Effect of adding carboxymethyl cellulose, zeolite and microcrystalline cellulose on the optical and mechanical properties of latex composite films

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Abstract. In this research, four-types of latex composite films which are carboxymethyl cellulose latex composite film, zeolite latex composite film, microcrystalline cellulose latex composite film and microcrystalline cellulose sodium hydroxide latex composite film were prepared by casting method. Drying time of all films formation is 24 hr. The average thickness of the dry film is 0.10 mm. The transparency of films were measured by UV-Vis spectrophotometer. It was found that the carboxymethyl cellulose latex composite film have more transparency than zeolite latex composite film, microcrystalline cellulose latex composite film and microcrystalline cellulose sodium hydroxide latex composite film respectively. The analysis of functional group of films were measured by ATR-FTIR technique. It was found that all types of films consist of O-H stretching group and C=O group without ether group of cellulose and Si-O-Al group of zeolite. The mechanical property of films were measured by Universal Testing Machine. It was found that the Young’s modulus of microcrystalline cellulose sodium hydroxide latex composite film was higher than microcrystalline cellulose latex composite film, zeolite latex composite film and carboxymethyl cellulose latex composite film respectively. The characteristic of stress-strain curve of films showed that all films were hard and brittle except microcrystalline cellulose latex composite films were hard and tough.

1. Introduction
Nowadays, many types of latex composite film have been prepared by mixing a fillers suspension with a latex polymer matrix [1]. The formation of latex films involved in four stages. The initial stage of film formation is termed the wet state. In second stage, when solvent evaporated, the latex particles arrange to form a close-packed structure. In third stage, deformation of particles arise to close the voids. In final stage, after the voids vanished particles cause diffusion across particle–particle boundaries which leads the film to form a homogeneous continuous latex film [10].
Inorganic filler materials (e.g. zeolites and halloysite nanotubes) have been widely used in the preparation of composite films [2-4]. Addition of zeolite improves the mechanical properties both the tensile strength and Young’s modulus of latex composite film. Moreover, Halloysite nanotubes filled in polymer latex not only prevents cracking in drying latex films but also enhances the pendulum hardness of latex film [4]. Organic filler materials (e.g. carboxymethyl cellulose (CMC) and microcrystalline cellulose (MCC)) are considered as the significant filler due to its biocompatible, biodegradable, nontoxic and abundantly available with good film forming property. Effects of adding MCC on mechanical properties of MCC-reinforced soy protein isolate (SPI)-gelatin (MSG) films reveal that increasing of MCC content in MCC-reinforced SPI-gelatin (MSG) films lead to increasing of tensile strength (TS) of MSG films [5]. In addition, increasing MCC loading in epoxidized natural rubber latex (ENR) can increase tensile strength of composite latex film [6].

Composite films derived from latex polymer matrix and loaded with fillers (e.g. CMC, zeolite, MCC and microcrystalline cellulose sodium hydroxide (MCCB)) have a wide variety of applications in comparison with pure latex films by reason of their improved mechanical performance and optical properties. The objectives of this work were to study of the effects of adding CMC, zeolite, MCC and MCCB on the mechanical and optical properties of latex composite films. The key idea of this work is shown in Figure 1.

![Figure 1. The key idea of this work.](image)

2. Experiment

2.1 Materials
The source of the latex used in the preparation of the composite films was TOA adhesive latex from the TOA Paint (Thailand) Public Company Limited. Commercial-grade carboxymethyl cellulose powdered (CMC), microcrystalline cellulose (MCC), commercial-grade zeolite clinoptilolite, analytical-grade sodium hydroxide (NaOH) with 99% purity and deionized water were used as starting materials.

2.2 Preparation of latex composite films
The latex composite films were prepared by mixing the starting materials and stirring at 1200 rpm for 60 min to obtain uniform mixtures with different compositions, as listed in Table 1. The mixtures 1000 μL were cast into 2x5 cm² glass slide. After a 24 hour, the samples were peeled off and kept in desiccator.

2.3 Characterisation
The transparency of the composite films was examined by UV-visible spectrophotometer (Jasco V-530). The Fourier-transform infrared spectra (FTIR) were analysed using a thermo scientific nicolet iS5 spectrometer to identify the chemical bonding. The mechanical property was examined using universal
testing machine (Conetech(H)-ZFA15). The film thickness of the composite films was measured by dial thickness gages (Mitutoyo-7301).

Table 1 Composition of latex composite films.

| Sample code | Latex (mL) | CMC (mL) | MCC (mL) | Zeolite (mL) | MCCB (mL) |
|-------------|------------|----------|----------|--------------|-----------|
| LCMC91      | 9          | 1        | -        | -            | -         |
| LCMC82      | 8          | 2        | -        | -            | -         |
| LCMC73      | 7          | 3        | -        | -            | -         |
| LCMC64      | 6          | 4        | -        | -            | -         |
| LCMC55      | 5          | 5        | -        | -            | -         |
| LMCC91      | 9          | -        | 1        | -            | -         |
| LMCC82      | 8          | -        | 2        | -            | -         |
| LMCC73      | 7          | -        | 3        | -            | -         |
| LMCC64      | 6          | -        | 4        | -            | -         |
| LMCC55      | 5          | -        | 5        | -            | -         |
| LZ91        | 9          | -        | -        | 1            | -         |
| LZ82        | 8          | -        | -        | 2            | -         |
| LZ73        | 7          | -        | -        | 3            | -         |
| LZ64        | 6          | -        | -        | 4            | -         |
| LZ55        | 5          | -        | -        | 5            | -         |
| LMCCB91     | 9          | -        | -        | -            | 1         |
| LMCCB82     | 8          | -        | -        | -            | 2         |
| LMCCB73     | 7          | -        | -        | -            | 3         |
| LMCCB64     | 6          | -        | -        | -            | 4         |
| LMCCB55     | 5          | -        | -        | -            | 5         |

a(Latex), latex 5 mL to water 5 mL, b(CMC), CMC 0.02 g to water 10 mL, c(MCC), MCC 0.02 g to water 10 mL, d(Zeolite), Zeolite 0.05 g to water 10 mL, e(MCCB), MCC 1.00 g to water 10 mL-NaOH(12%w/v) 30 mL

3. Results and Discussions

3.1 FTIR spectra of composite film

Figure 2(a)-(d) shows the spectra of latex composite films with CMC, MCC, zeolite and MCCB, respectively with different latex to fillers ratio of 9:1, 8:2, 7:3, 6:4 and 5:5. The bands at 1000 cm⁻¹ are attributable to R-O-R asymmetrical stretching vibrations of ether groups (Figure 2(a), (b), (d)) while the band at 1000 cm⁻¹ are attributable to Si-O-Al internal asymmetric stretching vibrations in zeolite (Figure 2(c)) [1]. The bands of functional groups in latex were observed at 1200 cm⁻¹, 1450 cm⁻¹, 1700 cm⁻¹, 2900 cm⁻¹ and 3300 cm⁻¹ indicate C-O stretching vibrations, -CH₂ bending vibrations, C=O stretching vibrations, C-H stretching vibrations and O-H stretching vibrations, respectively [2]. The band at 1600 cm⁻¹ are attributable to C=O asymmetrical stretching vibrations that relate to carboxymethyl cellulose (Figure 2(a)) [3]. It was demonstrated that the fillers were deposited on composite films than the fillers incorporated into the film structure.
Figure 2. FTIR spectra of latex composite films (a) CMC, (b) MCC, (c) zeolite and (d) MCCB.

3.2 Transparency of composite film

Apparent shape and transparency of the composite films were evaluated by measuring the light transmittance in the range of wavelength from 400 to 800 nm as shown in Figure 3. The average thickness of the dry latex composite film is 0.10 mm. The results from UV-Visible spectra show that adding CMC, MCC and zeolite in latex polymer films can increase the transparency of latex composite films while adding MCCB decrease the transparency of latex composite films. The reasons for increment in transparency might cause by the deformation of the matrix as a result of the incorporation of CMC into the latex polymer matrix [1, 10]. In addition, CMC is long chain polymer that consists of flexible part and rigid part so that adding it into polymer matrix lead to increasing transparency [1]. MCCB is short chain polymer that consists of only rigid part of cellulose in structure so that adding it into latex polymer matrix lead to decreasing of transparency because aggregation or agglomeration of rigid part occurred in latex polymer films.
Figure 3. Photos and light transmittance spectra of latex composite films (a) CMC, (b) MCC, (c) zeolite and (d) MCCB.

3.3 Mechanical property of composite film

The Young modulus of the latex composite films of CMC, MCC, zeolite and MCCB were shown in Figure 4. The results shown that the Young modulus of the CMC and MCC latex composite films is lower than the zeolite and MCCB latex composite films. It is evident from the results that zeolite as fillers can significantly increase the Young modulus of latex films compared to the CMC and MCC fillers. The Young modulus increases as the loading content of MCCB added to the latex polymer matrix, which is indicated to the interactions between the latex and the MCCB and the disruption of chain mobility resulting from the chain packing density as shown in Figure 4(d) [1,4]. No improvement of Young modulus was observed in the latex films with the addition of CMC, MCC and zeolite. It is known that interactions of filler types and latex polymer matrix contributes to the Young modulus of the latex film.
Figure 4. The influence of fillers content on Young’s modulus of latex composite films (a) CMC, (b) MCC, (c) zeolite and (d) MCCB.

4. Conclusion
The latex composite films were prepared by casting method using latex act as matrix and fours fillers consist of CMC, MCC, MCCB and zeolite. It was confirmed that the fillers types affected the transparency and mechanical properties of composite films. Increased transparency of latex composite films can be achieved by adding CMC. Increased mechanical properties of latex composite films can be achieved by adding MCCB.

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References
[1] Hubbe MA, Ferrer A, Tyagi P, Yin Y, Salas C, Pal L and Rojas OJ 2017 BioResources 12 (1) 2143-2233
[2] Hsu WJ, Huang PS, Huang YC, Hu SW, Tsao HK and Kang DY 2019 Langmuir 35 (7) 2538-2546
[3] Junqiang Q, Adams J and Johannsmann D 2012 Langmuir 28 8674–8680
[4] Denktaş C 2019 Journal of Applied Polymer Science 136 48549
[5] Li C, Luo J, Qin Z, Chen H, Gao Q and Li J 2015 RSC Advances 5 (70) 56518–56525
[6] Oun AA and Rhim JW 2016 Materials Letters 168 146-150
[7] Setthaya N, Chindapasirt P, Yin S and Pimraksa K 2017 Powder Technology 313 417-426
[8] Fang Q, Cui HW and Du GB 2012 Journal of Thermoplastic Composite Materials 26 (10) 1393-1406
[9] Tehseen R, Rabia Z, Faiza Z, Kanwal I, Nawshad M, Sher ZS, Abdur R, Syed AAR and Ihtesham UR 2018 Applied Spectroscopy Reviews 53 (9) 703-746
[10] Feng J, Winnik MA, Shivers RR and Clubb B 1995 Macromolecules 28(23) 7671–7682