THE Effect of Azido-Starch as Filler on Tensile and Tear Properties of Natural Rubber Latex Films

S Daud¹, A R Azura ² and M F Yhaya ³

¹ School of Materials and Mineral Resources Engineering, USM Engineering Campus, 14300 Nibong Tebal, Penang.
² School of Materials and Mineral Resources Engineering, USM Engineering Campus, 14300 Nibong Tebal, Penang
³ School of Dental Sciences, Health Campus, Universiti Sains Malaysia, 16150 Kubang Kerian, Kelantan.

E-mail: srazura@usm.my

Abstract. The azido starch/Natural Rubber (azo-starch/NR) latex films were prepared with control (0), 0.5, 1.0, 1.5 and 2.0 phr of azido-starch loadings. The azido starch functional groups were characterized by Fourier Transform Infra-Red (FTIR) analysis to observe the presence of significant peaks of azide (N₃). The control and azido starch-filled NR films were subjected to tensile test and tear test in order to investigate the effect of the addition of azido-starch on the mechanical properties of azo-starch/NR latex films. The tensile strength of azo-starch/NR latex films was increased with increasing azido-starch loading and slightly decreased after 1.0 phr loading. The optimum tensile strength of azo-starch/NR latex films is obtained at 1.0 phr loading. The moduli (M₁₀₀ and M₃₀₀) and tear strength also increased with increasing azido-starch loading. However, the elongation at break (EB) was almost similar with increasing azido-starch loading. The swelling test was done to determine the swelling index, crosslink density and rubber-filler interaction of azo-starch/NR films. The swelling index was decreased but the crosslink density increased with increasing azido-starch loading indicating the formation of crosslinks between azido-starch and rubber macromolecules.

1. Introduction

One of the most preferred types of polysaccharides is starch where the research has been carried on the utilization of starch as filler in the production of latex films [1][2]. The ultimate purpose of using lignocellulosic and polysaccharides materials into the rubber and polymer matrices are to induce biodegradation of the products. The incorporation of starches into rubber matrix not only cheapen the cost but also increased the rate of degradation and fragmentation of the rubber products upon disposal [3]. However, the utilization of starches on their own can deteriorate the vital properties of rubber products such as its mechanical properties. Starches are mostly unsuitable for applications without physical or chemical modification. The most common method of modification of starches normally acid hydrolysis, oxidation, esterification, etherification, substitution and crosslinking of the available hydroxyl groups on the α-D-glucopyranosyl units that make up the starch [4]. The starch granule consists of two constituents; amylose and amylopectin. The ratio of amylose and amylopectin varies depend solely on starch species [5]. The chemical reactivity of starch derives from the reactivity of hydroxyl groups of the anhydroglucose units (AGU). Each AGU contains 3 three OH groups, which react similarly to alcohols [6]. Cross-linkable functional group can be directly synthesized onto the starch. The crosslinking approached can be applied to any primary hydroxyl-containing starch. The extent of the modification reactions is generally expressed as the degree of substitution (DS), which
corresponds to the average amount of OH groups per AGU that have been substituted by another functional group [7].

Azido saccharides are usually synthesized for the amino group where the chemistry of azides allows it to be used for crosslinking purposes (8). Starch was chemically modified to improve interconnection between starch particles which increased the strength of the product. Azidated starch can be prepared by substituting the free hydroxyl groups with azide groups. Substituted starch with DS 0.2 and above increased the hydrophobicity of the starches, thus, increased the miscibility with a hydrophobic polymer that used as matrix [9]. Compared to native starches, crosslinked starch has superior properties in mechanical, thermal and chemical resistance [10]. The purpose of this research work is to investigate the potential use of azido- starch (azidated starch) as a reinforcing filler in natural rubber latex to increase the mechanical properties of the films produced. Furthermore, it also to develop a new potential cross-linker as an alternative to conventional sulphur/accelerator in natural rubber latex films using modified starch via click chemistry route.

2. Material and Methods

2.1 Materials

High ammonia NR latex with 60% total solid content (TSC) was purchased from Zarm Scientific and Supplies (Malaysia) Sdn Bhd. Sago starch was manufactured by Sago Link Sdn Bhd. Potassium hydroxide was supplied by Merck Sdn Bhd. Other compounding ingredients including anchoid, antioxidant, zinc oxide, zinc diethyldithiocarbamate (ZDEC) and sulphur in dispersions form were supplied by HH Saintifik Sdn Bhd and used as received. The tosyl chloride and sodium azide were manufactured Sigma Aldrich.

2.2 Preparation of azido-starch-filled NR latex films

The preparation of azido sago starch (azidated sago starch) involved the tosylation process. The synthesis of tosylated starch was carried out according to Elchinger [11] with a few modifications. First, a 50 g sago starch was mixed with 300 ml distilled water, 58.91 g of tosyl chloride, and 64.70 ml triethylamine under stirring for 24 hours at room temperature. The mixture was then filtered off and washed with distilled water followed by ethanol. Then the filtered product was dried at 40°C for 24 hours. Second, the tosylated starch was carried out by mixing the 50 g of tosylated starch powder with 9.1 g of sodium azide in water/ethanol (50/50 v/v) for 48 hours at 75°C. After that, the reaction was cooled down to room temperature, followed by the filtration process. The product obtained was subjected to centrifugation process in order to remove water and by-products using distilled water and finalized with ethanol. The starch cake obtained was dried at 40°C for 24 hours to obtain azido- starch powder. The 10% total solid content of azido starch dispersion was prepared by mixing the starch with anchoid, potassium hydroxide and distilled water using ultrasonic homogenizer at 50 Hz for 1 hour. The 0, 0.5 1.0, 1.5 and 2.0 phr of azido-starch loading mixtures were constantly stirred for 2 hours with stirring speed at 270 rpm. The latex mixtures were transferred into a pre-heated water bath at temperature 70°C and stirred at 270 rpm for another 20 minutes for the pre-vulcanization process to occur. The compound obtained was sealed and left for 12 hours at room temperature for the maturation process. The azido starch filled NR (azo-starch/NR) dipped latex films were prepared using the steel plates which were dipped in coagulant for 10 seconds and dried in an oven at 100 °C before cooled at room temperature. The steel plates were then dipped into NR latex compounds for 15 seconds and cured in an air oven for 20 minutes at 100 °C before cooled at room temperature for 24 hours.
2.3 Fourier Transform Infra –Red (FTIR)
Azido starch was characterized by Fourier Transform Infra-Red (FTIR), Perkin Elmer Spectrum One Spectrometer to identify the presence of azide group in the azido starch and compared with control starch. The scan was performed in the range of 550 cm\(^{-1}\) to 4000 cm\(^{-1}\).

2.4 Tensile and Tear Tests
Tensile test was conducted by using Instron 3366 according to ASTM D 412-06. The specimens were cut into dumbell shape and the thickness of each test piece was recorded. The crossheads speed was set at 500 mm/min. Five samples were prepared and the average values were calculated and reported. Tear test was conducted by using Instron 3366 according to ASTM D 624-00. The specimens were cut into a crescent shape (Die C) and the thickness of each test piece was recorded. The crosshead speed was set at 200 mm/min. Five samples were prepared and the average values were calculated.

2.5 Swelling Test
For the swelling test, small samples of the dried azo-starch/NR latex films were cut, weighed and placed in glass vials which were filled with toluene. The vials were stored at room temperature for 48 hours. The samples were taken out of the solvent, dabbed gently with a tissue to remove the solvent and quickly weighed. The swelling ratio, network density, rubber-filler interaction was calculated using Equation 1, 2, 3 and 4, respectively. The swelling ratio (Q) is calculated using the equation (1)

\[
\text{Swelling ratio (Q)} = \frac{W_1 - W_0}{W_o}
\]  
(1)

Where \(W_1\) is the swollen weight and \(W_o\) is the initial weight.

The crosslink density (v) can be calculated using the equation (2)

\[
v = \frac{1}{2M_c}
\]  
(2)

\(M_c\) is the molecular weight of polymer between crosslinks calculated using equation (2.1),

\[
M_c = \frac{-\rho V_s V_{rf}^2}{\ln [1 - V_{rf}] + V_{rf} + \chi V_{rf}^2}
\]  
(2.1)

\(\rho\), is the density of polymer, \(V_s\) is the molar volume of the solvent absorbed, and \(\chi\) is the interaction parameter, and \(V_{rf}\) is the volume fraction of rubber in the solvent swollen filled sample. The rubber-filler interactions are calculated using Cunneen-Russell [12] and Lorentz-Park [13] equations; The Lorentz-Park equation is given by equation (3). Where \(Q_f\) and \(Q_g\) is the amount of solvent absorbed for filled and unfilled latex films, respectively. \(Z\) is the weight fraction of filler, \(a\) and \(b\) are constant. While the Cunneen-Russell equation is derived from Lorentz-Parks equation (4)

\[
\frac{Q_f}{Q_g} = ae^{\chi Z} + b
\]  
(3)
\[ \frac{V_{ro}}{V_{rf}} = ae^z + b \quad (4) \]

3. Results and Discussion

3.1 Fourier Transform Infra-Red (FTIR)

The analysis of the FTIR spectra of the tosylated starch powder and azido starch powder were given in Fig.1 (a). The azido starch showed an increment of OH groups at 3420-3250 cm\(^{-1}\), 2831 cm\(^{-1}\), 1640 cm\(^{-1}\), 1150 cm\(^{-1}\), 1076 cm\(^{-1}\) and 1000 cm\(^{-1}\) due to the removal of amorphous region on the surface of the starch after tosylation, thus, more C-OH, C-O-C and C-C bonds have been exposed [14]. The peak at 1000 cm\(^{-1}\) indicates the presence of C-O bonds. The strong transmittance peak at 1000 cm\(^{-1}\) indicates the increase in crystallinity of starch [15]. The FTIR spectrum of tosylated and azidated starch contained the following characteristics peaks: a broad band between 3600 cm\(^{-1}\) to 3200 cm\(^{-1}\) due to stretching vibrations of O-H groups, C-H aliphatic stretching at peak 2927 cm\(^{-1}\), O-H bending due to water absorbed in an amorphous region of starch at peak 1650 cm\(^{-1}\), 1160, 1081, 1015 cm\(^{-1}\) attributed to stretching of C-O bond from the AGU ring [16]. The characteristics peaks of the AGU ring can be seen at 1154, 1081, 1025 and 930 cm\(^{-1}\) [17]. The IR spectrum showed a strong absorption peak of the C≡C corresponding to the azide group at 2118 cm\(^{-1}\) [18]. The absorption peaks at 1360 cm\(^{-1}\) and 1176 cm\(^{-1}\) (SO\(_2\)) confirmed the presence of tosyl chloride [19]. The primary peaks of NR latex spectrum are at 2961 -2852 cm\(^{-1}\) for C-H stretching, 1663 cm\(^{-1}\) for C=C stretching, and C-H bending vibrations of –CH2 and deformation of CH\(_3\) at peaks 1438 cm\(^{-1}\) and 1375 cm\(^{-1}\), respectively [20].

![Fig. 1. The spectra of tosylated starch powder and azido-starch powder (b) control NR film and azido-starch- filled- NR films](image)

3.2 Crosslink Density and Swelling

Fig. 2 shows the crosslink density and swelling index of azido starch-filled-NR latex films. The crosslink density is inversely proportional to swelling density which the values provide an idea about the rubber-filler interaction [21]. The results in Fig.2 shows that crosslink density of azido starch- filled NR films are increased significantly as azido starch filler loading increased. Addition of azido starch formed a good chemical crosslink between filler-rubber chains. Swelling index, on
the other hand, measured the solvent resistance of the specimens which indicates the restricted
diffusion of solvent molecules through the voids of the rubber. The higher crosslinks between
filler and matrix reduce the available free voids within the matrix, thus, less solvent was absorbed.
The interaction between rubber and filler can be assessed using Cunneen-Russell and Lorentz-
Parks equations [11]. As the filler loading increases, the Qf /Qg decreases due to the greater
interaction between filler- rubber. The Cunneen-Russell and Lorentz- Park plot give positive
slopes showed the greater extent of rubber-filler interaction present in the rubber matrix as
shown in Fig. 3 [12]. The reinforcing mechanisms might be explained by the catalytic effect of the
azido starch on the vulcanization or additional crosslinks are formed by azido starch filler acts as
complex crosslinks network [22]. The negative slope of the plot indicates the reinforcing effect by
azido starch on the rubber matrix. The ratio Vro / Vrf less than in Fig.3 shows that azido starch
has strongly adhered to the surrounding the rubber molecules preventing complete absorption of
solvent molecules.

![Graph](image_url)

**Fig. 2.** The crosslink density (Line) and swelling index (bar-chart) of control and azido starch-
filled NR latex films.
3.3 Tensile Properties

Fig. 4 shows the effect of incorporation of azido starch on tensile properties of NR latex films. According to Fig. 4, the tensile strength of azido starch-filled NR films increased at 0.5 and 1.0 phr compared to unfilled (control) sample but slightly decreased from 1.5 to 2.0 phr. It can be observed that the optimum tensile strength of the samples was at 1.0 phr. The increase in tensile strength for azido starch filled NR films was attributed from strong filler-rubber interaction and compatibility of NR latex and starch after surface modification of the starch. The azido starch capable of binding active chemical group in latex compounds through the formation of chemical bonding between starch and the NR latex. Thus, improve the interfacial adhesion and compatibility between the starch filler and NR latex. This leads to improve mechanical properties and better stress distribution between filler and latex particles during tensile stress application. Elongation at break (EB) in Fig. 5 slightly reduced with increasing the azido starch loading. Increased in azido starch loading has increased the stiffness of NR latex films hence, reduce its flexibility. The NR latex films become rigid due to increase in non-deformable characteristic of natural filler and less deformable rubber part in the NR films. The opposite trend was observed for tensile modulus (M100 and M300) which shown an increasing trend with increasing azido starch loading as shown in Fig. 6. Moduli of rubber matrix was increased by the enhancement in the surface activity of the fillers, the good dispersion of the filler in the rubber matrix and also better rubber-filler interaction [23]. The chemical surface modification of starch has improved the rubber-filler interaction. The increased of azido starch loading has reduced the chain mobility and increased the rigidity of the NR latex films. Modulus directly indicates the crosslinking density of the NR latex films. These changes related to changes in the main chain scission and crosslink modifications of the original crosslink structure. The crosslinks and bonding between NR latex and azido starch increased with the increment in the azido starch concentration region in the rubber matrix [24].
**Fig. 4.** The tensile strength of azido-starch-filled NR films

**Fig. 5.** The elongation at break of azido-starch-filled NR films
3.4 Tear Strength

Fig. 7 shows that the addition of azido starch loading has increased the tear strength of the NR latex films. The tear strength of the NR latex films increased with increasing azido starch loading but abruptly decreased at 1.5 phr azido starch loading. The tear strength in azidated starch-filled NR latex films was attributed by the ability of azido starch to form strong resistance towards crack and propagation where the rubber macromolecules to deviate the crack propagation during the tear test. The azidation surface modification on the starch particle acts as a barrier to the propagation of microcracks, thus provide higher tear strength. The presence of azido starch also contributes to a deviation of the tear path from a straight line, so that the tear becomes rougher which contribute to a higher tear strength. The tear strength also was largely dependent on the stiffness of the specimens, on other words, the higher the crosslinks density of the films, the higher the tear strength [12].
4. Conclusion

The azidation of sago starch via tosylation and azidation pathway of azidated sago starch overall has shown an increase in the mechanical properties of NR latex films. The tensile strength of azo-starch/NR films was optimum at 1.0 phr azido-starch loading and start to decrease at 1.5 phr azido-starch loading. These were due to increase in modulus which signified the increase in stiffness of the samples as an increase in azido-starch loading. The increased in the stiffness of azo-starch/NR films indicate the presence of filler-rubber crosslinks in addition to chemical crosslinks between NR chains. The greater extent of crosslinks in the rubber chains has reduced the ability of the azo-starch/NR films to resist breakage upon strain, thus, reduced in elongation at break of the samples. The evidence of increased crosslinks and the extent of rubber-filler interaction proved theoretically.

5. Acknowledgement

The authors would like to acknowledge the School of Materials and Mineral Resources Engineering of the Universiti Sains Malaysia for support and research facilities. This work is supported by the Bridging Research Grant (Grant No. 304 / PBAHAN / 6316180).
References

[1.] Izmar M H et al 2012 Compos. Part. B. Eng. 43, 2746–2750
[2.] Misman M A and Azura A R 2018 The Mechanical Properties Enhancement of Biodegradable Aminofunctional Starch/Carboxylate Nitrile Butadiene Rubber Latex Films Preprint gr-qc/201804
[3.] Misman M A et al 2016 Procedia Chem. 19, 770
[4.] Whistler R and Daniel J 2009 Molecular Structure of Starch (Starch: Chemistry and Technology vol 3) ed R Whistler (Oxford: Elsevier) chapter 6 pp.153-160
[5.] Alcazar-Alay S C and Meireles M A A 2015 Food Sci. Technol. 35 215
[6.] Song D et al 2009 J. Biobased Mater. Bioenergy 3 321
[7.] Rachta napun P et al 2012 Int. Food Res. J. 19 923
[8.] Shey J et al 2006 Carbohydrate. Polymers. 65 529
[9.] Song D et al 2009 Appl.Polym.Sci. 113 3019
[10.] Reddy N and Yang Y 2010 Food Chem. 118 702.
[11.] Elchinger P et al 2014 Ind.Eng.Chem.Res 53 7604
[12.] Rice A F A 2001 Raw Mater. Appl 5 242
[13.] John M J et al 2009 Lignocellulosic Fiber Reinforced Rubber (Natural Fibre Reinforced Polymer Composites: From Macro to Nanoscale) ed T Sabu (USA:Old City Publishing) chapter 10 pp 252–269
[14.] Masina N 2017 Carbohydr. Polym. 157 1226
[15.] Sevenou O et al J R 2002 Int. J. Biol. Macromol 31 79
[16.] Bastioli C et al 2013 Starch (Bio-Based Plastics:Materials and Applications) ed S Kabasci and C Stevens (West Sussex:Wiley & Sons) chapter 2 pp. 9-28
[17.] Apopei D F et al 2012 Digest Journal of Nanomaterials and Biostructures 7707
[18.] Elchinger P et al 2011 Polymers 3 1607
[19.] Heinze U 2001 New Highly Functionalized Starch Derivatives (Biorelated Polymers: Sustainable Polymer Science and Technology) ed E Chiellini (USA:Springer)chapter 17 pp. 205-210
[20.] Panrat K et al 2012 Procedia. Chem 4 322
[21.] Barkoula N M et al 2008 Polym. Compos 16 101
[22.] Taylor G L and Boonstra B B 1965 Rubber Chem. Technol 38 943
[23.] Egwaikhide A P and Okiemen F E 2013 Sci. J. Chem. 150
[24.] Liu C et al 2008 Polymer (Guildf) 49 2176

10