Studies on the Influenced of Dextrin Filler on the Mechanical Properties of Carboxylated Nitrile Butadiene Rubber (Xnbr) Films

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Abstract. Dextrin used in this experiment is a product of acidified sago starch being heated at high temperature. The use of dextrin as filler in latex films is to produce environmental friendly products. The synthesized dextrin dispersion was prepared by mechanical (ball milling). Dextrin (DX) is compounded with carboxylated nitrile butadiene rubber (XNBR) latex. The DX/XNBR films were prepared by incorporating dextrin at filler loading of 0, 5, 10, 15 and 20 phr into XNBR latex. The dextrin was then mixed with XNBR compound as a filler and a film was prepared by coagulant dipping technique. The effect of dextrin loadings on tensile properties of XNBR films were investigated. The results indicated that the tensile properties such as tensile strength, elongation at break, and crosslink density decreased with increasing filler loading. The changes of functional groups present in native sago, dextrin and DX/XNBR film were characterized using Fourier Transform Infra-Red (FTIR). The morphological properties of tensile fractured surfaces of the samples were observed using Scanning Electron Microscope (SEM).

1. Introduction

Carboxylated nitrile butadiene rubber (XNBR) latex is one of the largest contributors to world synthetic gloves. It is produced via emulsion polymerization technique where acrylonitrile, and 1, 3 butadiene are polymerized in an aqueous emulsion with presence of emulsifier (Lenko et al. 2013. Carboxylated nitrile butadiene rubber (XNBR) like other types of synthetic and natural latex, are not biodegradable due to nature of latex itself and other materials added to it such as conventional fillers to name a few carbon black, clay and silica. Degradation of XNBR mainly by means of physical processes such as thermal induction, photo-oxidation, ozonolysis, and radiation during the degradation process (Bhattacharjee et al. 1993). This causes serious threat to the environment. This results in a rise of awareness among researchers and people around the globe demanded for green-based products.

Demand for green based polymeric materials are increasing annually, due to increase awareness on environmental issue. Owing to this, researchers has found an alternative to conventional fillers used in latex and rubber industry by using lignocellulosic and polysaccharides natural fillers. The advantages of natural fillers include the biodegradability, renewable and environmental friendly (Blackburn, 2005). Natural fillers are also easily available, low density, cheap and non- abrasive (Muniandy et al., 2012). Thus, a blend of biodegradable fillers and synthetic polymer compound is seemed to be the best solution. The potential filler to be used is starch. In this experiment, dextrin is used as an alternative of sago
starch. Dextrin is a product of acidified sago starch heated at high temperature until brownish colour powder obtained. Dextrin has low molecular weight and shorter chains compared to starch which undergo chain fragmentation through chemical and pyrolysis reaction (Bai et al., 2014). The low molecular weight of dextrin increase the chances of the XNBR films to be broken down easily upon disposal. Thus, make them more environmental friendly and greener option compared to conventional filler used in latex films. The objective of this research is to study the potential of using dextrin as filler in XNBR latex with the aim to study the effect of dextrin loading on the tensile properties of XNBR latex films.

2. Experimental study

2.1 Materials

Carboxylated nitrile butadiene rubber (XNBR) latex classified as XNBR X6322 was supplied by Synthomer (M) Sdn Bhd. Other chemical ingredients include zinc oxide, zinc diethyl dithiocarbamate (ZDEC), sulfur, and antioxidant were supplied by Farben Technique (M) Sdn Bhd. Sago starch was supplied by Sago Link (M) Sdn Bhd. The material was in white powder form granule size of 10-20 µm.

2.2 Preparation of Dextrination

The sago starch (100 g) was suspended in 150 ml water. The pH of the slurry was adjusted to 3.0 by 0.5 M HCl and stirred for 30 minutes. The sago starch then filtered using filter paper. The starch flakes was dried in an oven at 40°C for 24 hours. The dried starch was grind, and strained through a sieve (100 mesh) and heated again in an oven at 170°C until the starch changed to darker colour (dextrin). The synthesized dextrin (50 g dry weight) then was dispersed in distilled water (45 mL), together with dispersing agent (5 g dry weight) to make dextrin dispersion. The compound was stirred for 1 hour and subjected to ball milling for 24 hours at 60 Hz.

2.3 Preparation of dextrin/carboxylated nitrile butadiene rubber (XNBR) latex films

The preparation of XNBR compounds was carried out by mixing all the ingredients in the beaker and was constantly stirred for one hour using Wise Stir HS-300 mechanical stirrer at stirring speed of 270 rpm at room temperature. The compounds were then pre-vulcanized for 1 hour at temperature of 80°C. Clean aluminum plate was dipped into coagulant (10% calcium nitrate) for 10 seconds and dried in convection oven for 15 minutes at temperature of 100°C. The plates was taken out and leave under at room temperature until the plate temperature reduced to 50-60°C. The plate then dipped into DX/XNBR latex compound for 17 seconds and cured in convection oven for 25 minutes at temperature of 100°C. The plate then cooled at room temperature for 24 hours before the films were stripped from the plate.

2.4 Tensile Properties of Dextrin/XNBR Films

Tensile test was conducted using Instron Machine according to ASTM 412-2006. AD/XNBR latex films was cut into dumbbell shape and thickness of each specimens was recorded.

2.5 Swelling Test

The swelling test was carried out according to ASTM D471 where a test piece weighing about 0.2 g was cut from the XNBR films. The films were immersed in 25 ml toluene and transferred into water bath and heated at 48 hours at 40 °C. The test piece was taken out and blotted using filter paper and the
swollen weight was immediately measured. The crosslink density of XNBR films \([X]\) were calculated using Flory-Rehner equation.

Flory Rehner Equation, \([X] = \frac{-[\ln (1-V_r) + V_r + \chi V_r^2]}{V_s (V_r^{1/3} - V_r^2)}\]

2.6 Fourier Transform Infra-Red (FTIR)

The Fourier Transform Infrared Spectrometry (FTIR) spectrometer used in this study was Perkin Elmer, Model Spectrum One. Analysis was done under room temperature within a typical wave number range of 4000 cm\(^{-1}\) to 550 cm\(^{-1}\) under transmission mode.

2.7 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) is a tool for visualizing the surface of solid samples. The morphologies of fillers and XNBR films were observed using Hitachi Tabletop SEM model TM3000. The filler powder was sprinkled on the black tape mounted on aluminum stubs. The samples were sputter coated with thin layer of gold before analysis to avoid electrostatic charging during analysis.

3. Results and discussion

3.1 Swelling Test

Figure 1 show the swelling values of unfilled and dextrin-filled XNBR films at different filler loading. The incorporation of dextrin gradually increased in swelling percentage with increasing filler loading. The increased in swelling percentage is due to the hydrophilic dextrin was incompatible with hydrophobic XNBR resulted in the poor interfacial interaction between rubber and filler, thus increased the toluene uptake in the films (Lin et al. 2011). The increase in toluene intake indicates minimal interaction between filler and rubber as a result of a few crosslinks forming per rubber chains. The higher dextrin loading could also interrupt the formation of crosslinks between XNBR chains, thus reduce the mechanical properties of XNBR films.

![Figure 1. Crosslink density and swelling index of unfilled XNBR and dextrin filled XNBR](image-url)
3.2 Mechanical Properties of Dextrin-filled XNBR films

The tensile strength of XNBR latex films attributed by three factors; the effectiveness of the dual crosslinking, the ability of ionic clusters to reform during stress and chain entanglement of XNBR macromolecules. The mechanical properties of the dextrin-filled XNBR latex films are shown in Table 1. The highest tensile strength of unfilled XNBR films ascribed the strength of the XNBR films. The presence of the different dextrin loadings showed decrement in tensile properties of XNBR films compared to unfilled XNBR films. The decreased in tensile strength was observed due to the breakage of sulfidic and ionic crosslinks (Blackley, 1997). The presence of polysaccharide molecules, the ionic crosslinks were hindered resulted from less sulfidic and ionic crosslinks. Dextrin with higher content of branched structures tend to reduce mechanical properties of rubber films compared to linear structure in latex films (Laurentin et al. 2003). The large particle size of dextrin also contributed to the decrement in tensile strength. Hence, the dextrin particle to become the stress concentrator during tensile test. The presence of weaknesses points on the films also restrict the ability of the films to elongate thus, reduce the elongation at break gradually with increasing dextrin loading as tabulated in Table 1. The moduli (modulus at 100% and modulus at 300%) of XNBR films were decreased as increase in dextrin loading. Modulus is related to the crosslinks density of the rubber. Higher dextrin loadings prevent the formation of crosslinks in the XNBR rubber.

Table 1. Tensile properties of unfilled XNBR and dextrin-filled XNBR films

| Samples       | Tensile strength (MPa) | Elongation at break (%) | Modulus at 100% (MPa) | Modulus at 300% (MPa) |
|---------------|------------------------|-------------------------|-----------------------|-----------------------|
| Unfilled XNBR | 20.137                 | 923.6                   | 2.3305                | 4.549                 |
| 5DX/XNBR      | 16.300                 | 706.120                 | 1.719                 | 4.4905                |
| 10 DX/XNBR    | 14.633                 | 663.920                 | 1.691                 | 3.5718                |
| 15DX/XNBR     | 11.380                 | 550.100                 | 1.514                 | 3.3781                |
| 20DX/XNBR     | 10.680                 | 517.617                 | 1.359                 | 2.5562                |

*DX/XNBR: dextrin/XNBR

3.3 Fourier Transform Infrared Analysis

Figure 2 indicates the functional groups shared by both native sago and dexrinized-sago. For starch, the peaks with representing its functional groups lies within major regions, 3600-3000 cm\(^{-1}\), 1700-1600 cm\(^{-1}\), and 1200-900 cm\(^{-1}\) which indicating the presence of –OH stretching, C-H stretch in starch main chain (CH\(_2\)) and CO stretching, respectively (Misman et al. 2013). The 3300-3310 cm\(^{-1}\) represents the OH group in starch and dextrin. The peaks within range 1630 cm\(^{-1}\) -1650 cm\(^{-1}\) were significant during dextrinization process as dextrin becomes more hygroscopic and soluble in water due to depolymerisation of the glucan as result of degradation by heat and acid (Yu et al. 2012). The crystalline region of starch can be detected within range 1047-1022 cm\(^{-1}\). Whereas, the amorphous region can be seen within region 1550-1750 cm\(^{-1}\) (Rajeev et al. 2010). It can be seen that the crystalline peak in the sago dextrin has diminished significantly and amorphous peak of dextrin appeared (Lin et al. 2011). The C-OH peak in carboxylic functionality can be found in both 1040 cm\(^{-1}\) unfilled XNBR and dextrin-filled XNBR films (Misman et al. 2016). There are two types of crosslinking exist in XNBR latex films. First one is the ionic crosslink that formed between carboxylic acid and zinc and the other one covalent bonding between sulphur and butadiene of XNBR. The absence of nitrile group band at 2238 cm\(^{-1}\) and presence of carbonyl group at band 1699 cm\(^{-1}\), it can be assumed that the crosslinks take place mainly with –CN group even though the –COOH group also participate in the reaction. The incorporation of dextrin as filler does not affect crosslink process, it does not favour the reaction with –CN nor with –COOH due to unreactive group present on the dextrin surface (Ibarra et al. 2008).
Figure 2. The Fourier Transform Infra-Red (FTIR) of sago starch, dextrin, unfilled XNBR and 10, 20 phr dextrin-filled XNBR films

3.4 Morphological Analysis

There is no obvious difference in the size and shape of starch granules detected between native sago starch and dextrinized sago starch after pyrolysis and acid treatment. The ball-milling method of preparing the dextrin dispersion did not efficiently reduce the particle size of the dextrin during preparations of dextrin dispersions. The only observation observed, that the structure of dextrinized sago starch particles are slightly cracked and damaged as pyroconversion leached out the crystalline ring growth consist of amylose content in native sago starch as shown in Fig.3 (a) and (b) (Karim et al, 2007; Dufresne, 2010). The SEM micrographs of tensile fractured surfaces of XNBR films are illustrated in Fig.3 (c) and (d). The presence of dextrin fillers sticking out of the fractured surface and formed holes indicate poor interfacial interaction between dextrin and XNBR due to polar characteristic of dextrin and non-polar characteristic of XNBR latex which lead to low tensile properties of XNBR films. Contrary, the unfilled XNBR (Fig. 3 (d)) has smooth fractured surface as no filler granule presents on the fractured surface.
4. Conclusion

In conclusion, the tensile properties of dextrin filled XNBR films, namely tensile strength, elongation at break, moduli 100 % and 300% decreased with increasing dextrin loading. The crosslink density of dextrin filled XNBR films also decreased as swelling index increased due to fewer formation of crosslinks hindered by presence of dextrin filler. The IR spectra showed that dextrin filler did not participate in crosslinking of rubber chains. The SEM showed that dextrin have poor adhesion with XNBR film due to hydrophilic nature of dextrin and hydrophobic nature of XNBR.

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