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Preparation of self-healing acrylic latex coatings using novel oil-filled ethyl cellulose microcapsules

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ABSTRACT

Novel oil-filled microcapsules were prepared by introducing a phase separation method using ethyl cellulose as a shell-forming containing rapeseed oil. The prepared oil-filled microcapsules were evaluated by optical microscopy, scanning electron microscopy and particle size analysis. Results showed that spherical microcapsules with a diameter of 10 to 45 μm and a rough porous shell were obtained. Carboxylated styrene/butadiene copolymer latex films containing various levels of these microcapsules were subjected to various levels of pre-elongation and their tensile properties were examined. The addition of oil-filled microcapsules resulted in a significant improvement in the modulus, strain-to-break, and toughness of the films. The self-healing mechanism of latex films was examined through the colorimetric measurements of the release of dye-containing following the pre-elongation of the samples. These measurements confirmed that pre-elongation of samples resulted in the release of oil within the latex films, hence plasticizing the surrounding polymeric network and partly restoring the mechanical properties of the pre-elongated films.

1. Introduction

Water-based polymeric coatings are used in a wide variety of applications ranging from decorative wall paints to packaging materials. However, due to the low strain-to-failure exhibited by these materials, unexpected damages and cracks often incur during their service life [1]. In many cases, physical and mechanical damages of polymeric coatings occur within the manufacturing and converting processes. In addition, water-based coatings usually provide relatively poor barrier properties against gases, high sensitivity to water and moisture, and inferior mechanical properties [2]. Some of conventional methods for improving these properties include; increasing the coating thickness [3], applying multiple coating layers [1], adding functionalized nanoparticles [4–6], increasing the crosslinking density of polymer [7] and introducing functionalized core-shell latexes into the coating formulation [8].

Among the aforementioned available methods [3–8], application of healable materials in coating formulations shows great potential for improving the durability and enhancing bulk mechanical properties of the coating layers. Such self-healing coatings possess the ability to repair in response to damage in the material [9].

In 2001, White and co-workers [10] introduced a novel method to repair the mechanical properties of thermosetting polymers following crack propagation through the micro-encapsulation of self-healing materials. Repairing has been obtained via the addition of urea-formaldehyde microcapsules containing dicyclopentadiene (DCPD) healing agent and through the ring opening polymerization of DCPD in the presence of Grubbs' catalyst [11]. Micro-encapsulation is an approach that consists of isolating a dispersed phase from an external medium by surrounding or coating it with a protective shell material having sizes typically ranging from submicron up to 1 mm [12]. The microcapsules containing healing agents have the capability of self-repairing upon crack propagation [13,14]. As the healing agent flows within the crack lines, it comes into contact with the active materials inducing polymerization and hence sealing up the crack [15]. The repairing of mechanical damage is particularly useful to coatings or composites where subsurface damage occurs that is difficult to detect and fix [15–18].

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A variety of self-healing chemistries have been introduced to enhance the interaction between the healing agent and a polymeric matrix. These include epoxy [10,19,20], isocyanate [21] and solvent welding [22] siloxane chemistries for vinyl ester matrices [23] and poly dimethyl siloxine (PDMS) [24].

An alternative to self-healing using chemical bonding agents is self-healing by plasticizing mechanism. This approach is a promising method for enhancing mechanical properties of polymeric coatings via increasing tensile strength and elongation at break.

In the current study, rapeseed oil was encapsulated in ethyl cellulose microcapsules using a robust phase separation route and the mechanical properties of the water-based latex coatings containing these oil-filled microcapsules were investigated. Latex films containing 1–3 wt% microcapsules and two microcapsule sizes were studied. The deformation and disruption of latex films containing microcapsules filled with colored rapeseed oil were examined under applied tensile load using color coordinate measurements.

2. Experimental

2.1. Materials

Ethyl cellulose (EC), rapeseed oil (RO), sodium dodecyl sulfate (SDS), Sudan Red 7B solvent dyestuff, and ethyl acetate were purchased from Sigma Aldrich (Oakville, Ontario, Canada). A non-ionic surfactant, Dynol 604, was provided by Air Products USA. A commercial carboxylated styrene-butadiene latex, Styronal ND 656 was supplied by BASF Corporation. This latex is an emulsion-type latex commonly used for paper coating applications for its film-forming properties, resistance to water and moisture, and relatively rapid drying with low porosity [25]. All chemicals were analytical reagent grade and used as received.

2.2. Microcapsules preparation

Microcapsules with oil to ethyl acetate ratio of 70:30 were prepared via a two-stage solvent evaporation method [2] following

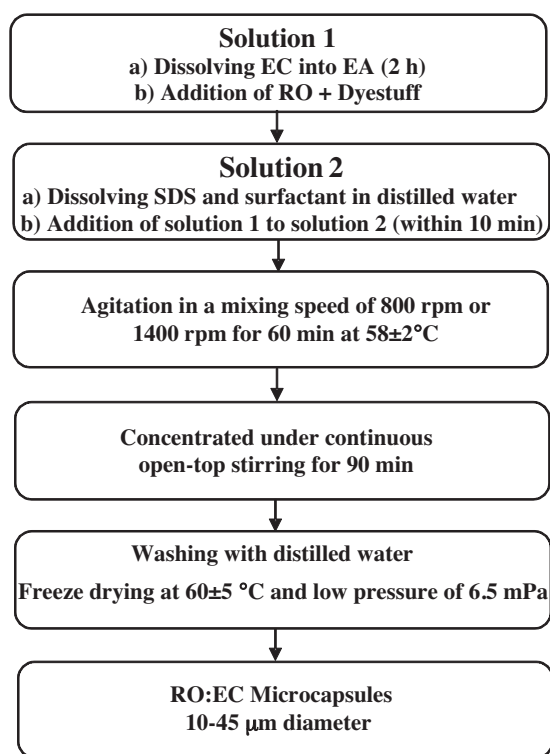


Fig. 1. Microencapsulation procedure.

the methodology reported elsewhere [26,27]. The flowchart for the synthesis of microcapsules is provided in Fig. 1. In brief, in the first stage, ethyl cellulose powder was dissolved in ethyl acetate (5 wt%) under magnetic stirring for at least 2 h at ambient temperature. RO and 0.005 wt% of red solvent dyestuff were then added to the above-mentioned solution and system was magnetically stirred for further 30 min. In the second stage, the solution was added drop wise to an aqueous solution of 1 wt% SDS and 0.05 wt%

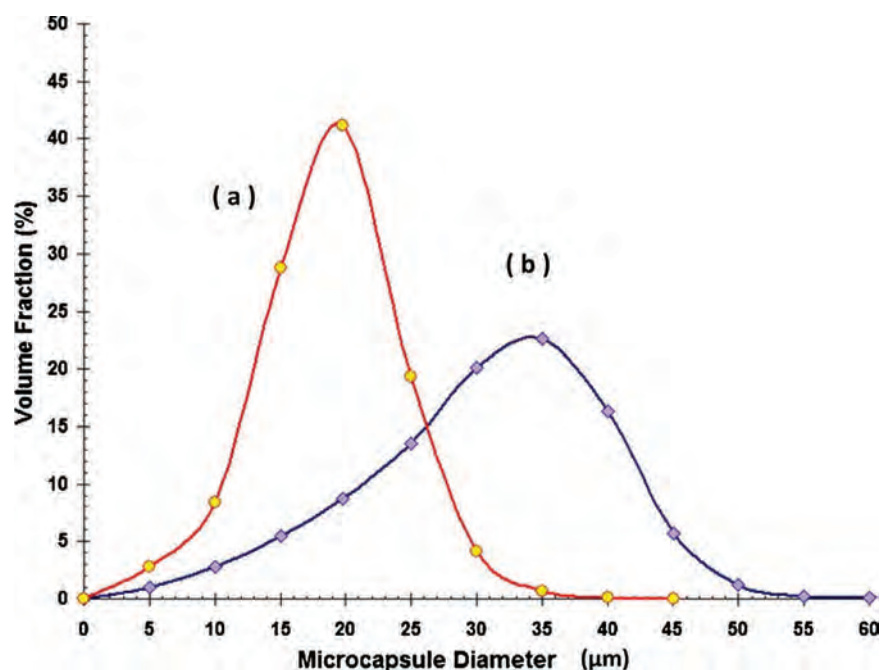


Fig. 2. Volume fraction (%) and the average diameter of 70:30 RO:EC microcapsules: (a) 1400 rpm ($d_m = 18.8 \mu\text{m}$, C.V. = 8.1%), and (b) 800 rpm ($d_m = 34.0 \mu\text{m}$, C.V. = 8.5%).

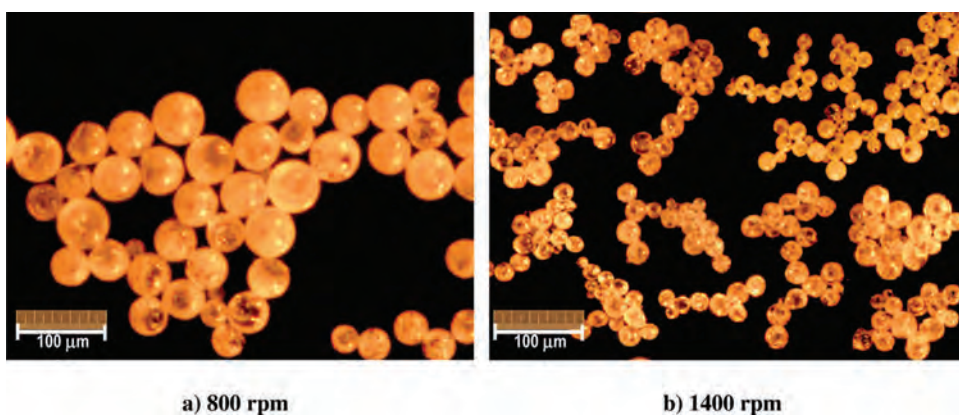


Fig. 3. Optical micrographs of microcapsules prepared at mixing rate of: (a) 800 rpm and (b) 1400 rpm.

Dynol 604 surfactant saturated with ethyl acetate, under mechanical mixing (BDC6015 Stirrer, Caframo Ltd., Warton, ON, Canada) at either 800 rpm or 1400 rpm at $25 \pm 2^\circ\text{C}$. The dispersion container was immersed in a temperature-controlled water bath on a programmable hotplate with external temperature probe (Canlab Co. New York, USA). The dispersion was stirred at a constant speed of either 800 rpm or 1400 rpm for 30 min, and the temperature was slowly increased up to $58 \pm 2^\circ\text{C}$. The dispersion was stabilized and concentrated by continuous open-top magnetic stirring at a temperature of $58 \pm 2^\circ\text{C}$ for about 90 min. These microcapsules were washed with deionized water and freeze dried at $-60 \pm 5^\circ\text{C}$ and 6.5 mPa for characterization. In addition, to examine the effects of oil encapsulation, a control sample was prepared where no oil was added in the synthesis procedure, producing solid ethyl acetate particles.

2.3. Microcapsules characterization

Multisizer 3 particle size analyzer (Coulter Counter, FL, USA), equipped with a $280\ \mu\text{m}$ aperture tube, was used to determine the average particle size and size distribution of microcapsules. Microcapsules (0.05 g) were dispersed into 250 ml deionized water using a stirring bar for about 10 min before particle size measurement.

The morphology and shape of microcapsules were evaluated using a Leica DMLA optical microscope (Leica Microsystems, Germany). The surface and morphology of microcapsules were also evaluated using a scanning electron microscope (HITACHI S-2500, Japan). The vacuum freeze-dried microcapsules [26] were mounted on a conductive stage and sputter coated with a thin layer ($\sim 10\ \text{nm}$) of gold for 90 s under Ar atmosphere and SEM micrographs were recorded in the secondary electron mode at 10 kV.

2.4. Mechanical properties

Various wt% of oil-filled microcapsules were added to the latex suspension and magnetically stirred for 30 min. The suspension was then applied on the degreased glass plate using a standard coating rod with a wet film thickness of $200 \pm 10\ \mu\text{m}$. The latex samples were then dried at $50 \pm 5^\circ\text{C}$ for about 30 min.

Tensile properties of free-standing latex films containing various levels of RO:EC microcapsules were evaluated according to ASTM D 638 standard. Rectangular tensile specimens ($0.15\ \text{mm} \times 15\ \text{mm}$) were prepared by cutting the latex film to shape. The experiments were carried out on a Universal computerized system for material testing machine (Sintech 1).

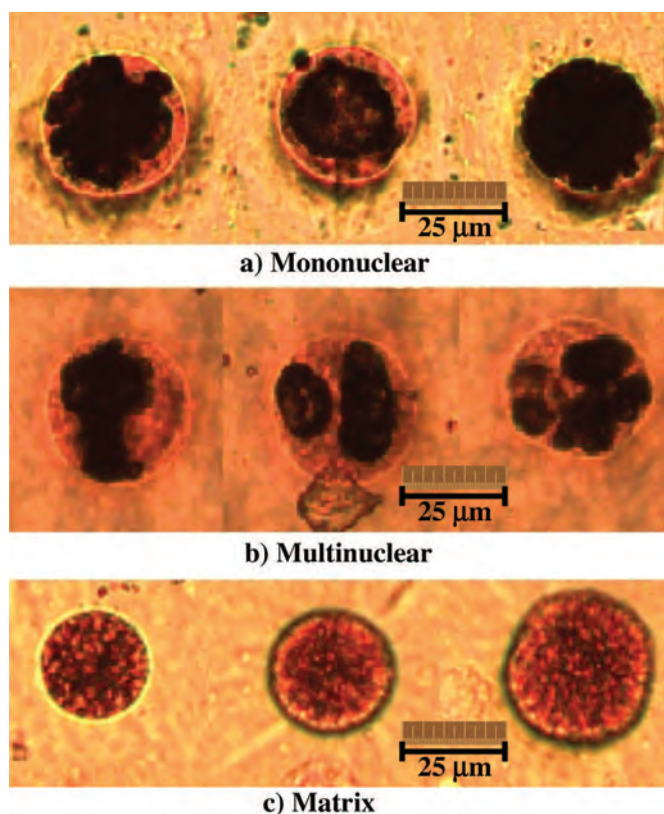


Fig. 4. Optical micrographs of latex film containing microcapsules with different morphologies.

The crosshead moved with a constant speed of $50\ \text{mm min}^{-1}$ at $23 \pm 2^\circ\text{C}$. At least seven individual replicates were tested for each formulation.

2.5. Color measurements

To visualize the oil released during the mechanical testing of latex films, after being subjected to different elongation percentages (0, 25, 50, 100 and 150%), color measurements were performed according to ASTM D 65 standard using a X-Rite 530 spectrodensitometer. Total color change, ΔE , as a function of pre-elongation %

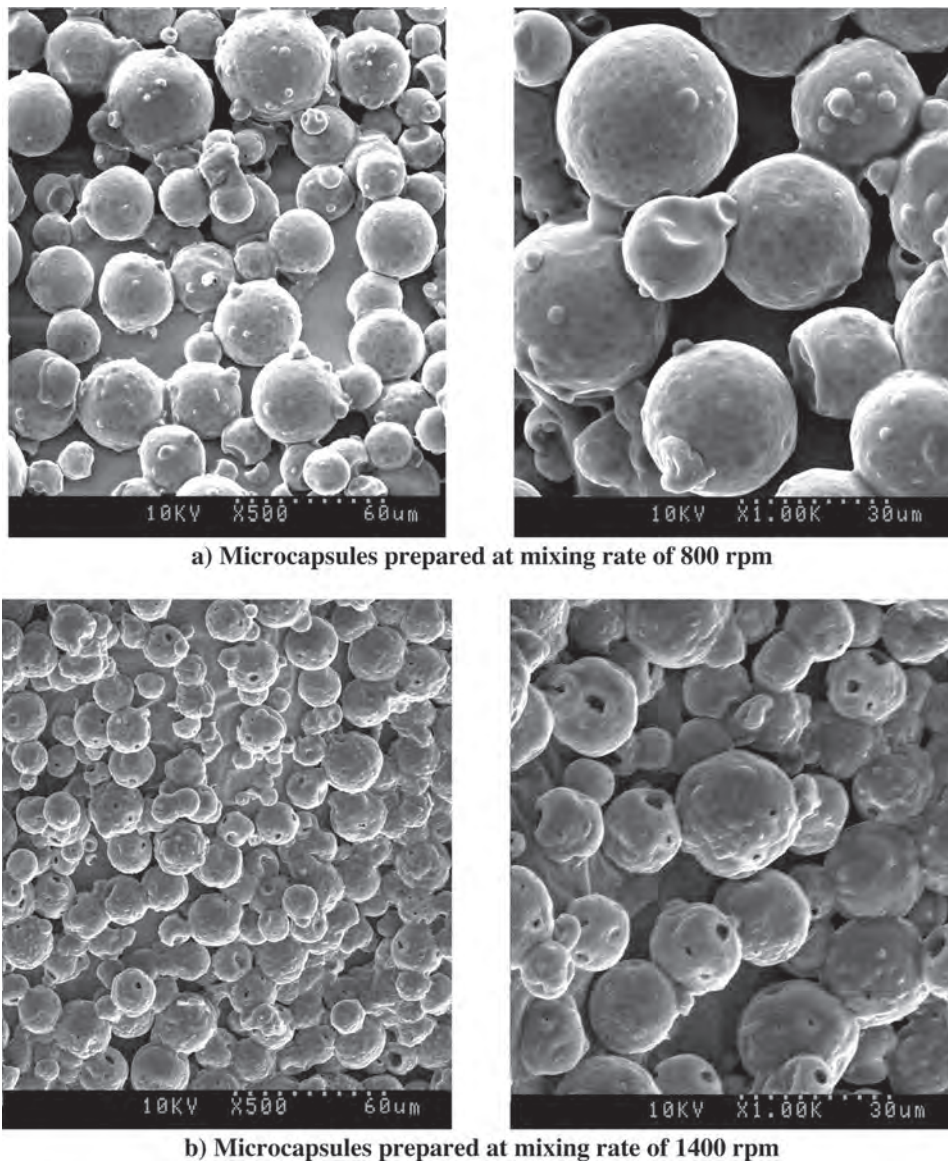
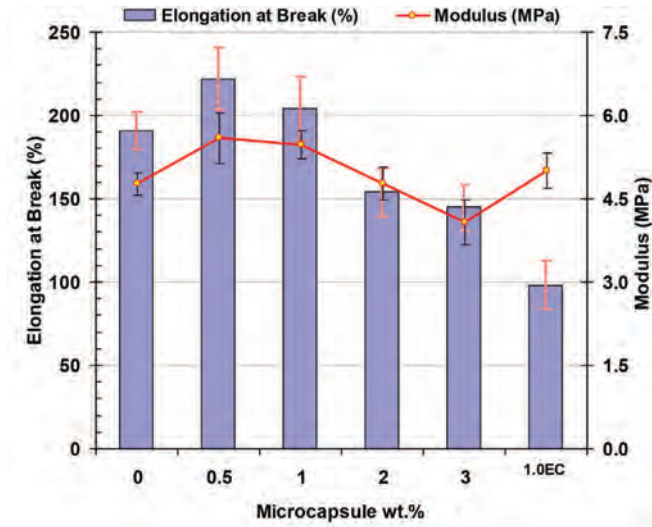


Fig. 5. Scanning electron micrographs of RO:EC microcapsules synthesized at mixing rate of (a) 800 and (b) 1400 rpm.

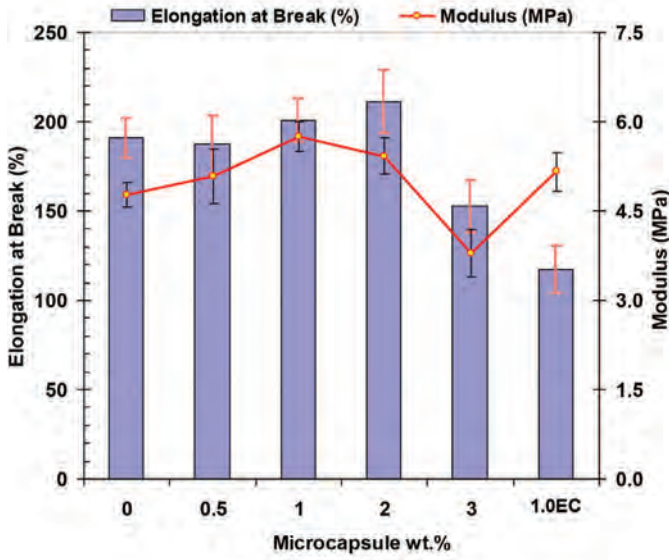
Table 1
Summarized mechanical properties of latex films containing oil-filled microcapsules.

Sample coding ^a	Elongation at break (%) ±14	Young modulus (MPa) ±0.25	Yield stress (MPa) ±0.15	Yield strain (MPa) ±0.17	Toughness (MPa) ±0.23
NLa	191	4.77	0.74	2.70	3.84
0.5R-800	222	5.59	1.40	3.03	4.36
1.0R-800	204	5.47	2.19	4.38	5.85
2.0R-800	154	4.75	1.15	2.00	2.68
3.0R-800	145	4.08	0.87	1.49	1.55
1.0EC-800	98	5.00	2.35	3.80	3.15
0.5R-1400	187	5.08	1.82	3.28	4.18
1.0R-1400	201	5.74	2.05	3.38	4.65
2.0R-1400	211	5.42	2.23	3.08	3.10
3.0R-1400	153	3.79	1.80	2.60	2.61
1.0EC-1400	117	5.16	2.40	3.85	3.05

^a NLa, R and EC in sample coding stand for Neat latex film, RO:EC microcapsules, non-oil filled microcapsules, respectively. The first digit symbol represents the wt% of each type of microcapsule embedded in latex film and the second digit corresponds to mixing speed of either 800 or 1400 rpm. 1.0EC-800 and 1.0EC-1400 show latex films containing 1 wt% oil free microcapsules prepared at mixing speed of 800 and 1400 rpm, respectively.



a)



b)

Fig. 6. Tensile properties of latex films containing various wt% of RO filled microcapsules prepared at mixing speed of: (a) 800 and (b) 1400 rpm.

was calculated from CIE (Commission Internationale de l'éclairage) ($L^*a^*b^*$) 1976 [28]:

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

here L^* is on the black–white ($L^*=0$ for black, $L^*=100$ for white) axis, a^* is on the red–green (positive values are red, negative values are green) axis, and b^* is on the yellow–blue (positive values are yellow, negative values are blue) axis.

3. Results and discussion

3.1. Microcapsules characterization

It has been reported that functionality, mechanical properties and appearance of microcapsules are affected by their size [29–31]. Also, in the case of self-healing coatings, the amount of healing

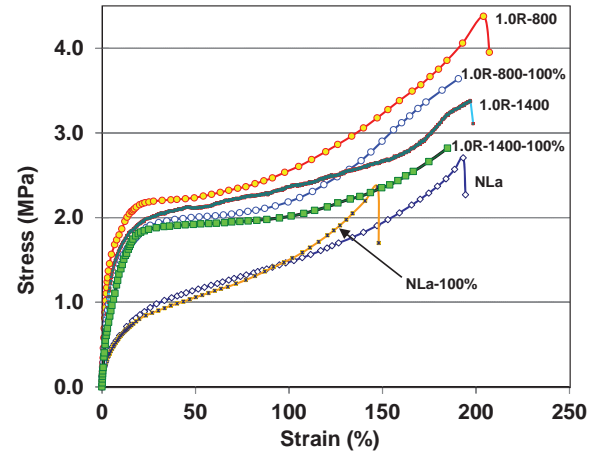


Fig. 7. Stress–strain plots for latex films containing 1 wt% of RO microcapsules prepared at 800 and 1400 rpm mixing speeds, before and after 100% pre-elongation.

agent available for delivery to the crack area depends on the microcapsule size [31].

The particle size distribution plots of the RO microcapsules and the volumetric average (d_m) and the coefficient of variation of particle size (CV) are shown in Fig. 2. With increasing mixing rate from 800 rpm to 1400 rpm, the average diameter of microcapsules decreased from $34.0 \mu\text{m}$ to $18.8 \mu\text{m}$ while the coefficient of variation (CV) of particle size remained almost constant at about 8.1–8.5%. These results reveal that the average diameter of microcapsule can be controlled by varying mixing speed.

Shell wall integrity, aggregation phenomena, and microcapsule shape and size were also evaluated by optical microscopy and scanning electron microscopy (SEM). The optical micrographs of microcapsules prepared at mixing speed of 800 rpm and 1400 rpm are shown in Fig. 3. The prepared microcapsules were poly-dispersed spherical particles ranging in size from about 5 to $50 \mu\text{m}$ without any inter-capsule bonding. No free oil was visible in these micrographs, suggesting that oil was well encapsulated in the shell material [1,26].

Fig. 4 shows optical micrographs of latex films representing the range of morphologies of prepared microcapsules observed in this study. The morphology of microcapsules mainly depends on the core material and the deposition process of the shell. Based on their morphology, microcapsules may be classified as mononuclear (or core-shell), multinuclear and matrix [32]. In mononuclear microcapsules core material is surrounded by a continuous shell. Multinuclear microcapsules on the other hand contain a number of small droplets of core material embedded within a single shell. Finally, in matrix microcapsules, the core material is distributed uniformly in the shell material. It is expected that a more efficient self-healing property of microcapsules within the coating film can be achieved by mononuclear morphology.

SEM micrographs of the freeze-dried microcapsules are shown in Fig. 5. With increasing mixing speed, shell structure became more porous and the number of “holes” appeared on the surface of microcapsules increased. The porous surface structure of microcapsules is expected to affect the self-healing properties of the latex films. Microcapsules with higher porosity and surface holes, could release the oil under a relatively lower level of mechanical stress. However, to avoid premature oil release, it is necessary that oil-filled microcapsules withstand mechanical stresses occurred during the processing of latex films. On the other hand, for non-porous microcapsules, breakage of the

Table 2

P-value results obtained from *t*-test statistical evaluation for mechanical properties of latex films containing various amounts of microcapsules.

A) Microcapsules synthesized at mixing speed of 800 rpm

-	NLa	0.5R-800	1.0R-800	2.0R-800	3.0R-800	1.0EC-800
NLa	-	0.004	0.15	0.001	3.7×10^{-5}	2.6×10^{-8}
0.5R	0.003	-	0.10	8.3×10^{-6}	3.0×10^{-6}	1.7×10^{-8}
1.0R	0.14	0.38	-	0.001	6.3×10^{-8}	1.5×10^{-8}
2.0R	0.46	0.006	0.005	-	0.41	1.1×10^{-8}
3.0R	0.02	3.7×10^{-4}	2.3×10^{-4}	0.03	-	2.7×10^{-8}
1.0EC	0.22	0.02	0.03	0.34	0.008	-

B) Microcapsules synthesized at mixing speed of 1400 rpm

-	NLa	0.5R-1400	1.0R-1400	2.0R-1400	3.0R-1400	1.0EC-1400
NLa	-	0.62	0.14	0.03	0.001	1.0×10^{-7}
0.5R	0.06	-	0.10	0.02	0.001	1.8×10^{-6}
1.0R	0.01	0.07	-	0.22	2.5×10^{-5}	3.4×10^{-8}
2.0R	0.01	0.11	0.57	-	2.3×10^{-5}	1.7×10^{-7}
3.0R	0.13	0.02	0.003	0.004	-	0.001
1.0EC	0.05	0.47	0.23	0.44	0.01	-

*: Elongation at break point (horizontal), Young's modulus (vertical)

microcapsule is the initiating event for oil release and the repairing process. Therefore, it is essential to synthesize microcapsules with appropriate shell morphology, wall thickness and mechanical properties [33].

3.2. Mechanical properties

Summary of the mechanical properties of latex films samples are given in Table 1. The results plotted in Fig. 6 show that with the addition of microcapsules, yield stress and yield strain initially increased before decreasing again at high microcapsule contents. However, statistical analysis revealed no significant difference between the mechanical properties of the samples up to 2 wt% microcapsule addition levels (Table 2).

Stress-strain curves for latex films containing 1 wt% RO microcapsules with and without pre-elongation are plotted in Fig. 7. These samples exhibited a three-part stress-strain plot: an elastic region, a plastic region, and a strain-hardening region. Compared to the neat latex films (NLa), the addition of oil-containing microcapsules resulted in a more extended plastic region. Furthermore, the latex films containing microcapsules prepared at 800 rpm exhibited a better mechanical properties compared to those containing microcapsules prepared at 1400 rpm. Modulus, toughness and elongation at break of microcapsule containing samples after 100% and 150% pre-elongation are plotted in Fig. 8. As expected, increased levels of pre-elongation generally deteriorated the mechanical properties of samples. However, this effect was less pronounced for the latex films containing RO microcapsules.

In particular, microcapsules prepared at 800 rpm better restored the mechanical properties of latex films after pre-elongation. The dependency of mechanical properties on the microcapsule size has been reported for polyurethane composite [34,35], where smaller particles had less of an effect on the tensile properties of the composite film [34].

To better examine the oil release within the latex films during the elongation process, optical micrograph images were taken at various elongation levels of latex films. As discussed before, in order to better visualize the oil release in these experiments, a red dyestuff was added to the rapeseed oil. According to Fig. 9, as the specimen was elongated, the oil was released and spread in the surroundings polymeric matrix. After removing the tensile force, the specimen retracted to its initial dimensions but the released oil; as characterized by the spreading of darker regions in the image area, remained within the polymer matrix. Close examination of the samples showed that the oil release mainly occurred via oil penetration through the porous wall of microcapsules and without capsule rupture.

3.3. Colorimetric analysis

The oil release properties from microcapsules were characterized by evaluation of changes in the color coordinates of samples. The results of color measurements (Table 3) show that for all microcapsules embedded samples, a^* values (redness) increased significantly after pre-elongation up to about 50%, then followed

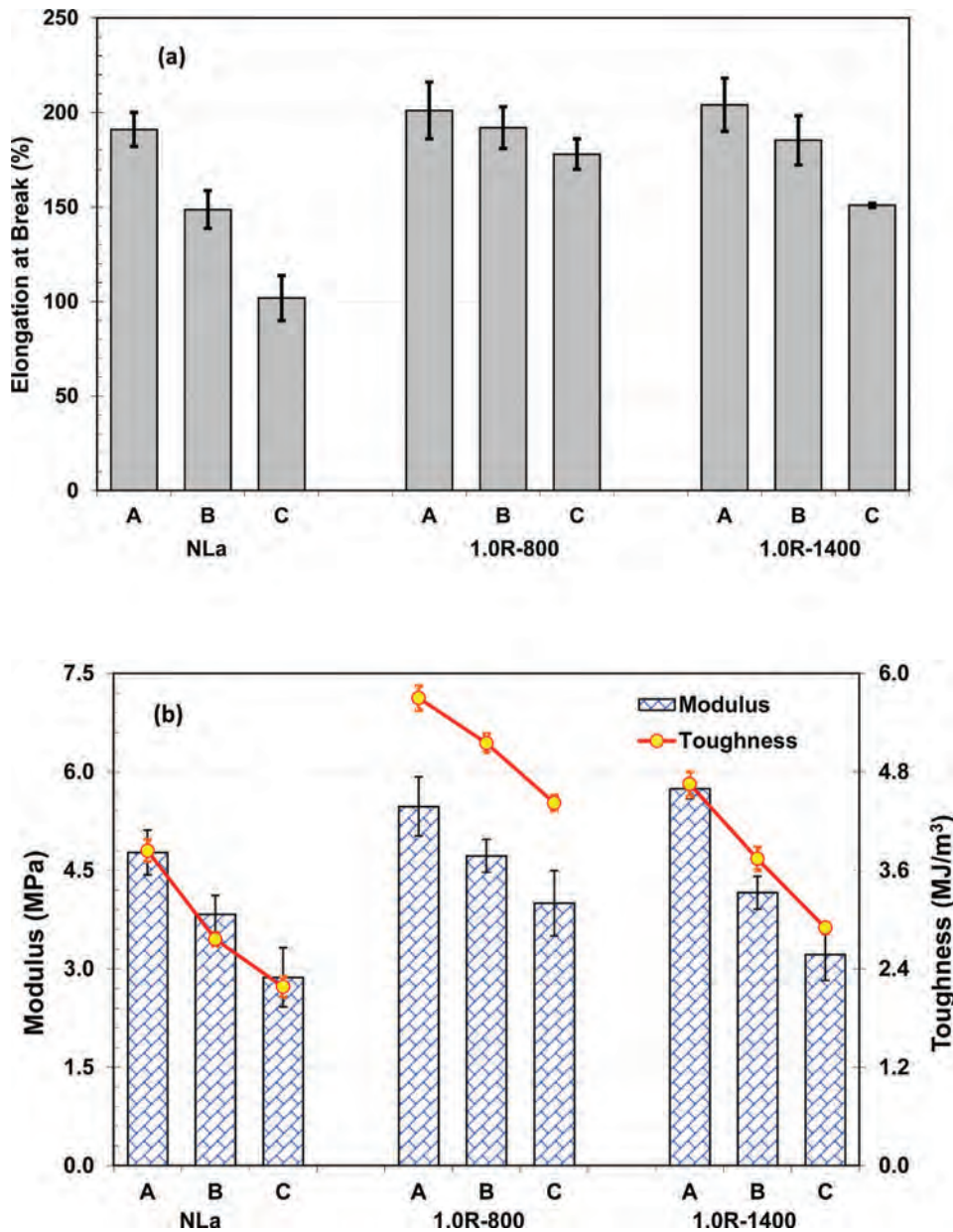


Fig. 8. Tensile strength test results for latex films containing 1 wt% EC:RO microcapsules (A) before elongation, (B) After 100% pre-elongation, (C) after 150% pre-elongation.

by a gradual increase at higher elongation %. Specimens containing 2 wt% of microcapsules prepared at mixing speed of 800 rpm had a higher increase in a^* value, due to more colored oil released from the bigger microcapsules within the polymeric matrix. The smallest Δa^* and the highest L^* value were observed for un-filled latex specimens. This is attributed to the fact that the latex film is colorless, transparent and has no particles. For all specimens, L^* values were decreased by addition of microcapsules. Specimens containing 2 wt% of capsules revealed higher reduction in L^* value, due to more light scattering by the particles. L^* values were decreased with increasing elongation %, resulting of microcapsules rupture, possible stress-whitening and better orientation of polymeric chains, therefore more lights are scattered through the latex film.

Fig. 10 shows that the total color change (ΔE) of various latex samples increased rapidly with increasing the pre-elongation from

25% to 50%. The color change, ΔE had a similar trend compared to redness, a^* , and increased after pre-elongation. Specimens containing 2 wt% of microcapsules prepared at mixing speed of 800 rpm had a higher increase in ΔE value. A higher value of ΔE is indicative of more oil being released within the sample. The specimens containing 2 wt% of larger capsules revealed maximum color changes ($\Delta E = 1.15$) after 150% pre-elongation, while the ΔE for the specimen containing 2 wt% of smaller capsules was 1.01. Unfilled coating revealed the lowest color change ($\Delta E = 0.323$) after 150% pre-elongation.

These color measurements confirm the release of oil was released among the polymeric network and the surrounding latex matrix with increasing the % elongation. The released oil could act as a healing agent and restore mechanical properties of the latex film by filling the micro-cracks generated during the tensile testing of the sample.

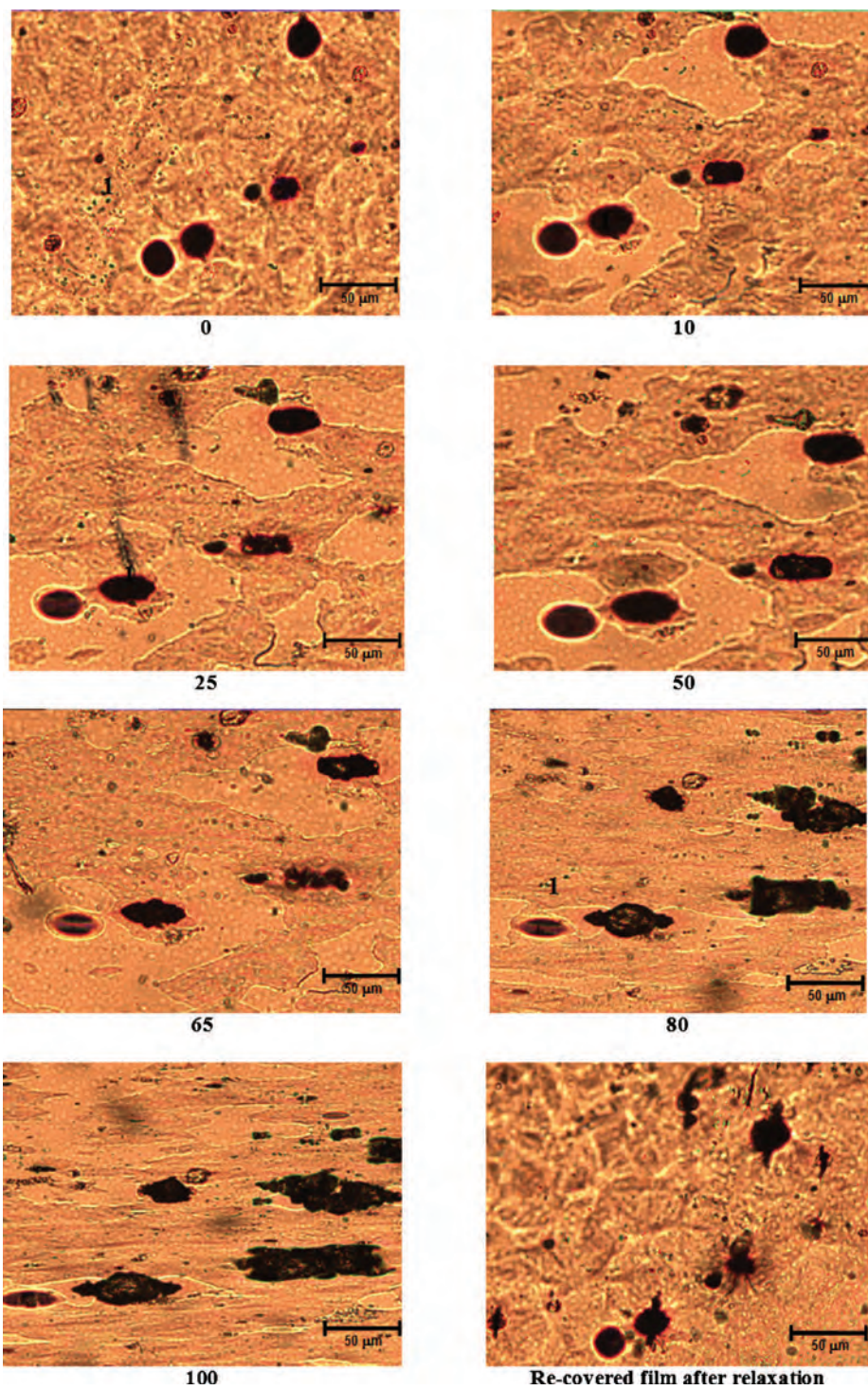


Fig. 9. Optical micrographs of latex films containing 1.0 wt% EC:RO microcapsules during various elongation percentages and after recovery.

Table 3
Color coordinates changes of specimens before and after various elongation percentages.

Sample coding	Pre-elongation (%)	Average color coordinates			Total color changes	
		L^*	a^*	b^*	ΔE	STD
NLa	0	90.13	-1.43	3.90	0	0
	25	90.05	-1.40	3.80	0.132	0.061
	50	90.04	-1.37	3.85	0.119	0.037
	100	89.98	-1.39	3.84	0.166	0.073
	150	89.85	-1.37	4.05	0.323	0.081
1.0EC-800	0	73.00	-1.15	2.10	0	0
	25	72.85	-1.18	2.04	0.166	0.012
	50	72.77	-1.17	1.98	0.262	0.07
	100	72.67	-1.20	2.13	0.330	0.065
	150	- ¹	-	-	-	-
1.0R-800	0	79.80	12.35	-0.70	0	0
	25	79.65	12.98	-0.72	0.643	0.1
	50	79.48	13.13	-0.68	0.842	0.052
	100	79.26	13.21	-0.67	1.016	0.034
	150	79.20	13.27	-0.472	1.121	0.1
2.0R-800	0	82.50	10.70	-0.09	0	0
	25	82.47	11.29	-0.13	0.595	0.116
	50	82.30	11.53	-0.17	0.854	0.112
	100	82.08	11.61	-0.12	1.027	0.149
	150	81.92	11.69	-0.13	1.149	0.121
1.0R-1400	0	72.79	25.80	-4.40	0	0
	25	72.71	26.26	-4.33	0.474	0.052
	50	72.60	26.45	-4.32	0.683	0.056
	100	72.51	26.54	-4.27	0.801	0.174
	150	72.35	26.59	-4.23	0.926	0.109
2.0R-1400	0	73.90	25.05	-4.10	0	0
	25	73.81	25.47	-4.09	0.433	0.075
	50	73.71	25.75	-4.06	0.726	0.106
	100	73.55	25.84	-4.13	0.860	0.169
	150	73.39	25.93	-4.11	1.013	0.133

¹ Specimens disrupted for the elongation greater than 100%.

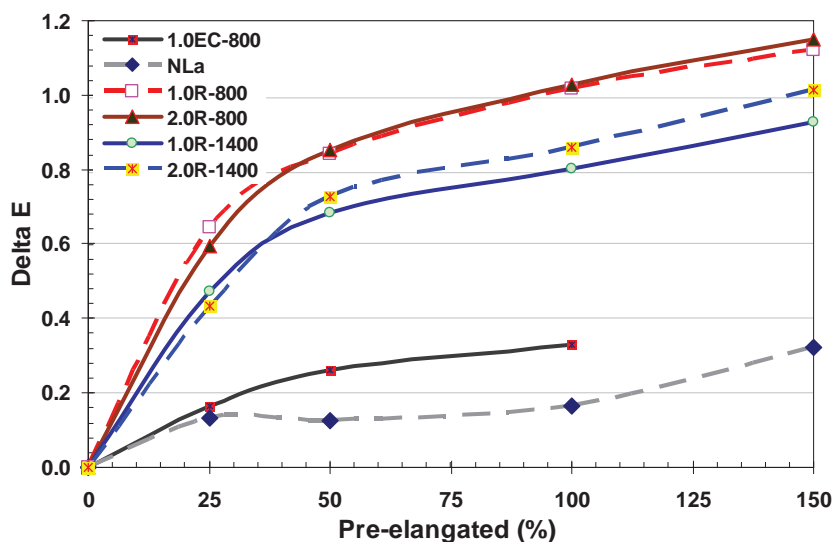


Fig. 10. The color difference, ΔE , versus the pre-elongation for latex films containing RO:EC microcapsules.

4. Conclusion

In this study, new self-plasticizing microcapsules with enhanced mechanical and healing properties of latex film were prepared by introducing a robust solvent evaporation method using ethyl cellulose as a shell-forming polymer containing rapeseed oil. These results suggest that the oil was released from the capsules under mechanical stress into the microcapsules surrounding through capillary force, and sliding of molecular chains on each

other, resulting in improved mechanical properties through plasticization of the latex films.

The results also reveal that latex films containing larger microcapsules, prepared at mixing rate of 800 rpm, showed slightly better tensile strength properties in second and third tensile measurements runs, compared with those counterparts having smaller microcapsule.

The improvement in the mechanical properties of latex film was due to the release of oil within the latex network that plasticized

the surrounding polymeric network thus restoring the integrity of the film.

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