a filler. The amount of the TiO_2 in the composite was varied to determine the corresponding effects on the thermal and mechanical properties of the polybutadiene rubber composite. The PBR/TiO_2 nanocomposite was prepared using solvent mixing followed by two roll milling. By applying this technique, the homogeneity of the compound was significantly improved. This can be seen from the morphology observed by the scanning electron microscope (SEM). It was found that the increment of mechanical properties of the PBR/TiO_2 composites with increased contents of nano-size TiO_2. At 2 pphr, the TiO_2/PBR nanocomposites exhibited better tensile test, hardness, and compression properties where it reaches 7.7 MPa, 47.1, and 9.33 MPa, respectively. Also, the thermal conductivity of PBR was improved with the addition of TiO_2.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

Nowadays, rubber technology has become an important part of various industries because of its wide applications in many fields like in the production of tires, balloons, gloves, rubber seals, and others. Natural rubber in the past decades has been widely used in various applications as a polymeric material due to its outstanding elastomeric properties. Nevertheless, rubber has limited applications due to its low Young modulus and strength. Hence, natural rubber needs to be improved by using a variety of fillers to attain an optimum specification for industrial applications [1-5]. Polybutadiene rubber is one type of synthetic rubber which have a superb resistance to wear over natural rubber and styrene-butadiene rubber, which is a key competitor in the rubber industry because of their low-cost rubber and lower glass transition temperatures. [6]. Rubber is typically stuffed with high quantities of reinforced materials such as carbon black and silica to enhance its stiffness and strength. The extent of reinforcement is a function of the strength of filler–filler and polymer-filler interactions [7-10]. Rubber nanocomposites are the kind of packed rubbers during which no less than one

dimension of the fillers is within the nanometer scale. The most widely used nanofillers are carbon nanotubes, graphene, and clay. [6, 11]. Different types of nonblack fillers have been utilized in the rubber industry to modify and improve the properties of the elastomeric material. Adding fillers to natural rubber generally results in a modulus increase and thereby produces a significant improvement in tear and abrasion resistance. Calcium carbonate, precipitated silica, titanium dioxide, and clay are used in rubber compounds to impart desired mechanical and physical properties [12]. TiO_2 has been extensively used as fillers in several polymers' applications because of the enhanced physical and mechanical specifications it creates. The reinforcement of rubber composites is usually influenced by the type of TiO_2 used as a filler. The use of TiO_2 nanoparticles as fillers prevent the occurrence of active hydroxyl groups on the surface of the polymeric materials which is contrary to the use of silica nanoparticles as fillers which often allows the occurrence of surface hydroxyl groups. The absence of the hydroxyl group typically facilitates the propensity to form aggregate, thus leading to an improved homogeneity of the TiO_2

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nanoparticles. This phenomenon is often associated with strong interfacial adhesion in the polymer composites between matrix and filler [13, 14]. Several studies have reported the use of white fillers through the incorporation of TiO_2 into rubber composites [15]. The studies revealed that the tensile strength, modulus, and tear strength increased with increasing TiO_2 loading. In the studies, scanning electron microscopy and atomic force microscopy were employed to examine the morphology, mechanical properties, and adhesion strength of the dispersed filler in the polymer matrix. The characterization revealed that the TiO_2 filler significantly improve the polymer matrix. Seentrakoon et al. [16] reported the efficient reinforcement of nano-sized TiO_2 with a large surface area on natural rubber. The findings revealed that a well dispersed and homogeneity of the nano TiO_2 was attained in the rubber matrix. An increase in the TiO_2 content resulted in the improved mechanical performance of NR/TiO_2 composites. Nano-sized titanium dioxide was studied for the effect in reinforced natural rubber composites by Hayeemasae et al. [13]. The incorporation of the nano TiO_2 into the natural rubber composite improved its mechanical properties. This study, therefore, aimed to investigate the effect of incorporating nano TiO_2 in polybutadiene rubber composites which have not been previously reported in the literature. The morphology, mechanical and thermal properties of resulting nanocomposites.

2. Experimental

Polybutadiene rubber was used as the matrix and it was obtained from Robinson Rubber Products Company, Inc, USA. Carbon black (CB_ N330) with particle < 53 μm, and 99.99% purity was used in the composite formulation. Precipitated silica was purchased from Henan Zhong ya Fine Chemical Engineering (HE NAN, China). The particle size of silica was 100 μm and 99 % purity. The curing system consisted of sulfur was obtained from Almeshraq, Iraq. TiO_2 from Cgangsha Santech Co. with purity > 99.8% and particle size 30 ± 5 nm. Toluene solvent was obtained from SDFCL Co. (S D Fine-Chem Limited, India).

2.1. Preparation of nanocomposites

The composition of the PBR utilized in this study is summarized in Table 1. The inclusion of the TiO_2 into PBR was done using the solvent mixing method. In the first instance, the TiO_2 was dispersed in toluene using ultra-sonication techniques for 2 h. Thereafter, the PBR was added to the toluene solution and the mixture was stirred and kept overnight until the rubber has dissolved uniformly in the toluene. The toluene solution of TiO_2 was subsequently dispersed into the PBR mixture with a continuous stirring for 1 h. Finally, the PBR mixture was evaporated at 50 °C for 48 h to obtain the TiO_2/PBR mixture. Vulcanizing

agent was added to the TiO_2/PBR nanocomposites in an open two-roll mill at room temperature with a rotor speed of 24 rpm and 40 min mixing time [17].

Table 1: the formulation of the PBR composites

Materials	TiO_2/PBR (pphr)
Poly butadiene rubber	100
Carbon black	20
Silica	5
Sulfur	3
TiO_2	0.5, 1 and 2

2.2. Characterization

The morphology of the nanocomposites was examined by scanning electron microscope (SEM, VEGA 3 LM) with an acceleration voltage of 20 kV. Fourier Transforms Infrared spectroscopy recorded on a (Bruker Tensor 27) spectrometer was used to characterize the chemical structure between the nano TiO_2 with rubber. FTIR spectra were collected in the range 4000– 500 cm^{-1} at room temperature. The X-ray diffraction analysis patterns of the nanocomposites were recorded by a Shimadzu-6000 instrument.

Tensile property tests on the nanocomposite samples were made at room temperature according to ASTM D412 using a testing machine (Zwick/Roell). An electronic Shore A (Zwick, Germany) was used to determine the hardness of the PBR composite based on ASTM D2240 standard. The compressive strength of the samples was measured using the compression test instrument (type: Hydraulic Press, England). The Lee's Disk was employed to determine the thermal conductivity of the PBR nanocomposite using an electric potential of 6V and an electric current of 0.25A.

3. Results and Discussion
3.2.1 Tensile Test

The effects of TiO_2 incorporation on the tensile strength of the PBR-based composite are illustrated in Figure 1. It can be seen that the tensile strengths of elastomers increase gradually with an increase in the amount of TiO_2. The tensile strength of the polybutadiene rubber reaches 7.7MPa at a loading level of 2pphr for TiO_2. It can be observed from the results that the TiO_2 reinforcing fillers improve the tensile strength of the PBR matrices. This is due to the bonding force between the fillers and rubber molecules prohibiting the movement of the polymer chain and reduced chain slippage. Another reason is the well-dispersed nanomaterials which are which explain the improvement of the tensile strength. The improvement in the interaction between the matrix and the filler can be ascribed to the adhesion of the polymer to the filler and improved tensile in the composites. The relationship between elongation percentage at break and loading level of reinforcing fillers for PBR is shown in Figure 2. It can be

observed that the elongation at the break (%) decreases gradually with an increase in the additional quantity of TiO_2. The reduction of the elongation at break may be attributed to the stiffening of the rubber matrix by the added nanomaterial. Moreover, the increase in the amount of added filler reduces the movement of the associated molecules due to the formation of the physical bonds that bind the filler particles and the rubber chains that stiffen the matrix. This observation is consistent with Datta et al. [18].
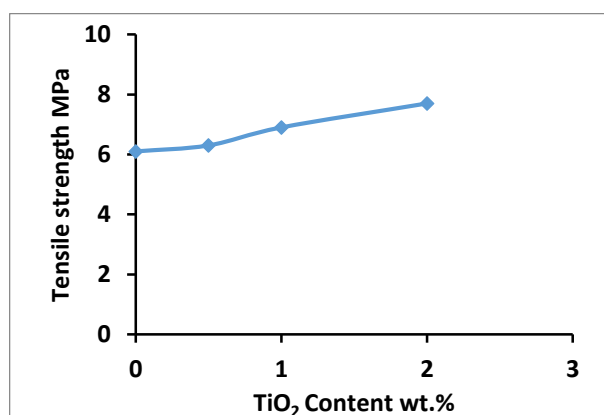
Figure 1: Tensile strength for PBR composite with reinforcing filler TiO_2.
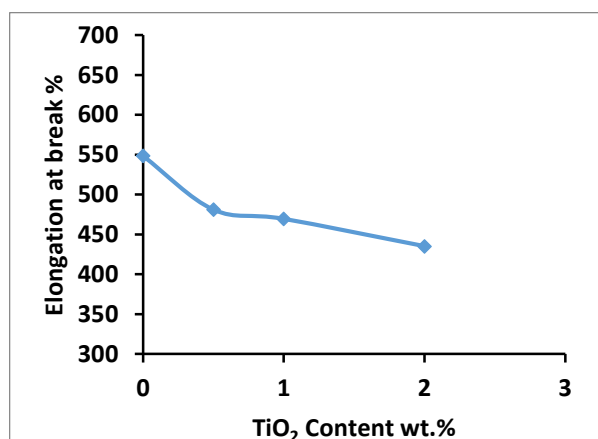
Figure 2: Elongation at break of PBR composite with reinforcing filler TiO_2.

3.2.2 Hardness Test

Figure 3 represents the effect of incorporating TiO_2 nanoparticles on the hardness of the PBR composites. It can be observed that the hardness of the PBR composite increases with an increase in TiO_2 reinforced fillers which inturn improves the surface resistance. Also, it can be seen that TiO_2 reinforcing fillers increase hardness at a rate higher than the PBR matrix. This is due to increase adhesion between nanomaterials and rubber matrix consequently increases cross-linking density. These results are in agreement with Datta et al. [18].
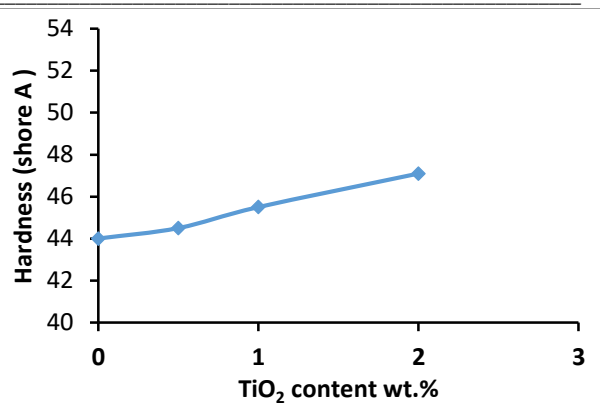

Figure 3: Hardness of PBR composite with reinforcing filler TiO_2.

3.2.3 Compression Test

The relationship between compressive strength and nano-additive concentration for rubber specimens was shown in Figure 4. The compression strength of the TiO_2 at 2 pphr resulted in the highest stress value of 9.33 MPa compared to 6.66 MPa for the PBR. This occurrence can be attributed to the increase in the compression strength of the TiO_2 compared to the pristine PBR in the de-aggregation of the filler particles. Besides, there is a uniform dispersion of the individual particles in the matrix, and the secondary causes is the particle size of nanofiller, aspect ratio, filler/matrix interface adhesion, and particle loading in the rubber. The interaction between filler and the rubber led to an increasing cross-linking property which could result in a large surface area that could help to connect with all chain polymers and increase the resistance to the load [19].
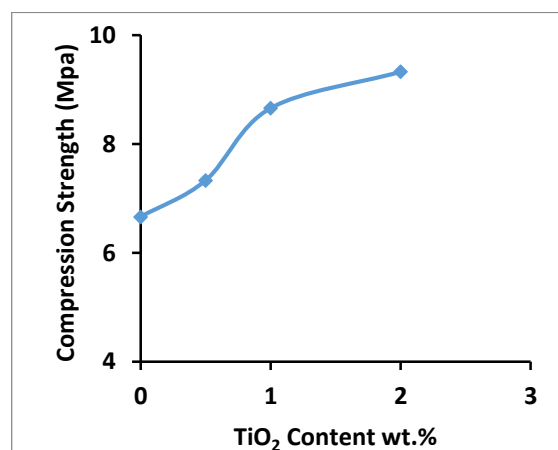

Figure 4: Compression strength of PBR composite with reinforcing fillers TiO_2

3.3 Thermal Properties

The thermal conductivity of the PBR composites based on the effect of incorporating the nano TiO_2 loading is shown in Figure 5. It can be seen that the thermal conductivity gradually increases with an increase in the amount of TiO_2. The thermal conductivity of the PBR composite filled with TiO_2 is higher than the unfilled composite nanomaterial. This

can be attributed to the effect of the incorporated TiO_2 nanoparticles on the rubber which is higher than the thermal conductivity of the pristine rubber. Moreover, it can also be attributed to the large interface thermal resistances between TiO_2 and polybutadiene rubber as reported in [20, 21].
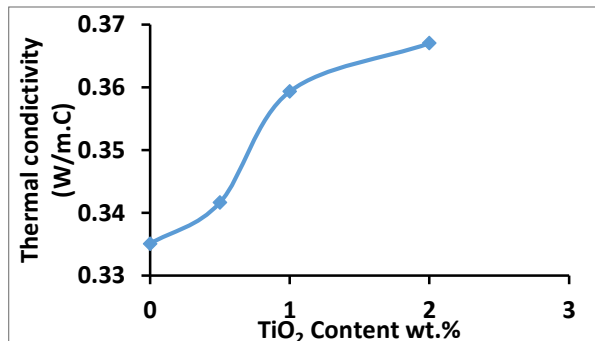

Figure 5: Thermal conductivity of PBR composite with reinforcing filler TiO_2.

3.4 Structural Characterization
3.4.1 Scanning Electron Microscopy (SEM)
Uniform dispersion of TiO_2 in the nanocomposites was observed through scanning electron microscopy as shown in Figures 6 and 7. The nano-titanium dioxide was dispersed homogenously in the polybutadiene rubber matrix, indicating that using the ultrasonic-assisted mixing roll mill to prepare the nanocomposites produced a better dispersion. Well-dispersed nano TiO_2 in PBR composite is regarded as the most important factor to obtain excellent mechanical and thermal specifications. The results of the present work are in agreement with [14].
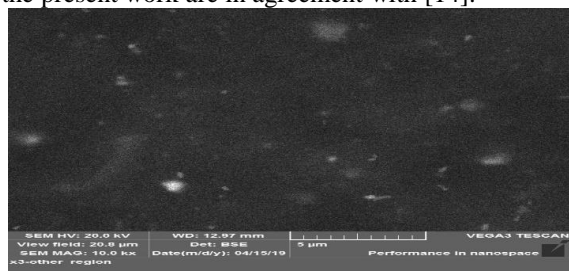

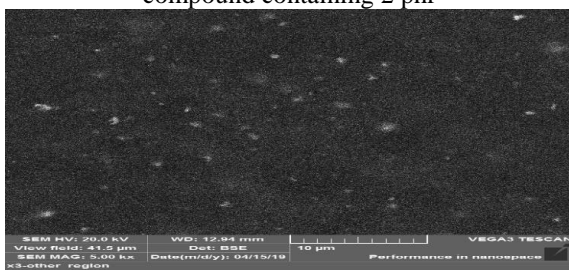**Figure 6:** SEM images of TiO_2-filled PBR compound containing 2 phr

Figure 7: SEM images of PBR filled with additives
3.4.2 Fourier Transforms Infrared Spectroscopy
The chemical structure of PBR-TiO_2 composites was analyzed as indicated by the FTIR spectra shown in

Figure 8. As shown in Figure 8, asymmetric stretching vibrations at 2848.10– 2915.84 cm^{-1} represent the bands assigned to the CH_2 symmetric. Whereas the peaks at 2954.56 cm^{-1} could be ascribed to the CH_3 asymmetric stretching vibration. It can be observed that the peak at 3340 cm^{-1} corresponds to the hydroxyl groups' presence on the surface of the TiO_2 nanoparticle. The unfilled composites with a peak at 959.71 cm^{-1} can be attributed to the C=CH vibration bond that disappeared after the addition of TiO_2 into the rubber matrix. Similarly, the C=CH vibration bond can be found at 1429.07 cm^{-1}. Besides, at 660 cm^{-1}, a broad peak can be observed which corresponds to the absorption band of Ti–O and O–Ti–O flexural vibrations. Also, the peak at 1016.09 cm^{-1} can be ascribed to the C=CH deformation vibration in the PBR composite as reported by [20].

Figure 9 shows the FTIR spectra of PBR. The broad peak at 3380 cm^{-1} and 1468.76 cm^{-1} signifies the occurrence of O–H and C=O stretching vibration in the PBR composite. Similarly, the stretching vibration of C–O, and C–OH can be ascribed to the peaks at 1366.25 cm^{-1} and 1228.67 cm^{-1}, respectively while the peak at 1388.64 cm^{-1} signifies the presence of C = C stretching vibration in the PBR composite as reported by [22-23].
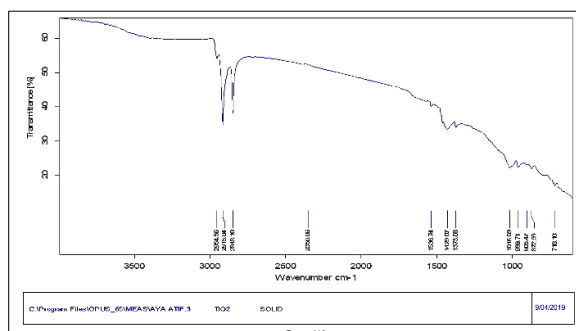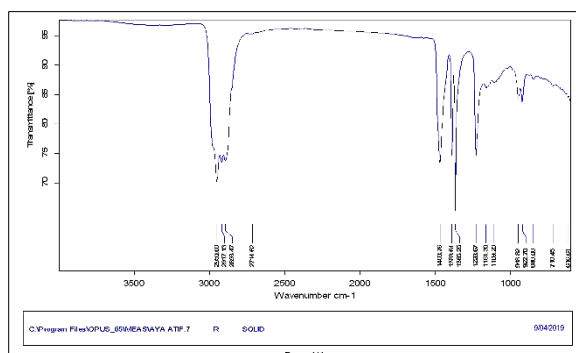

Figure 8: FTIR spectra of PBR/TiO_2 nanocomposites

Figure 9: FTIR spectra of PBR composites

3.4.3 X-Ray Diffraction
The XRD patterns of the PBR-TiO_2 and PBR nanocomposites are shown in Figures 10 and 11. The broad diffraction peak of the TiO_2 in the rubber composites around 20° implies the presence of a non-

crystalline form of PBR. Whereas the diffraction peaks between 30–70°indicated a crystalline structure. All the samples display no clear characteristic peaks of TiO_2, suggesting that the TiO_2 is uniformly dispersed in the polymer matrix. The XRD pattern for matrix PBR is shown a characteristic peak at $2\theta = 14.5°$ and 43°. The results of the present work agree with the reference [13].
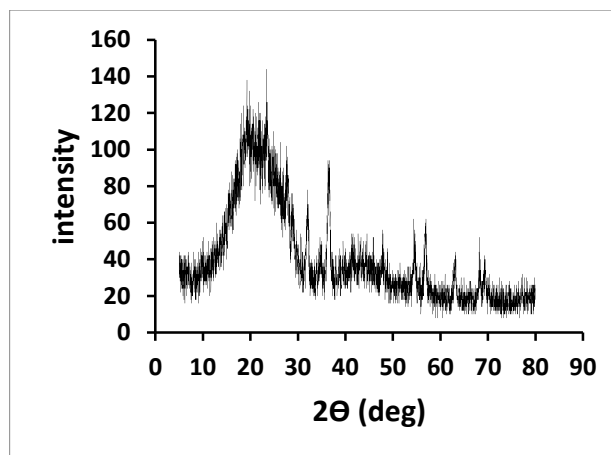

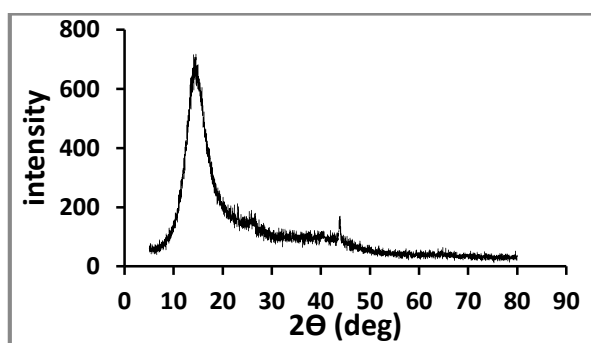***Figure 10:*** *X-ray diffraction patterns of PBR- TiO₂ nanocomposites with 2pphr*

Figure 11: *X-ray diffraction patterns of PBR composites.*

4. Conclusions

The results showed that incorporating TiO_2 as filler resulted in a robust PBR composite with enhanced mechanical properties and thermal stability. The Prepared PBR composites exhibited higher tensile strength, hardness, and elongation at break than the unfilled polybutadiene rubber. The nano-sized TiO_2-filled composites exhibited better dispersion in the elastomeric matrix, shown by SEM micrographs. The XRD pattern of the matrix PBR-filled TiO_2 is a broad diffraction peak around 20° depicts the noncrystalline structure of PBR, while the diffraction peaks between 30–70° depict the crystalline structure. All the samples show no obvious characteristic peaks of TiO_2, indicating that TiO_2 is homogeneously dispersed in the polymer matrix. The FTIR spectra conclude the presence of functional groups including hydroxyl groups and carbonyl groups on the surface of rubber nanocomposite.

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