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Potential Bio-filler Cellulose Derived from Cucumber Pomace Filled Natural Rubber Latex Films

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The aim of this work was to study the tensile properties and the swelling behaviour of natural rubber latex (NRL) incorporated with different loadings of cellulose derived from cucumber pomace. Cellulose was extracted from cucumber pomace by acid hydrolysis process. The amount of cellulose fillers added in NRL was varied from 2 to 10 phr. The unfilled NRL and NRL/ cellulose films were prepared through dipping process. The NRL/cellulose films were subjected to tensile testing to determine the tensile strength (TS), the elongation at break (EB), and the modulus (M100, M300, M500). Swelling test was also conducted on NRL/cellulose films to measure the crosslink density of the samples. In this study, the highest tensile strength of NRL/cellulose films was recorded at 10 phr loading of cellulose. However, the fluctuation values of the tensile strength could be caused by the poor dispersion of the cellulose in NRL. The swelling test also found that the swelling percentage of NRL films decreased with increased cellulose loading, due to free spaces in NRL compounds that filled with cellulose which restricted the diffusion of the solvent. The overall result showed that cellulose derived from cucumber pomace can be potentially developed as bio-filler in NRL.

Keywords: Bio-filler; cellulose; natural rubber latex; tensile properties; swelling behaviours

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Natural rubber (NR) is the most used elastomers in worldwide due to its unique properties. Generally, elastomers are polymers that viscoelastic and exhibit very weak intermolecular forces. In comparison with other materials, elastomers possess low Young's modulus and high failure strain, as well as high elongation that prevent potential breaking and cracking when subjected to external load [1,2]. Theoretically, rubber compound consists of elastomers compounded with five or more additives depending on the applications of the final products [3]. In rubber industries, compounding additives such as fillers are commonly added to improve the mechanical properties of rubber materials, to reduce the cost and to ease the processability [4, 5]. Carbon black and silica are often used as reinforcing fillers and their impact on the rubber mixture are mainly influenced by the type of surface area and the formation of aggregation or agglomeration [6]. However, high loading of these fillers causes the filled rubber particulates to have relatively high density which opposes the unique light-weight properties of rubber materials.

For centuries, natural rubber latex (NRL) have been used widely in various applications including gloves, catheters, balloons and pacifiers [7]. Latex is a colloidal dispersion extracted from rubber tree, *Hevea brasiliensis* consisting of rubber particles which surrounded by a thin layer of proteins, lipids and fatty acids [8]. Owing to the outstanding properties of latex like sustainability, renewability and processability, making it highly utilized from household applications to industrial manufacturing [9]. Gloves are the most used product that take up large percentage of latex consumption in health and laboratory sectors. However, as the glove applications market begins to grow, there are few downsides that must be improved. For instance, the requirement of a thin film which offers good physical properties such as flexibility and good mechanical properties to produce a high-quality glove. Therefore, nanofillers such as clay and carbon nanotubes are incorporated in latex to improve the mechanical properties of latex. Nevertheless, the poor dispersion, the incompatibility and the toxicity of commercial nanofillers have become common especially at higher filler loadings [10–12].

Cellulose was introduced to become one of the promising fillers in rubber industries where it offers versatility of chemical and physical properties, biodegradable and environmentally-friendly [13]. Its capability of being a reinforcing filler along with having high stiffness and low density properties [14,15], have drawn attentions of many researchers especially with the rising concern of the depletion of synthetic and non-renewable resources. Cellulose is obtained through acid hydrolysis process of a renewable resources where this process isolates the cellulose from any other materials like lignin and pectin that usually f in plants [10]. Apart from being

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fertilizer and feedstock for animals, pomace can also be used as a source of general dietary fibre. Furthermore, this derivative of natural fibres is abundant, compostable and biocompatible. Environment Canada has listed cellulose as a 'non-toxic' substance which directly proved that it poses low health hazard during handling it in large scale production [16].

Cucumis sativus L. (C. sativus) or also known as cucumber is one of the most popular plants that belongs to Cucurbitaceae family and is grown world-wide. These cucumbers can either be consumed fresh, cooked or as pickles. However, cucumber wastes including their peels and slices were found around 12% from residual wastes after they were processed [17]. In addition, Begum (2018) stated that the extract contains antioxidant and analgesic activities which are used as carminative and antacid. Meanwhile, cucumber seeds suppress good sources of protein, calcium and minerals [18]. Therefore, many studies have been conducted to develop pomace-waste as potential bio-filler in NRL [19]. By incorporating natural fillers, the properties of polymeric materials can be tailored in order to improve their properties in terms of mechanical and biodegradability.

Hence, this paper consists of a new study on the reinforcement of NRL with cellulose extracted from cucumber pomace. This study focused on the reinforcing effect of the cellulose and its potential as biodegradable filler in NRL.

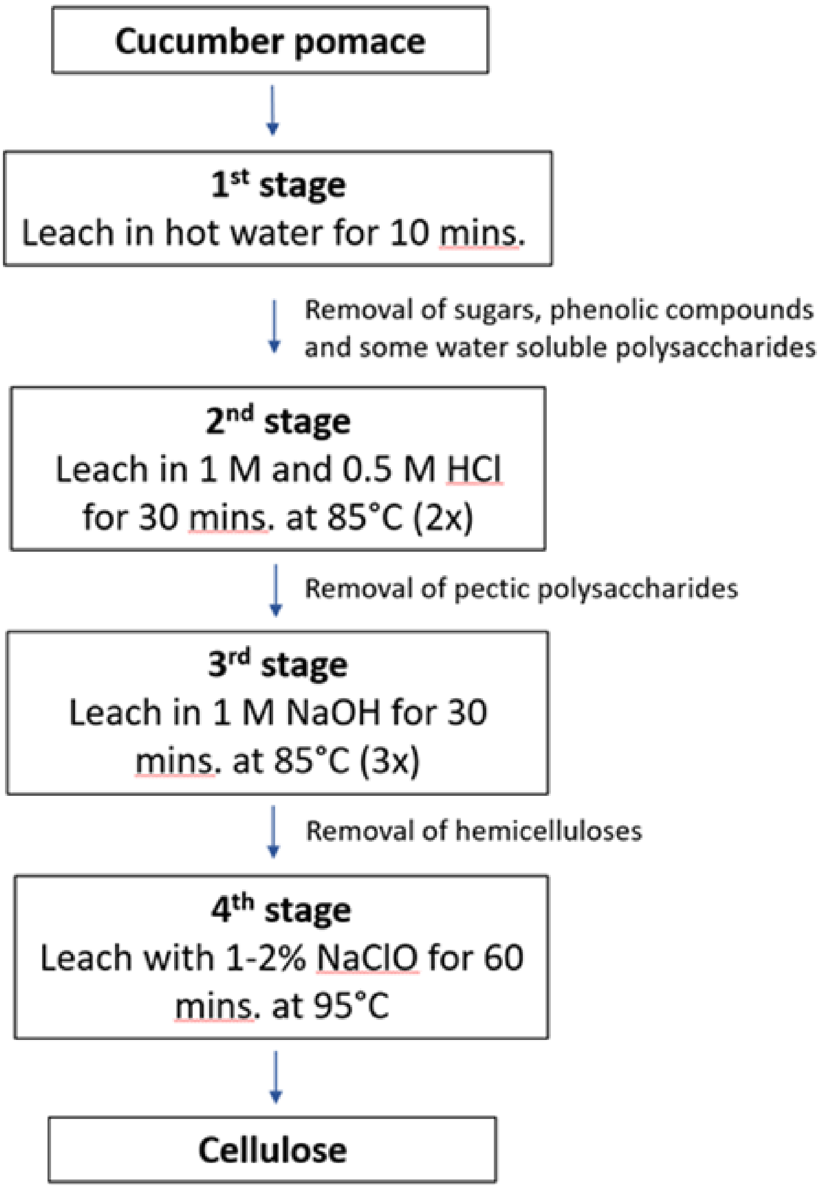

Figure 1. Extraction process of cellulose from cucumber pomace Source: Szymanska-Chargot et al. (2017).

METHODOLOGY

Pre-vulcanised NR latex with 60 w/w% dry rubber content was purchased from Getahindus Sdn. Bhd., Tangkak, Johor, Malaysia. Cucumber was obtained from local grocery market. The cucumber pomace was prepared in a de-pulping slow juicer (Model HUROM H-AA, Korea) which contained fragments of pulp, skin and seeds. All other chemical reagents were purchased from Sigma-Aldrich (M), Subang Jaya, Selangor and used without further purification.

1. Extraction of Cellulose from Cucumber Pomace (CP)

Firstly, the fresh cucumbers were blended using food processor. Then, 500 g of cucumber pomace was boiled for 10 mins and filtered. During this process, part of water solvent polysaccharides was removed along with phenolic mixes and sugars. Then, 3 L of 1 M hydrochloric acid (HCl) solution was added and stirred at 200 rpm and 85 ℃ for 30 mins in the previous filtered residue. The mixture was again filtered, and the step was repeated with 0.5 M HCl solution to remove pectic polysaccharides by acid treatment.

Next, 3 L of 1 M sodium hydroxide (NaOH) was stirred at 200 rpm and 85 ℃ for 30 mins, before filtering the residue. The steps were repeated for 3 times to remove the hemicelluloses through alkali treatment. Then, the obtained residue was bleached with 1%–2% of sodium hypochlorite solution for 60 mins at 95–96 ℃ and this step was repeated twice to obtain cellulose. To maintain a neutral pH, the cellulose was washed with hot deionized water for few times. Figure 1 shows the four stages involved for the extraction of the cellulose and Figure 2 shows the cucumber solutions obtained after each treatment.

In Figure 2, solution (a) contained sugars, phenolic compounds and water-solvent polysaccharides after leached in hot water. Solutions (b) and (c) were obtained after acid treatment where pectic poly-saccharides were removed, while (d), (e) and (f) were the solutions obtained after alkali treatment where hemicelluloses were removed. Solutions (g) and (h) were obtained after the remaining cucumber residue was bleached to obtain cellulose. Lastly, solution (i) was obtained after cellulose was washed to maintain neutral pH.

2. Preparation of NRL/Cellulose Film

The extracted cellulose was mixed with pre-vulcanized NRL in varying fractions of 2 to 10 phr (dry basis). Latex dipping process was conducted to obtain the NRL/cellulose films. Magnetic stirrer was used to stir the mixture for 4 hours before dipping the boiling tubes into the mixture. Any presence of bubbles was removed. The NRL/cellulose film was dried overnight at 60 ℃ and the thickness obtained were between 0.4 to 0.6 mm, depending on the amount of filler loading. Figure 3 shows the samples of NRL/cellulose films after dipping process and were left to dry in the oven, while Figure 4 shows the films after dried.

Figure 2. Cellulose solutions after treatment.

Figure 3. Drying of NRL/cellulose film.

Figure 4. NRL/cellulose films.

3. Characterization of NRL/Cellulose

3.1. Fourier Transform Infrared (FTIR) Analysis

FTIR was used to analyse the functional groups and their interactions in the extracted cellulose and solution using FTIR Perkin Elmer 90325. All spectra were recorded in the range of 4000–650 cm^{-1} resolution. The attenuated total reflectance method was used to examine the obtained cucumber pomaces and the cucumber solutions.

3.2. Tensile Test

NRL/cellulose film was prepared in the shape of dumb-bell according to ASTM D412. Digital thickness gauge was used to measure the thickness of the film prior tensile testing. The test was conducted using an Instron machine with a 500N loaded cell with crosshead speed of 500 mm/min at room temperature.

3.3. Swelling Behaviour

For swelling behaviour test, 1 cm × 1 cm of NRL/cellulose film was immersed in toluene for several days until equilibrium weight was achieved. The container was sealed tightly and kept in dark environment at room temperature to prevent evaporation of the solvent. The initial weight of the samples was recorded until a constant weight was reached. The swelling index was calculated using:

$$\%\ Swell = \frac{W_1 - W_2}{W_2} \times 100\% \qquad (1)$$

where W_1 is the weight of the swollen rubber and W_2 is the weight of the original dried rubber. The calculation of crosslinked density was determined using the Flory-Rehner equilibrium swelling equation (2). The equation is stated as below:

$$-\ln(1 - V_r) - V_r - \varphi\, V_r^2 = 2\rho V_o [X]_{phy} V_r^{1/3} \qquad (2)$$

Where V_r is the volume fraction of swollen rubber; V_o is the molar of solvent; ρ is the density of rubber and φ is the rubber-solvent interaction parameter.

RESULTS AND DISCUSSION

1. FTIR Analysis

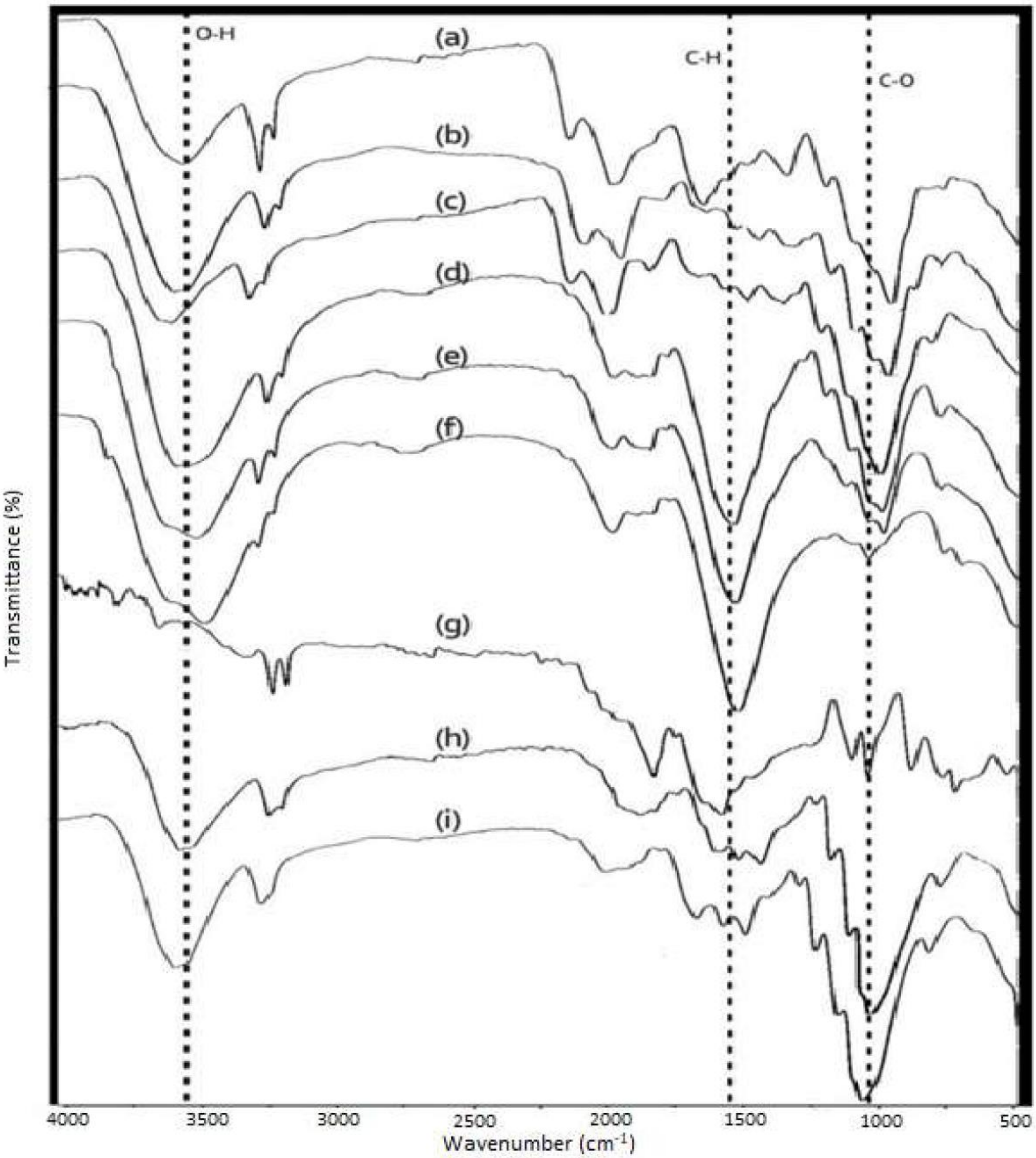

Figure 5. FTIR spectra of cellulose pomaces (CP): **(a)** CP after boiling with H_2O **(b)** CP after treatment with 1 M HCl **(c)** CP after treatment with 0.5 M HCl **(d)** CP after 1st treatment with 1 M NaOH **(e)** CP after 2nd treatment with 1 M NaOH **(f)** CP after 3rd treatment with 1 M NaOH **(g)** CP after 1st treatment with H_2O_2 **(h)** CP after 2nd treatment with H_2O_2 and **(i)** CP after leaching with DI H_2O.

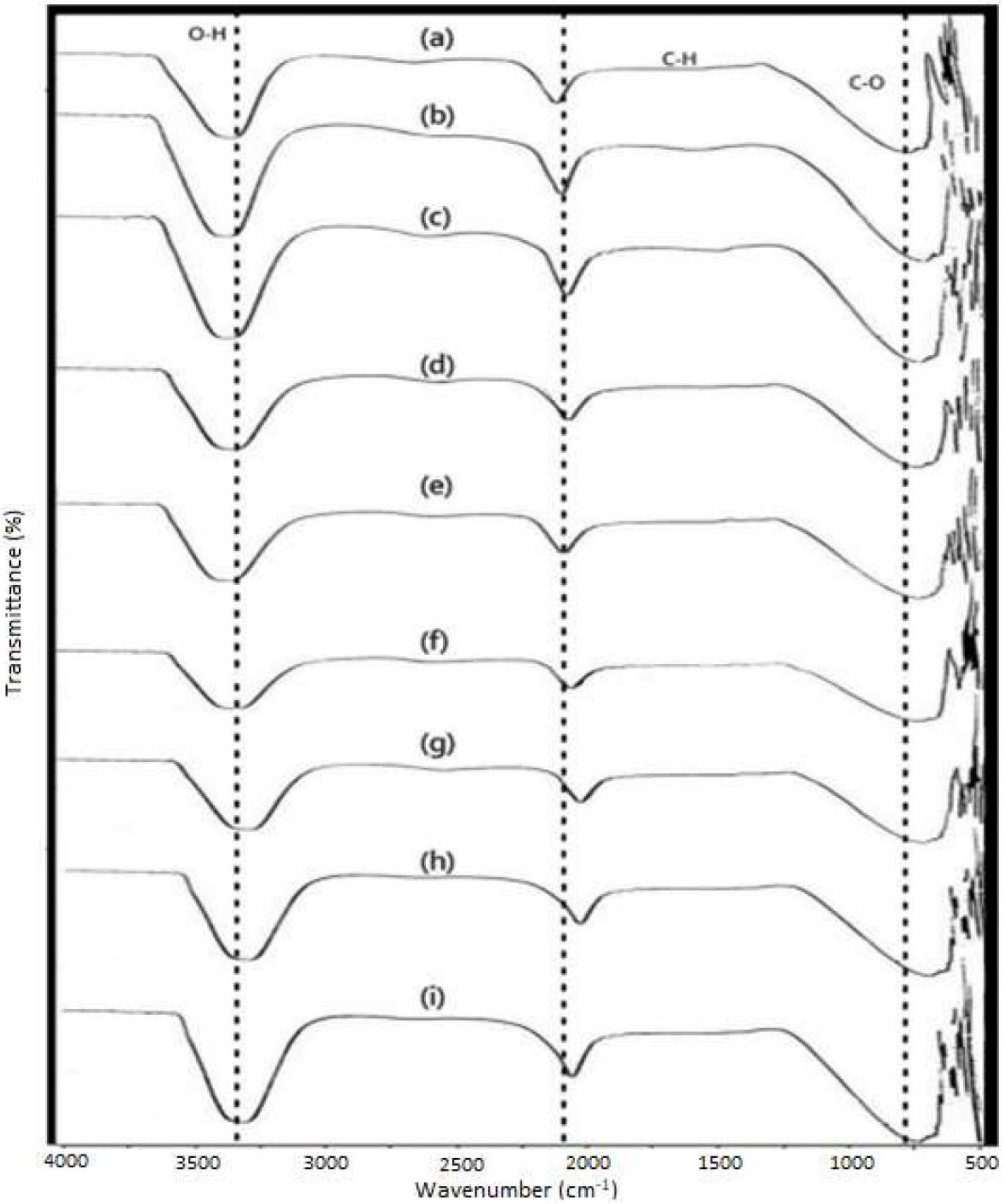

Figure 6. FTIR spectra of cellulose solutions (CS): **(a)** CS after boiling with H_2O **(b)** CS after treatment with 1 M HCl **(c)** CS after treatment with 0.5 M HCl **(d)** CS after 1st treatment with 1 M NaOH **(e)** CS after 2nd treatment with 1 M NaOH **(f)** CS after 3rd treatment with 1 M NaOH (g) CS after 1st treatment with H_2O_2 **(h)** CS after 2nd treatment with H_2O_2 and **(i)** CS after leaching with DI H_2O.

Based on Figure 5, all samples of CP were analysed to observe the structural changes of the CP after each stage of treatment. Spectrum obtained showed characteristic bands at 1154 cm^{-1} and 998 cm^{-1} which assigned to the C–O stretching vibration and the glycosidic-CH deformation, respectively. A trace of aromatic compounds was also observed at the widened peaks in the range of 1650–1537 cm^{-1}. The region of 1090–816 cm^{-1} (C–H out-of-plane bending) might be due to the vibrations of the aromatic compounds as phenolic compounds. Whereas the broadening in region 1500–1300 cm^{-1} can be associated with the trace of proteins [19]. Figure 6 depicts the spectra of the solutions obtained that showed a slight stretched at 2250–2000 cm^{-1} towards the end of the treatment. This may occur due to the losses of proteins and carbohydrates that were presented in the early stages of the extraction solutions until the solutions were completely bleached after treatments [17].

2. Tensile Test

Table 1. Tensile properties of unfilled NRL and NRL/cellulose films at different cellulose loading.

Samples	TS (MPa)	EB (%)	M100 (MPa)	M300 (MPa)	M500 (MPa)
Unfilled NRL	2.08 ± 0.62	9.41 ± 403.14	2.33 ± 1.09	3.74	3.75
2 phr cellulose filled NRL	2.01 ± 0.43	510.25 ± 412.14	0.28 ± 0.20	2.57	6.90
4 phr cellulose filled NRL	1.61± 0.19	655.09 ± 482.80	1.56 ± 0.23	2.24 ± 0.23	6.56 ± 1.24
6 phr cellulose filled NRL	2.69 ± 1.44	17.55 ± 248.03	1.37	1.43	-
8 phr cellulose filled NRL	1.79 ± 0.51	243.25 ± 362.08	1.76 ± 0.46	2.21 ± 0.14	5.51± 0.92
10 phr cellulose filled NRL	2.84 ± 1.29	244.44 ± 558.90	3.30 ± 1.76	5.73 ± 3.76	7.52 ± 1.37
Mean	**2.08**	**9.41**	**2.33**	**3.74**	**3.75**

Based on the result obtained in Table 1, the highest tensile strength was found at 10 phr filler loading. According to Daud et al. (2020), as the amount of filler increased, the tensile strength of the films varied and this might occur due to the poor dispersion of cellulose in the NRL compound, resulting a more significant filler-filler interaction than rubber-filler interaction. The formation of agglomerates between filler particles at stress concentration point causes the film to easily break [20]. Hence, the elongation at break of the films decreased with increased cellulose fillers. The formation of agglomerates can be observed from a study conducted by Yazid et al. (2018) as in Figure 7, where higher filler loading caused higher possibilities of agglomeration.

However, a study by Mekonnen et al. (2019) on cellulose nanocrystals (CNC) derived from kraft pulp displayed a significant increase in tensile properties with the addition of CNC in NRL due to its excellent dispersion. The tensile strength increased with incorporation of CNC at 2.5 and 5 phr by 31% and 80%, respectively. Nevertheless, the incorporations of 10 and 20 phr of CNC in NRL did not show a big difference on the increased tensile strength due to the formation of aggregates as the amount of CNC increased [22].

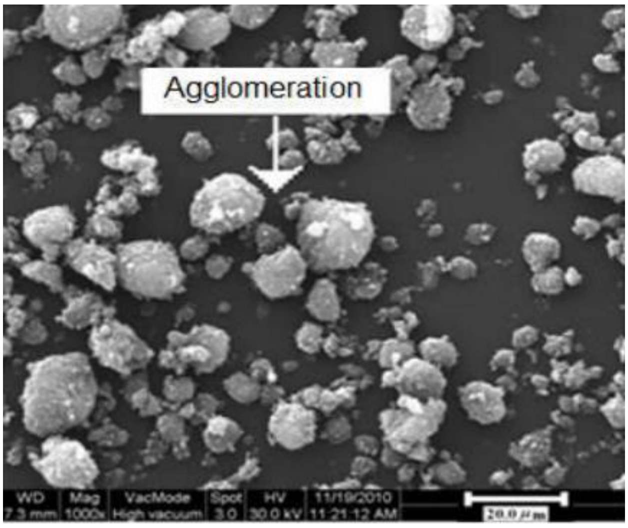

Figure 7. SEM image of filler agglomeration. Source: Yazid et al. (2018).

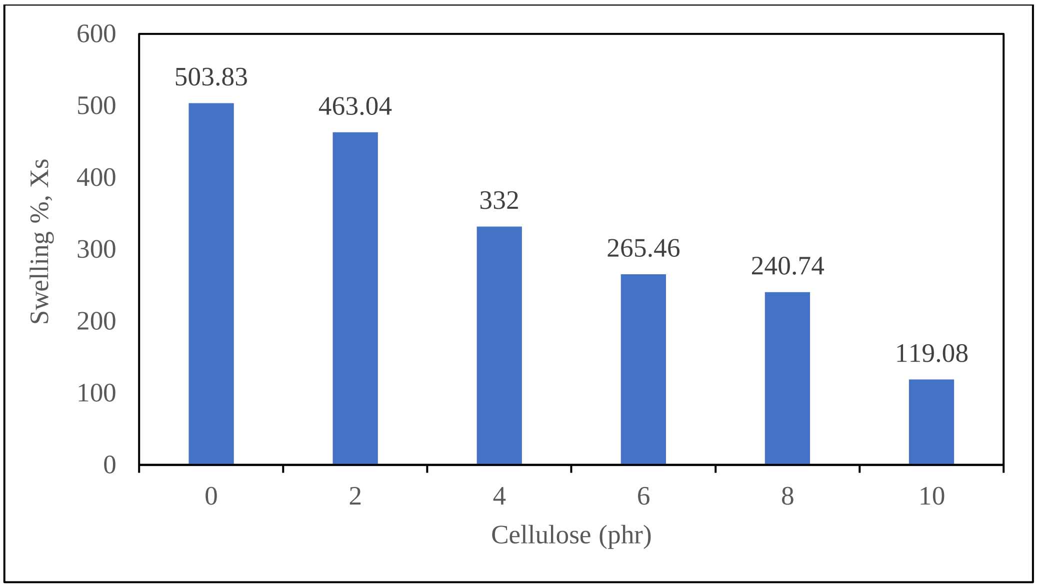

Figure 8. Swelling percentage of unfilled NRL and filled NRL/cellulose films at different cellulose loading

3. Swelling Test

Figure 8 shows the swelling percentage of NRL latex with different loading of cellulose. According to Sallehuddin & Ismail (2020), as the amount of cellulose filler increases, the percentage of swelling decreases due to spaces and voids of the rubber molecules that are occupied with the cellulose filler, causing the restriction of solvent materials to diffuse into the samples [23]. From Figure 8, sample with 10 phr cellulose showed the lowest swelling percentage due to its high crosslink density as it contained the highest amount of cellulose filler which increased the restriction for the diffusion to occur [10, 20]. This statement can be proven by referring to Figure 9 where the highest crosslink density was obtained in the highest loading of cellulose filler, which was at 10 phr. High crosslink density would result in greater tensile strength as mentioned previously.

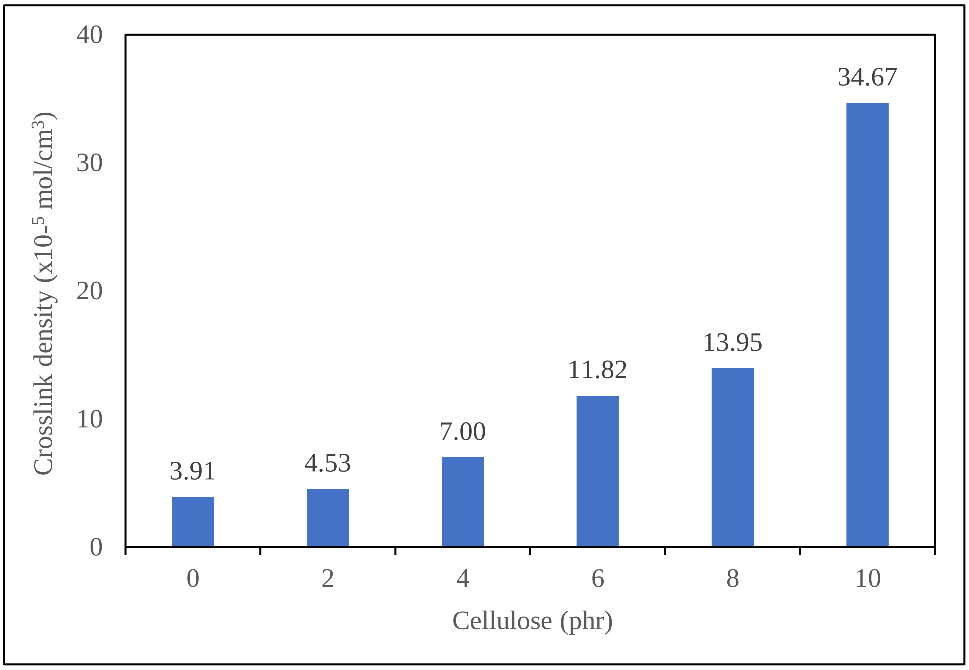

Figure 9. Crosslink density of unfilled NRL and filled NRL/cellulose films at different cellulose loading.

CONCLUSION

The new findings on the addition of cellulose derived from cucumber pomace (CP) into natural rubber latex (NRL) improved the mechanical properties of NRL, making it compatible to be utilized as fillers. With the addition of cellulose, the mechanical properties including tensile strength, swelling behaviour and crosslink density of NRL films were improved compared to the unfilled NRL. As for tensile test, NRL/cellulose at 10 phr showed the highest tensile strength, in line with the crosslink density result. Meanwhile, the lowest swelling result was observed at 10 phr of cellulose. Although with small amount of cellulose filler incorporated in NRL, it could be potentially developed as biodegradable fillers that meet the standard and industrial requirements of latex products. In future, this study could be enhanced by incorporating dispersing agent in the NRL/cellulose mixture to promote a good dispersion of the cellulose in NRL. Moreover, more tests can be conducted such as scanning electron microscope (SEM) to observe the surface morphology of NRL filled with cellulose. In addition, soil burial test also can be conducted to investigate the degradation process of the NRL film filled with cellulose bio-filler. The results can contribute to the development of biodegradable latex dipping products such as gloves, balloons, latex catheters, and condoms.

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