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Chitosan-reinforced nitrile rubber – a step towards sustainable development

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ABSTRACT

This work aims to investigate the effect of chitosan powders on the mechanical, morphological and thermal behaviour of nitrile rubber (NBR). The chitosan content has been varied between 0 and 15 phr. NBR was initially loaded with chitosan using a two-roll mixing mill along with compounding agents and then cured by compression moulding using accelerated sulphur vulcanisation strategy. The results indicate that the mechanical properties of NBR increase at a critical loading of chitosan (12 phr). A new Chitosan Efficacy Index has been proposed to understand the effect of chitosan loading on overall mechanical properties. Morphological examinations by using scanning electron microscopy pointed towards the presence of voids and discontinuities within the fractured surfaces of the composites. Thermogravimetric analysis and water absorption studies have also been carried out to complement the results from the investigation of mechanical properties.

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Chitosan; nitrile rubber; cure time; mechanical properties; tensile test; morphology; TGA; water absorption

Introduction

Synthetic rubbers are mainly made from petroleum-based monomers. About 65% of the rubbers being used in the world belong to this category. Acrylonitrile–butadiene rubber, butadiene rubber, solution styrene–butadiene rubber, styrene–butadiene rubber, polychloroprene, ethylene–vinyl chloride copolymers and polybutadiene are some of the rubbers being utilised in industries now [1–4]. Among them, acrylonitrile–butadiene rubber (NBR), commonly known as nitrile rubber, is of significant commercial and academic interest as it is extensively employed for the manufacture of various products such as fuel hoses, O-rings, shoe soles, seals and automotive parts; owing to its excellent oil resistance and chemical stability [5–7]. It is a copolymer of acrylonitrile (ACN) and butadiene (BR) having physical and chemical properties varying based on the composition. The amount of acrylonitrile content determines the oil resistance of the rubber. The advancement in industrial requirements and quality concerns pushes researchers now to modify the intrinsic features of NBR through different routes. The reinforcement of NBR with compatible fillers is considered an ideal strategy in this regard [8–10]. However, disposal issues, by the end of the service life of synthetic rubbers like NBR, suggests researchers employ biodegradable fillers preferentially [11,12].

In view of the above, nowadays, the rubber industries are showing great interest in using biological fillers such as bamboo, cuttle-bones, oil palms,

wood, rice husk, starch, coconut shell floor, and chitin. Biodegradability, low cost, lightweight, and great versatility for chemical modifications made them attractive candidates for the design of innovative elastomeric materials having specific properties for niche applications [13–15]. Among the existing natural fillers, chitosan is an excellent candidate that can be used as fillers in synthetic rubber due to its biocompatibility and biodegradability [16,17]. The primary sources of chitosan fillers are the renewable resources from marine crustaceans like crabs, crayfish, squid, shrimp, lobster and prawns. These biomasses remain highly abundant across the globe due to the enormous number of food and canning industries. The wide applications of chitosan ranging from pharmaceutical to water treatment and plant protection are attributed to its premium film-forming ability, good antimicrobial activity, and decent mechanical properties [18,19].

Chitosan-based composites have been investigated by different research groups who subsequently reported the efficiency of chitosan to interact with matrices, with good dispersion features, and thus to cause an elevation in mechanical properties [20], packaging properties [21] and adsorption properties [22]. Typically, the effect of chitosan on elastomers such as polypropylene [23], vulcanised natural rubber [24] and epoxidised natural rubber [25] has been investigated. However, no systematic studies have yet been reported on the effect of chitosan on nitrile rubber compounds with a combined focus on cure

time, mechanical properties, thermal degradation, morphology and water absorption. Therefore, a streamlined investigation has been carried out on the effect of chitosan loading on the cure, morphological, mechanical, thermal and water sorption features of NBR, through the present work.

Experimental details

Materials

NBR containing 33% acrylonitrile was obtained from Common Facility Service Centre (CFSC), Manjeri, India. Chitosan particles of average size less than 100 μm , were obtained from Kerala Mathsafed Corporation, Kollam, India. It was obtained by processing the shells of shrimp, crab, squid, etc. Chemically it is an amino-polysaccharide. The compounding agents like zinc oxide (ZnO), stearic acid (SA), tetramethylthiuram monosulfide (TMT) and sulphur (S) of commercial-grade; obtained from local suppliers.

Sample preparation

The nitrile rubber compounds with varying chitosan loading were prepared as per the formulations shown in Table 1. The mixing was performed on a two-roll mixing mill. NBR was initially masticated for 5 min within the rollers of the mill. The temperature was maintained below 40°C by the circulation of cold water. The compounding ingredients were added one by one in sequence as shown in Table 1. The uncured specimens (5–10 g, each) were analysed in a Monsanto Rheometer at 150°C to determine their corresponding cure time as per ASTM D-2084-07. The samples were then compression moulded using a hydraulic press up to the cure time so noticed.

Assessment of mechanical properties

The ASTM D412 standard specimens for tensile testing were cut from the moulded sheets which were previously conditioned for a minimum of 24 h at room temperature. Tensile tests were performed at a temperature of 25°C by using a Universal Testing Machine (Instron 4411) at a crosshead speed of 500 ± 50 mm/min. Tensile modulus, tensile strength and percentage elongation at break (or tensile strain) were determined from the data of tensile tests. The hardness of the samples was also evaluated by using a Shore A hardness tester (ASTM D2240) at a temperature of 25°C.

Scanning electron microscopy

The cross-sectional morphology of tensile fractured surfaces was studied using a field emission SEM (Hitachi SU6600, Japan). The objective of this study was to

explore the dispersion of chitosan fillers within NBR. To eliminate the building up of electrostatic charges, the samples were sputter-coated with gold before the SEM analysis.

Thermogravimetric analysis (TGA)

Analysis of thermal stability by TGA can ensure the safe working conditions of NBR products as they are being subjected to high temperatures during different practical applications. TGA was performed using a Perkin Elmer Diamond TG/DTA instrument. For this, 5–10 mg of the samples were heated from 40 to 740°C at a heating rate of 10°C/min under a nitrogen atmosphere. The peak temperature and residual weight percentage of the NBR-chitosan compounds were compared with unfilled NBR compounds.

Absorption studies

Oven-dried samples of diameter 25 mm and thickness 2 mm were immersed in distilled water kept at atmospheric temperature. Initial weight (W_i) and weight of the samples after immersion (W_f) in grams for a duration of 1-day was recorded. The samples were gently wiped using tissue paper to remove water from the surface before weighing. The absorption (%) by the samples have been expressed as:

$$\text{Increase in weight (\%)} = \frac{(W_f - W_i)}{W_i} \times 100 \quad (1)$$

Results and discussion

Cure time

The Monsanto Rheometer gives the rheographs of the samples as time-torque plots. The torque elevation with time is a reflection of crosslink density and hence the modulus of samples. The maximum torque is indicated by a plateau region in the plots. The time to reach this torque is represented as t_{100} . However, for the safety of products, they are cured only to 90% of the maximum torque (T_{90}) initially, giving allowance for the remaining 10% curing during service. The time to reach T_{90} is called the optimum cure time (t_{90}) which is the normal cure time for all industrial rubber products. Figure 1 shows the influence of chitosan loading on the optimum cure time (t_{90}) of NBR. The cured NBR sample shows a t_{90} of 14 min. However, with chitosan loading, the t_{90} has been found to get reduced regularly up to a threshold value. Thereafter, the value gets increased. The reduction in t_{90} is an indication of the effective interaction of chitosan with NBR. The polar groups in chitosan ($-\text{NH}_2$ and $-\text{OH}$) can interact with the polar group in NBR ($-\text{CN}$) through hydrogen bonding making the

Table 1. Chemical compositions of prepared NBR compounds.

Order	Ingredients	Properties	Composition (in phr)
1	NBR	Elastomer	100
2	Chitosan	Filler	0, 2, 4, 6, 8, 10, 12, 15
3	Zinc oxide (ZnO)	Activator component	5.0
4	Stearic acid (SA)	Activator component	1.5
5	Tetramethylthiuram monosulphide (TMT)	Accelerator component	1.0
6	Sulphur (S)	Vulcanising agent	2.0

matrix rigid and subsequently enhancing the torque [26]. Thus the polar-polar interactions between the matrix and filler would contribute significantly to the elevation in cure behaviour and modulus.

The reduction in cure time, reaching optimum cure earlier, is often a favoured feature in industries as the moulding of real-time products can be done within shorter periods and hence more products can be made in a single shift of operation. In comparison with the unmodified NBR, the cure time has been observed to be dropped by more than 55% for compounds containing 12 phr chitosan. This indicates that chitosan can act as a cure accelerator for NBR compounds. These observations are in good agreement with the study of chitosan/agar compounds reported by El-Hefian et al. [27].

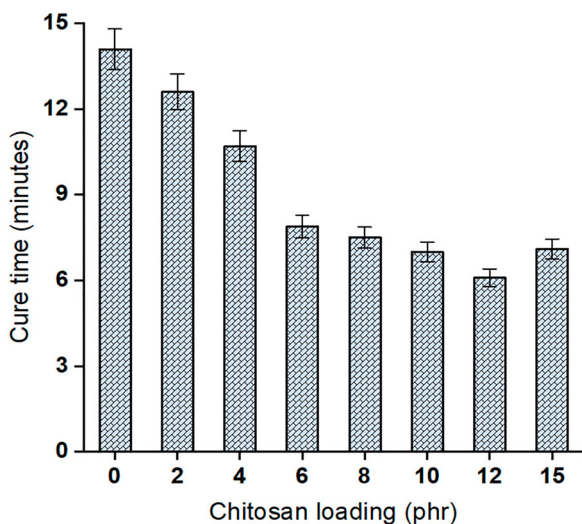
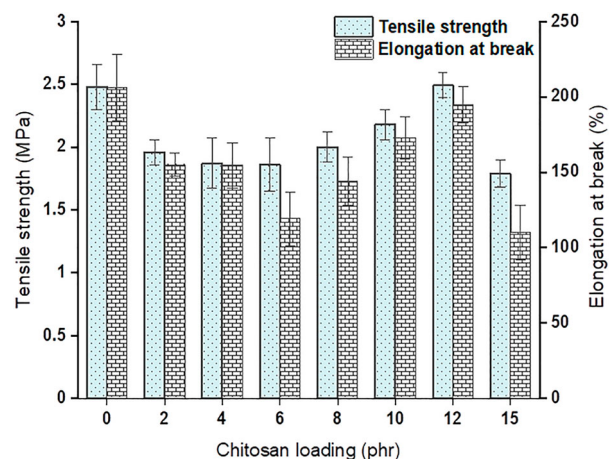
Mechanical properties

Figure 2 shows the variation of tensile strength with chitosan loading in the NBR matrix. Initially, with 2–8 phr loading of chitosan, the tensile strength has been found to be decreased. Later it increases for 10 and 12 phr loading. The initial drop in tensile can be attributed to the insufficient filler loading with high discontinuity within the matrix. This discontinuous nature would disturb the original load-bearing efficiency of NBR through localised stress concentration [28]. However, at higher loadings, up to a threshold value, a continuous morphology would be

derived with minimum stress-concentration centres; with a dominant stress relaxation [29,30]. Under such a condition, the tensile load would be distributed uniformly within the matrix and a high tensile strength would have resulted. This also indicates that there is a critical filler concentration for the system which would offer better tensile properties. At this loading, every point within the macro-system is being duly supported by the filler particles with a large number of filler–matrix contact points that are mutually complementary.

The continuous distribution of fillers would provide the system with physical crosslinks in addition to the chemical crosslinks being introduced by the accelerated vulcanisation process [31,32]. Such a system can withstand a higher load compared to the unfilled systems or the systems with discontinuous filler loading. A schematic representation in this regard is given in Figure 3. Loading with 12 phr of chitosan is ideal for NBR. The drop in tensile strength beyond 12 phr can be attributed to the increased filler–filler interactions than the filler–matrix interactions due to possible filler agglomeration [33].

Figure 2 also shows the variation in elongation at break or tensile strain. This variation is found to be quite similar to that of tensile strength. Rubber elongation primarily happens through the de-coiling of the macro-chains. Under a discontinuous filler loading, the intrinsic elongation of NBR is being blocked at several points due to the stress concentration centres. At the optimum loading, filler

**Figure 1.** Variation of cure time with chitosan loading.**Figure 2.** Variation of tensile strength and elongation with chitosan loading.

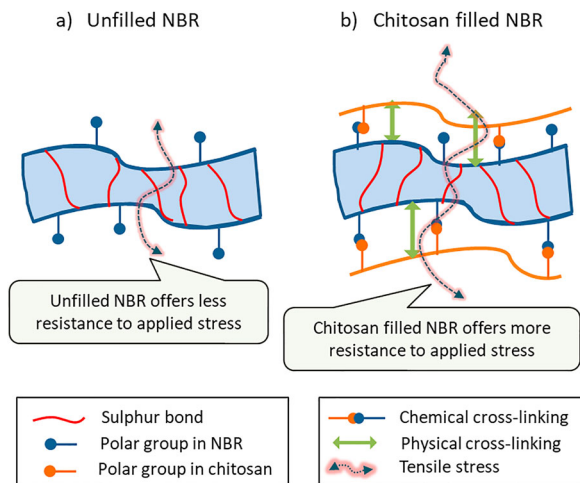


Figure 3. Schematic representation of filled and unfilled NBR compounds.

distribution is relatively uniform and the matrix and filler particles yield together to accommodate the load giving better elongation features. This tendency would decrease later after a threshold value of filler loading due to agglomeration of filler particles which would again regenerate stress concentration centres. The overall decrease in tensile strength and ductility below and above the threshold loading is attributed to the following reasons [34–36]:

- Ineffective filler distribution at lower loadings and agglomeration occurring at higher loading.
- Dominant filler-filler interactions than matrix-filler interactions.
- The absence of physical crosslinks to support chemical crosslinks.

Figure 4 shows an increase in overall modulus at 100% elongation with chitosan loading. The modulus shows a significant increase of 20.5% (for optimum loading of 12 phr) compared to NBR without any

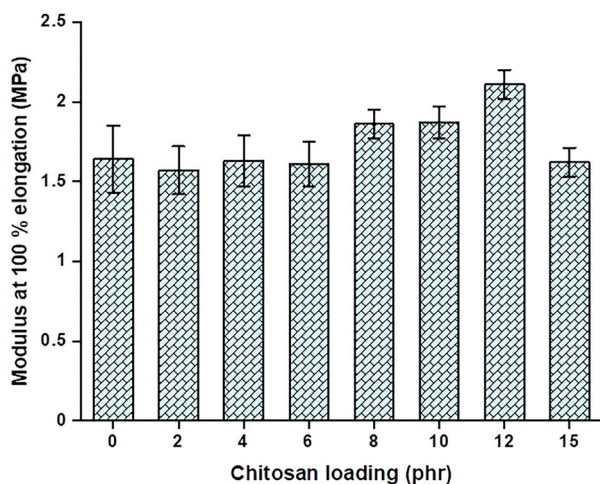


Figure 4. Variation of modulus at 100% elongation with chitosan loading.

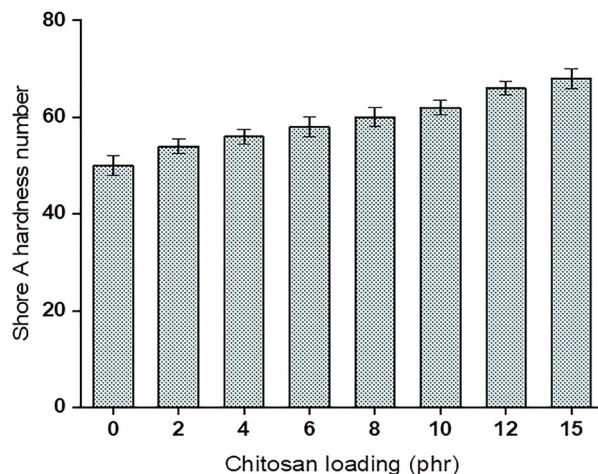


Figure 5. Variation of hardness with chitosan loading.

chitosan. Effective chitosan distribution would restrict the overall chain mobility of NBR making the system rigid. However, beyond 12 phr the dominant filler-filler interactions, due to the possible particle agglomerations, would lead to the weakening of the matrix. This observation is perfectly in agreement with the results from rheometric studies as discussed under Section 3.1.

The hardness of the NBR/chitosan system was measured by using a Shore A hardness tester. The variation of hardness was measured as an average of at least five points is represented in Figure 5. The hardness value has been found to be increased linearly with the chitosan content. This further confirms the effective interaction between NBR and chitosan. The presence of chitosan would modify the surface of the matrix and because of the combined resistance offered by NBR and chitosan particles, the hardness is seen to be increased [37].

The combined effect of changes in tensile strength, percentage elongation at break, modulus at 100% elongation and Shore A hardness values of NBR due to chitosan loading is represented through a new index called Chitosan Efficacy Index (CEI). It is a dimensionless, positive value and an expression of the effect of chitosan loading on the overall changes in the mechanical properties. The CEI was calculated using Equation (2) from normalised tensile strength, normalised elongation at break, normalised modulus at 100% elongation and Normalised Shore A hardness as shown in Table 2.

$$CEI = (NT_x)(NE_x)(NM_x)(NS_x)^2 \quad (2)$$

Figure 6 shows the variation of the CEI with chitosan loading. A value of CEI higher than 1 would indicate better overall mechanical properties for the filled systems compared to NBR without chitosan loading. Figure 6 indicates further that the optimum chitosan loading is 12 phr as the corresponding composite offers the best CEI value.

Table 2. Normalised values of mechanical properties and CEI for different Chitosan loading.

Chitosan loading (phr)	Normalised tensile strength (NTx)	Normalised elongation at break (NEx)	Normalised modulus at 100% Elongation (NMx)	Normalised shore A hardness (NSx)	CEI
2	0.8163	0.7023	0.9697	1.0784	0.6466
4	0.7755	0.6977	1.0182	1.1176	0.6881
6	0.7347	0.6279	0.9697	1.1569	0.5987
8	0.8163	0.6744	1.1212	1.1765	0.8544
10	0.9184	0.8140	1.1515	1.2157	1.2721
12	1.0082	0.9302	1.3636	1.2549	2.0139
15	0.6939	0.5116	1.0303	1.2941	0.6126

Mathematical modelling

The obtained mechanical properties were compared with the theoretical models, using a Python programming tool, defined by the following quadratic and trigonometric Equations (3–6):

$$\text{Tensile strength} = 2.5 + 0.05 C^2 - 0.36 C - 0.002 C^3 \quad (3)$$

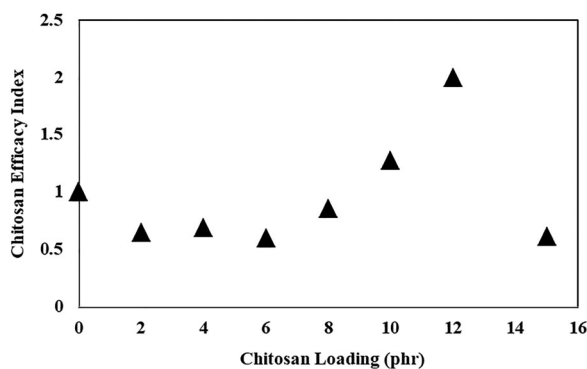
$$\% \text{Elongation} = 164.5 + 41.46 \cos(-8.96C) \quad (4)$$

$$\text{Tensile modulus} = 1.96 + 0.4 \cos(2.5 + 9.6C) \quad (5)$$

$$\text{Hardness} = 51.34 + 1.1 C \quad (6)$$

where C is the volume fraction of chitosan.

The comparison between experimental values of mechanical properties and a mathematical model is presented in Figure 7. The experimental data is in good agreement with the theoretical predictions as both show a similar trend for all the properties. The R^2 value for tensile strength shown in Figure 7(a) has 0.93 which is quite acceptable. The R^2 value for % elongation and tensile modulus comes around 0.96 while for hardness the R^2 value is 0.99. Though the R^2 value can be as close as 1.0 indicating appreciable agreement between the predicted and desired values; lower values are also accepted as generally. The deviations are due to the non-uniform behaviour of the materials under test with the increase of chitosan content. Further tests can be performed to accurately model the tensile strength as a function of chitosan loading.

**Figure 6.** CEI as a function of chitosan loading.

Surface morphology of fractured surface

The morphology of tensile fractured surfaces of the samples with different chitosan loadings is shown in Figure 8. Better load-bearing capability is achieved by a composite when the size of filler particles are smaller and the dispersion is uniform throughout the matrix [38–40]. The filled systems have been found to possess a heterogeneous morphology attributed to the surface energy mismatch between NBR-matrix ($26.95 \times 10^3 \text{ J/m}^2$) [31] and chitosan-filler ($41.10 \times 10^3 \text{ J/m}^2$) [41]. Though a heterogeneous nature is observed for the composites, the constituents are being interlocked through physical interactions. A relatively uniform morphology has been observed for the NBR matrix loaded with 12 phr chitosan. It reflects the affinity of polar chitosan towards the polar NBR matrix. The surface morphology can further be improved by choosing suitable surface modification methods for the filler particles as reported by Kamal et al. [42].

Thermal analysis

Rubber compounds are usually exposed to thermal events during service. Typically, NBR hoses may be employed for the transport of hot oils. In view of this, the effect of chitosan loading on the thermal features of NBR has been examined through TGA. Figure 9 highlights the improvement in the thermal stability of NBR due to chitosan addition. The peak temperature during TGA for chitosan filled compounds was increased by 10°C . The residual weight percentage at 740°C has also been found to be significantly improved after chitosan loading from 5.5 to 13.3%. The aforesaid results highlight that the incorporation of chitosan fillers would effectively enhance thermal stability. In comparison, the chitosan loading with 12 phr exhibited the highest thermal stability. The improvement in thermal stability can be attributed to the strong interfacial adhesion between the chitosan filler and the NBR matrix [43,44].

Absorption studies

Chitosan being hydrophilic, due to the presence of OH and NH_2 functional groups, may adversely affect the

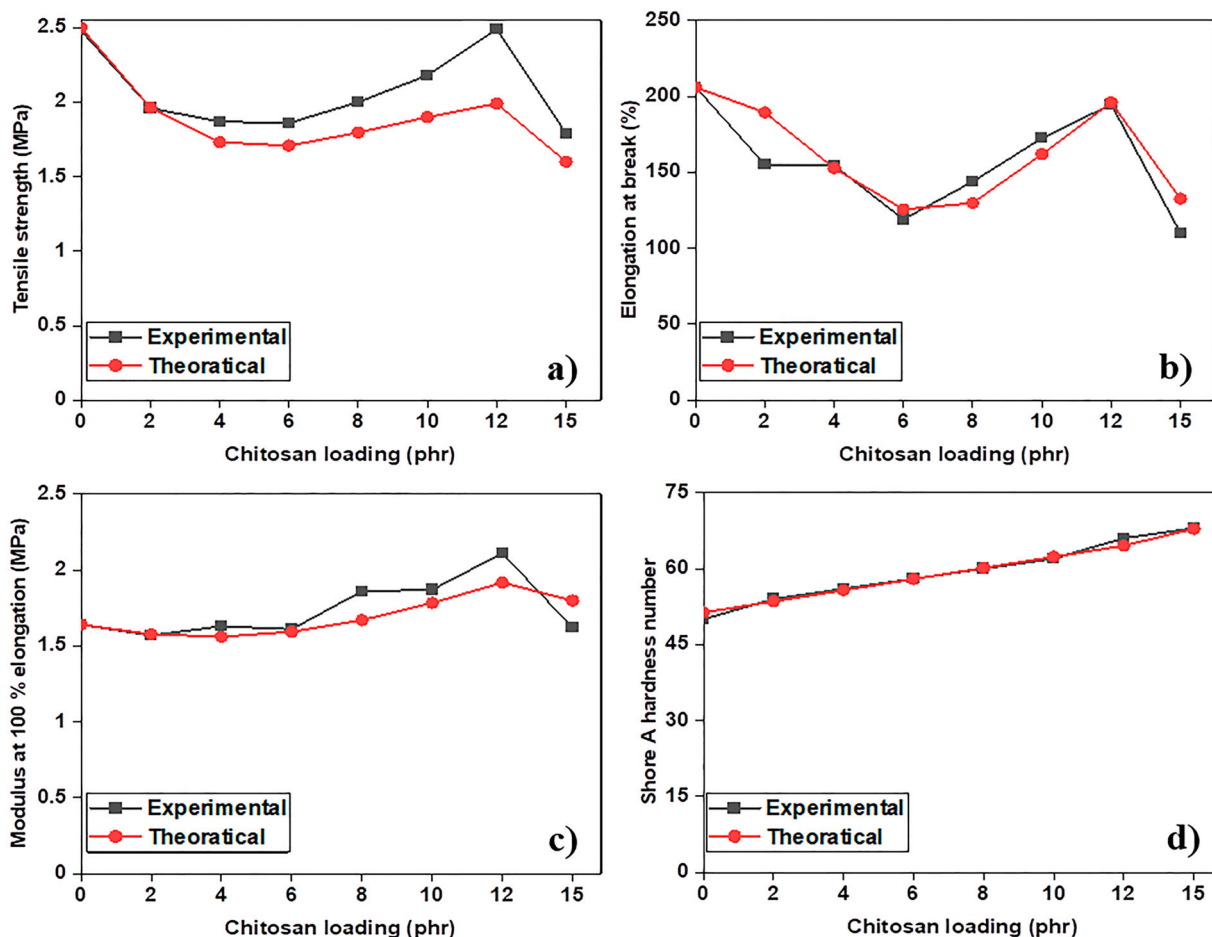


Figure 7. Comparison of experimental results with theoretical model.

intrinsic hydrophobic nature of NBR during service. Therefore an investigation has been carried out on the water-resistance of chitosan-NBR composites. Figure 10 shows the water absorption behaviour of NBR samples with different filler loadings. Nitrile rubber compounds are hydrophobic and they show only negligible water absorption without fillers. As the filler concentration increases, the system exhibits comparatively higher water sorption characteristics. However, the maximum water absorption for the

prepared rubber compounds is less than 2%, even for the highest filler loaded condition, which highlights that the hydrophobic applications of NBR would not be hindered due to the use of biodegradable chitosan particles as fillers within them. Interestingly, it has been reported that, with appropriate surface treatment for the filler particles, the hydrophilicity of biodegradable polymers can be effectively reduced to complement the matrix features in a composite system [45,46].

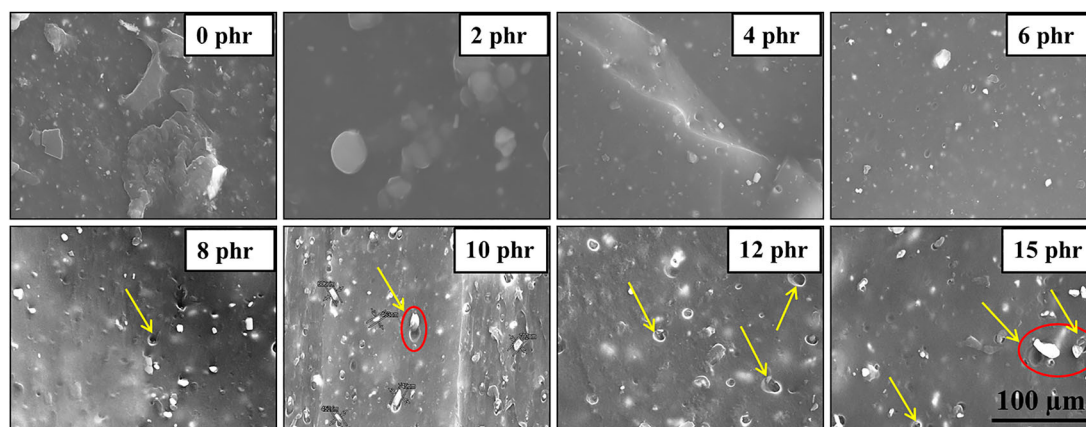


Figure 8. SEM Micrographs of fractured surfaces for different compositions.

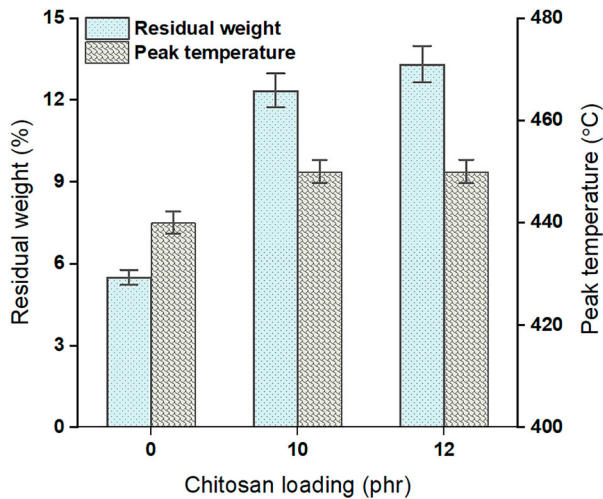


Figure 9. TGA of samples showing residual weight and peak temperature.

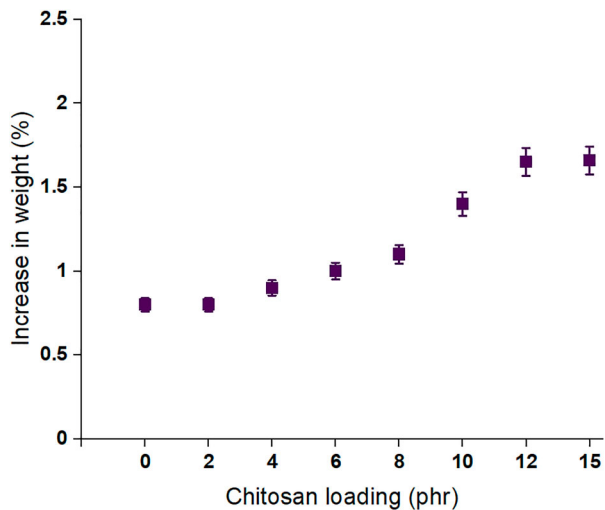


Figure 10. Increase in weight due to water absorption for different loading.

Conclusion

Chitosan reinforced NBR compounds were successfully prepared by using a two-roll mixing mill followed by compression moulding. The investigations indicated that the mechanical properties of NBR increased significantly at a critical loading of chitosan within the matrix (12 phr). A CEI has been suggested to highlight the effect of chitosan loading. The observed mechanical properties are in good agreement with the mathematical model derived through a Python programming tool. The cure time of NBR has been found to efficiently modified with chitosan loading which is a significant achievement in terms of industrial aspects. Morphological examinations pointed towards the heterogeneous nature of the filled matrix; with voids and discontinuities. However, the polar-polar interactions between the filler particles and the matrix have been found to offer a significant reinforcement effect. Thermogravimetric analysis (TGA) and water absorption studies have also been executed to

complement the results from the investigations of mechanical properties. This study offers the possibility for modifying the NBR formulations which are currently being employed for the fabrication of products such as O-rings, gaskets, and hoses.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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