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The role of dicumyl peroxide in the preparation of chloroprene rubber/starch/sodium acrylate water-swellable composites

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ABSTRACT

Water-swellable composites were prepared by blending sodium acrylate (NaAA), additives, and chloroprene rubber (CR)/starch masterbatch which was pre-formed by latex compounding method. The effects of the content of dicumyl peroxide (DCP) on the properties of the composites were investigated. We found that an increase in DCP amount led to a large increase in water swelling ratio and meanwhile a decrease in the mass loss ratio. Further, the composites were swollen uniformly in water and thus kept their original shapes well. The hardness and stresses at 100% and 300% increased with the increase in DCP amount. The addition of DCP facilitated the homopolymerization of NaAA while decreased the esterification reaction between NaAA and CR, which was verified by vulcanization curves, DSC and FT-IR. The morphology of the composites before and after water immersion was observed by optical transmission microscopy and indicated that the starch was homogenously dispersed in the composites.

1. Introduction

Water-swellable rubbers (WSRs) as a novel class of functional materials can stop water through elastic sealing and in particular swelling in water (Park & Kim, 2001; Sun, Zhang, Shi, Tang, & Wu, 2002; Zhang, Zhang, et al., 2004). Based on their unique characteristics, WSRs have found wide applications in sealing in civil building, underground engineering, flood protection, and water conservation. But it is not easy to prepare WSRs simultaneously showing good mechanical properties and high water-swelling capacity. Natural rubber, ethylene propylene diene terpolymer (EPDM) rubber, chloroprene rubber (CR) and other rubbers used as the matrix provide the elasticity of WSRs, and reinforcing fillers such as carbon black, silica, attapulgite and starch are used to improve the mechanical properties of rubbers (Liu, Ding, Zhou, & Chen, 2006; Park & Kim, 2001; Song, Qi, & Wu, 2010; Sun et al., 2002; Tang et al., 2006; Wang, Li, & Chen, 1999). We recently prepared several rubber/starch composites by co-coagulating starch paste and rubber latex which exhibited better mechanical properties than the corresponding composites prepared by direct blending (CN, 2003; Wu, Ji, Wang, & Zhang, 2004; Wu, Qi, Liang, & Zhang, 2006). In most WSRs, the water-swelling capacity is mainly achieved by incorporating water-absorbing components (Liu et al., 2006; Wu, Lin, Wei, & Lin, 2005; Wu, Wei, Lin, & Lin, 2003; Zhang, Li, & Wang, 2006), e.g., sodium polyacrylate, starch grafts, and cellulose grafts. Among these additives, sodium polyacrylate shows some advantages including high water swelling ratio and rate, stable structure, and low price. Further, it can be prepared in situ by the polymerization of acrylate salt initiated by dicumyl peroxide (DCP) at elevated temperatures in the rubber matrix (Ren, Peng, Zhang, & Zhang, 2005; Song et al., 2010). Accordingly, sodium acrylate (NaAA) was utilized in the present study, and the effects of DCP were investigated, as will be reported below.

The present study developed a novel type of water-swellable composites, consisting of CR, starch, NaAA, DCP and other additives. CR/starch masterbatch was prepared by latex compounding method (CN, 2003) to ensure the fine dispersion of starch. The effects of the content of DCP on the mechanical and water-absorbing properties of the composites were investigated in detail. It is proved that the addition of DCP facilitates the homopolymerization of NaAA and at the same time decreases the reaction between NaAA and CR, which is favorable in terms of increasing the water swelling ratio of the WSRs. Of particular interest is the finding that the mass loss ratio decreased with increasing water swelling ratio, which would help to prolong the life time of WSRs. In addition, the microscopic morphology of the composites before and after water immersion was observed by optical transmission microscopy (OTM). We believe that the results will open new possibilities for preparing novel high performance WSRs.

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Table 1
Formulations for CR/starch/NaAA composites (parts per hundred rubber, phr).

Ingredients	Loading
CR	100
Zinc oxide	5
Magnesium oxide	4
Stearic acid	1
Accelerator NA-22	0.5
Accelerator DM	0.5
Starch	20
NaAA	30
DCP	0/0.75/1.5/2.25

Table 2
Effects of DCP amount on vulcanizing characteristics of CR/starch/NaAA composites.

DCP amount/phr	0	0.75	1.5	2.25
MH/dNm	45.7	49.1	51.3	53.6
ML/dNm	5.6	4.9	4.8	4.5
t_{10}/min	2.6	2.6	2.7	2.4
t_{90}/min	32.4	30.8	28.8	27.4

2. Experimental

2.1. Materials

CR latex (3211) was obtained from Shan Xi Company, China. Corn starch (100% amylopectin, 12 wt% moisture content) was purchased from Changchun Dacheng Special Corn Modified Starch Development Co, Ltd., China. NaAA was prepared in our laboratory. All other ingredients including zinc oxide, magnesium oxide, stearic acid, DCP, 2-imidazolidine thione (accelerator NA-22), and dibenzothiazole disulfide (accelerator DM) were of chemical grade and commercially available.

2.2. Preparation of CR/starch masterbatch and CR/starch/NaAA composites

2.2.1. CR/starch masterbatch

1 wt% starch aqueous suspension was prepared by vigorously stirring a given content of starch at 95 °C in a water bath for 25 min until the suspension became transparent. Then, the starch paste was added in the CR latex and stirred vigorously for 20 min at room temperature. A 1.5 wt% $CaCl_2$ solution was used to coagulate the mixture. The coagulum was thoroughly washed with water and then dried in an oven at 60 °C for 72 h until the moisture content dropped below 2 wt%.

2.2.2. CR/starch/NaAA composites

The as-prepared coagulum was masticated on a two-roll mill for 3 min, and then the vulcanizing ingredients and other additives including NaAA, stearic acid, DCP, DM, NA-22, magnesium oxide and zinc oxide were added and mixed continuously until the mixture reached homogeneity. The compounds were obtained. The related formulations are shown in Table 1.

After the compounds prepared above were kept at room temperature for ca. 2 h, the vulcanization characteristics were measured in an oscillating disc rheometer operating at 153 °C to evaluate the optimum cure time (t_{90}). After being kept at room temperature for about 12 h, the compounds were cured for t_{90} at 153 °C and 15 MPa in a plate press machine, providing the composites.

2.3. Tests

2.3.1. Mechanical tests

Tensile strength and hardness were measured according to Chinese standards GB/T 528-1998 and GB/T 531-1999, respectively. The mechanical tests were conducted on samples both before and after water immersion, in which the samples were dipped in deionized water at 70 °C for 22 h. Five samples for each composite were tested, and the median value was regarded as the final value.

2.3.2. Water swelling ratio and mass loss ratio tests

The composites were cut into square pieces 20 × 20 × 2 (in mm), and each piece was weighed and then immersed in 300 mL deionized water at 70 ± 2 °C. After 334 h, the samples were taken out and mildly mopped with tissue paper to remove the excess water on the surface. The weights of swollen samples were recorded. Then the samples were dried in an oven at 60 °C to constant weight. Water swelling ratios by mass (Δm) and by volume (ΔV), and mass loss ratio (Lm) were all the average values of three samples and were calculated by the following equations:

$$\Delta m = \frac{m_3 - m_1}{m_1} \times 100\%, \qquad \Delta v = \frac{(m_3 - m_4) - (m_1 - m_2)}{m_1 - m_2} \times 100\%,$$

$$Lm = \frac{m_1 - m_5}{m_1} \times 100\%$$

where m_1 and m_3 are the weights of the sample in air before and after water immersion, respectively; m_2 and m_4 the weights of the sample in water before and after water immersion, respectively; and m_5 the weight of the dried swollen sample. The density of water is taken as 1.0 g/cm^3.

2.4. Characterization

2.4.1. DSC analysis

Pure CR, CR/30 phr NaAA, CR/20 phr starch/30 phr NaAA and CR/20 phr starch/30 phr NaAA/0.75 phr DCP were tested with DSC (DSC1, Mettler Toledo, Switzerland). The temperature scanning is from 30 to 300 °C at 10 °C/min.

2.4.2. FT-IR spectroscopy

FT-IR spectra of the CR/30 phr NaAA before and after heat pressing at 153 °C for t_{90} and 15 MPa in a plate press machine were recorded on a FT-IR spectrometer (Tensor 27, Bruker Optik Gmbh, Germany). The measurement mode is attenuated total reflectance.

2.4.3. Optical transmission microscope

The microscopic structure of the composites before and after water immersion was observed with an optical transmission microscope (OTM, BP201, Chongqing Optical Instrument Factory, China). The samples were prepared as follows: First, the compounds were re-milled six times on a two-roll mill. Then about 0.2 g of a compound was sandwiched between two smooth flat plates and cured in a plate press machine at 153 °C and 15 MPa for t_{90}. Nearly transparent film samples with a thickness of about 0.02 mm were obtained. Finally, the as-prepared films before and after water immersion were stained for about 10 min by a 2% tincture of iodine. The stained films were observed at a magnification of 400 times. The immersion time of the specimens in de-ionized water was approx. 1 h.

3. Results and discussion

3.1. Effects of DCP amount on vulcanizing characteristics

The effects of DCP amount on the vulcanizing characteristics of the compounds are shown in Table 2 and Fig. 1. From Table 2 and Fig. 1, it is found that with an increase in the content of DCP, the maximum torque value (MH) increases, while t_{90} decreases gradually. It is thus indicated that an increase of crosslinking density

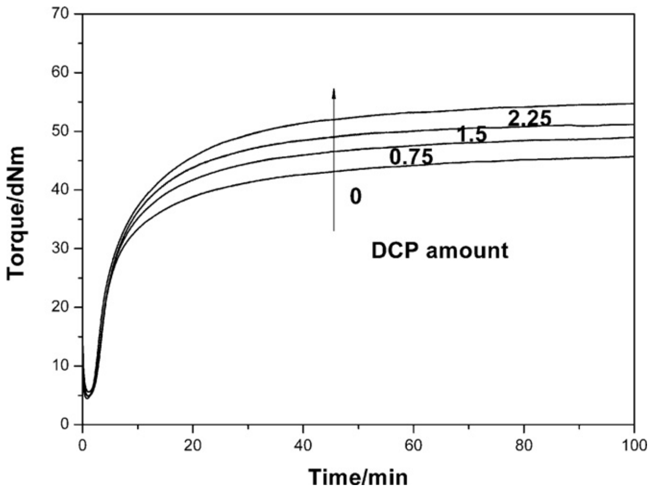

Fig. 1. Vulcanization curves of compounds with varied DCP amounts at 153 °C.

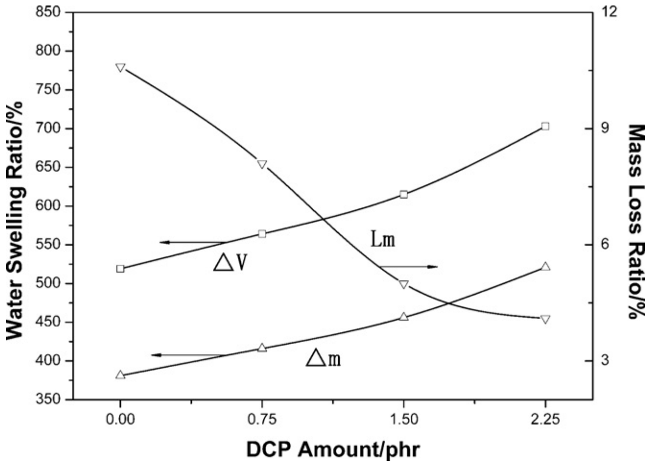

Fig. 2. Plots of water swelling ratios by mass (Δm) and by volume (ΔV) and mass loss ratio (Lm) versus DCP amount.

occurred in the CR/starch/NaAA composite, caused by DCP serving as a co-curing agent.

3.2. *Effects of DCP amount on the mechanical properties*

Table 3 shows the effects of DCP amount on the mechanical properties of the composites before and after water immersion. As can be seen from Table 3, the tensile strength and elongation at break of the composite without DCP before water immersion showed the highest values of 9.1 MPa and 670%, respectively; the hardness was the lowest, 64. An increase in DCP amount from 0 to 2.25 phr resulted in a gradual decrease in the tensile strength and elongation at break. It also caused a gradual increase in the stress at 100% and 300% and Shore A hardness. All these observations can be explained by the increase in crosslinking density of the composites which resulted from the addition of DCP, as mentioned above (Fig. 1).

The mechanical properties of the composites after water immersion changed in a similar way to those before water immersion. However, the composites lost some mechanical properties after immersion in water. This observation can be attributed to the absorbed water which acted as a plasticizer (Song et al., 2010).

3.3. *Effects of DCP amount on water swelling ratio and mass loss ratio*

The effects of DCP amount on the water swelling ratio and the mass loss ratio of CR/starch/NaAA composites are presented in Fig. 2. From Fig. 2, both Δm and ΔV increase gradually with an increase in DCP amount. When the DCP amount is 2.25 phr, Δm and ΔV reach the maximum, 521% and 703%, respectively. In theory, if DCP increases the crosslinking density only, the water swelling ratio should decrease with increasing DCP amount. Moreover, Fig. 2 shows that mass loss ratio decreased from 10.6% to 4.1% with increasing DCP amount from 0 to 2.25 phr. This is an interesting result, considering that the mass loss ratio generally increases with the increase of water swelling ratios (Ismail & Gamal, 2010; Liu et al., 2006; Zhang, He, Zou, & He, 2004). These unexpected observations can be understood by the fact that DCP could initiate the polymerization of acrylic acid salt (Ren et al., 2005). The higher the DCP amount, the higher the amount of the main water-absorbing component sodium polyacrylate formed. Since the composites contained up to 30 phr NaAA, the increased DCP amount should lead to a stronger network of sodium polyacrylate, which caused an improved water swelling ratio and a decreased mass loss ratio.

In Fig. 2, it should be mentioned that ΔV reaches 519% for the composite without DCP. In our investigated system, the main water-absorbing component is sodium polyacrylate, and NaAA could not polymerize into sodium polyacrylate without DCP. We thus assume that certain reactions occurred between CR and NaAA in the absence of DCP, which contributed to the high ΔV. More discussion will be made later.

3.4. *Effects of DCP on the reaction among CR, NaAA and starch*

To explore the possible reaction among CR, NaAA and starch and the role of DCP, we prepared the following four samples: (a) pure CR (S1), (b) CR/30 phr NaAA (S2), (c) CR/20 phr starch/30 phr NaAA (S3), and (d) CR/20 phr starch/30 phr NaAA/0.75 phr DCP (S4). Then we measured the vulcanizing behavior and thermal transitions of these samples. Pure CR as the reference was included in the investigation.

Table 3
Effects of DCP amount on mechanical properties of CR/starch/NaAA composites before and after water immersion.

DCP amount/phr		0	0.75	1.5	2.25
Before immersion	Tensile strength/MPa	9.1	7.4	6.0	4.7
	Stress at 100%/MPa	2.1	2.2	2.3	2.6
	Stress at 300%/MPa	3.8	3.9	4.0	4.4
	Elongation at break/%	670	571	487	335
	Shore A hardness	64	65	67	68
After immersion	Tensile strength/MPa	3.8	3.1	2.5	1.7
	Stress at 100%/MPa	0.8	0.9	1.0	1.1
	Stress at 300%/MPa	1.9	2.4	–	–
	Elongation at break/%	406	329	265	192
	Shore A hardness	30	31	34	35

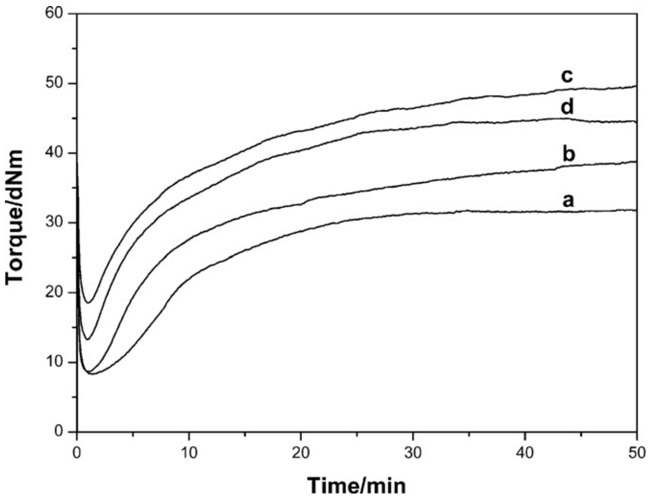

Fig. 3. Vulcanization curves of four samples at 153 °C: (a) pure CR (S1); (b) CR/30 phr NaAA (S2); (c) CR/20 phr starch/30 phr NaAA (S3); (d) CR/20 phr starch/30 phr NaAA/0.75 phr DCP (S4).

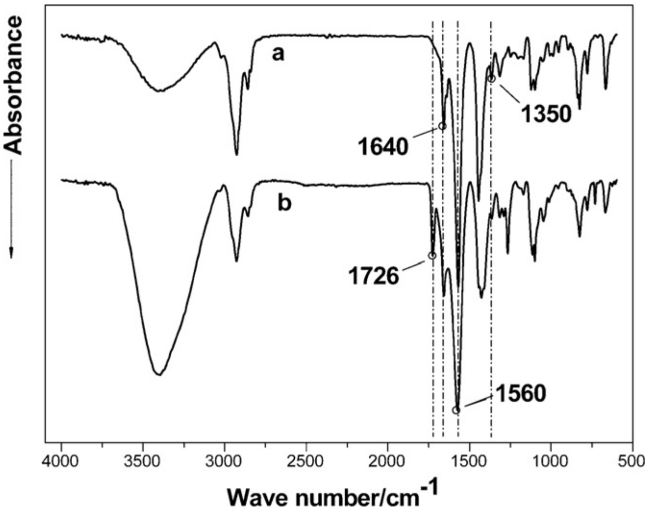

Fig. 5. FT-IR spectra of (a) CR/30 phr NaAA before heat processing and (b) CR/30 phr NaAA after heat processing at 153 °C.

The vulcanization curves of the four samples are shown in Fig. 3. S1 is found to undergo curing, because this kind of chloroprene rubber latex (CR, 3211) contains a small amount of vulcanizing agent (Liu, 1980). The torque of S2 is higher than that of S1, most likely due to the reaction between NaAA and CR. The maximum torque of S3 is higher than that of S2. The reason for this result is that starch can act as reinforcing filler for rubber; in addition, reactions occurred between CR and starch (Song et al., 2010). Nevertheless, the torque of S4 is lower than that of S3, indicating that the addition of DCP facilitated the homopolymerization of NaAA while inhibited the reaction between NaAA and CR. In order to verify this assumption, we conduct the DSC measurement, as discussed below.

The DSC curves of the four samples are displayed in Fig. 4. A common endothermic peak is observed around 160 °C. For S1, the exothermic peak at about 160 °C demonstrates the crosslinking reaction observed in Fig. 3 (curve a). The heat capacity of S2 increased due to the reaction between CR and NaAA. The exothermic peak of S3 increased relative to S2, which is derived from the reaction between CR and starch (Song et al., 2010). However, the heat capacity of S4 (18.12 J/g) is lower than that of S3 (18.96 J/g) because of the addition of DCP, again indicating that DCP initiates the homopolymerization of NaAA, and hinders the reaction between NaAA and CR. This analysis is consistent with the observations in Fig. 3.

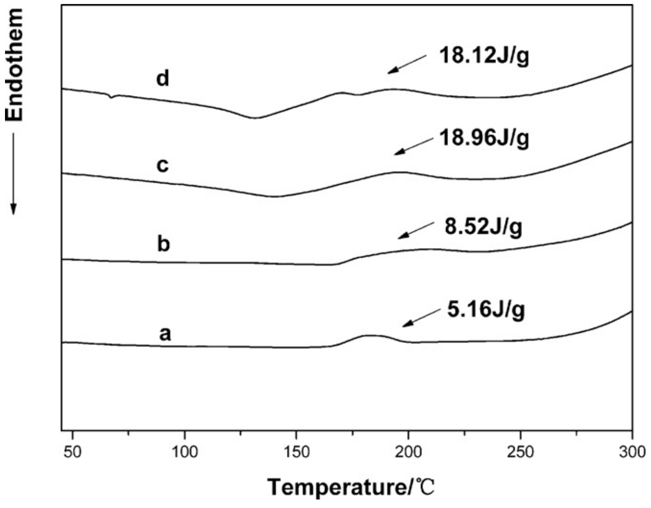

Fig. 4. DSC curves of four samples: (a) pure CR (S1), (b) CR/30 phr NaAA (S2), (c) CR/20 phr starch/30 phr NaAA (S3), and (d) CR/20 phr starch/30 phr NaAA/0.75 phr DCP (S4).

To further investigate the reaction between CR and NaAA, FT-IR spectra of CR/30 phr NaAA before and after heat pressing at 153 °C for t_{90} were measured, as illustrated in Fig. 5: (a) CR/30 phr NaAA before heat pressing and (b) CR/30 phr NaAA after heat pressing. By comparing the curves a and b, a new strong absorption peak (1726 cm^{-1}) appears in curve b. This peak can be attributed to the ester carboxyl group connected to a C=C double bond, demonstrating ester groups (Ruckenstein & Chen, 2000) formed between carboxylic acids and chloromethyl groups of CR. In addition, the absorption peaks (1560 and 1350 cm^{-1}), which are asymmetric stretching vibration and symmetric stretching vibration of carboxylic acid ion (–COO–), of curve b are weaker than the corresponding absorption peaks of curve a, indicating a decreased amount of NaAA resulting from the reaction between NaAA and CR.

3.5. Morphology

The surface morphology of CR/starch/NaAA composites after water immersion is shown in Fig. 6. It is found in this figure that the surface morphology of the composites remained flat and regular even after they absorbed a lot of water, revealing that the composites were swollen uniformly in water and further the water-absorbing component and starch were well dispersed inside the composites.

Fig. 7 shows the OTM micrographs of the composites with varied DCP amounts before and after water immersion. The dark-colored parts in the micrographs indicate the starch particles. The starch seems to be dispersed homogeneously in the composites. It should be noted that the starch particle size is smaller via the latex compounding technique than via the melt blending process (Song et al., 2010), which is very important to keep its shape after absorbing water. After the CR/starch/NaAA composites absorbed water, their thickness increased and the color became darker due to easily staining. After water immersion, the image of the composite with 2.25 phr DCP seems to be obscure when compared to that of the composite without DCP because the former absorbed more water than the latter.

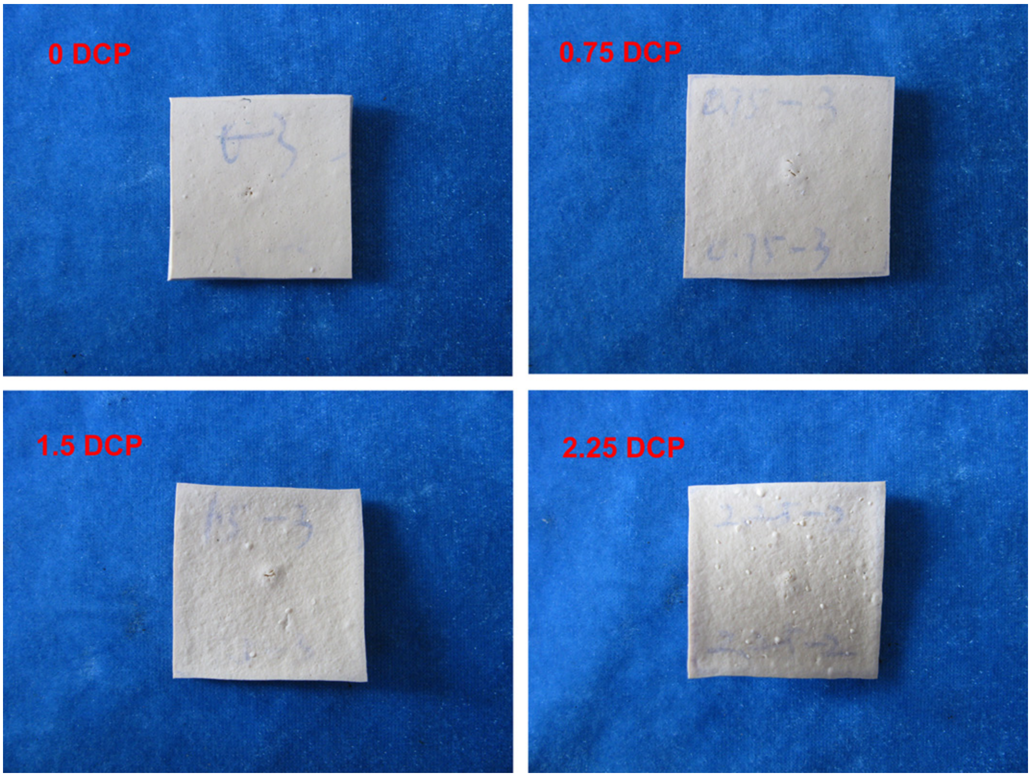

Fig. 6. Surface morphology of CR/starch/NaAA composites with varied DCP amounts as taken by a digital camera.

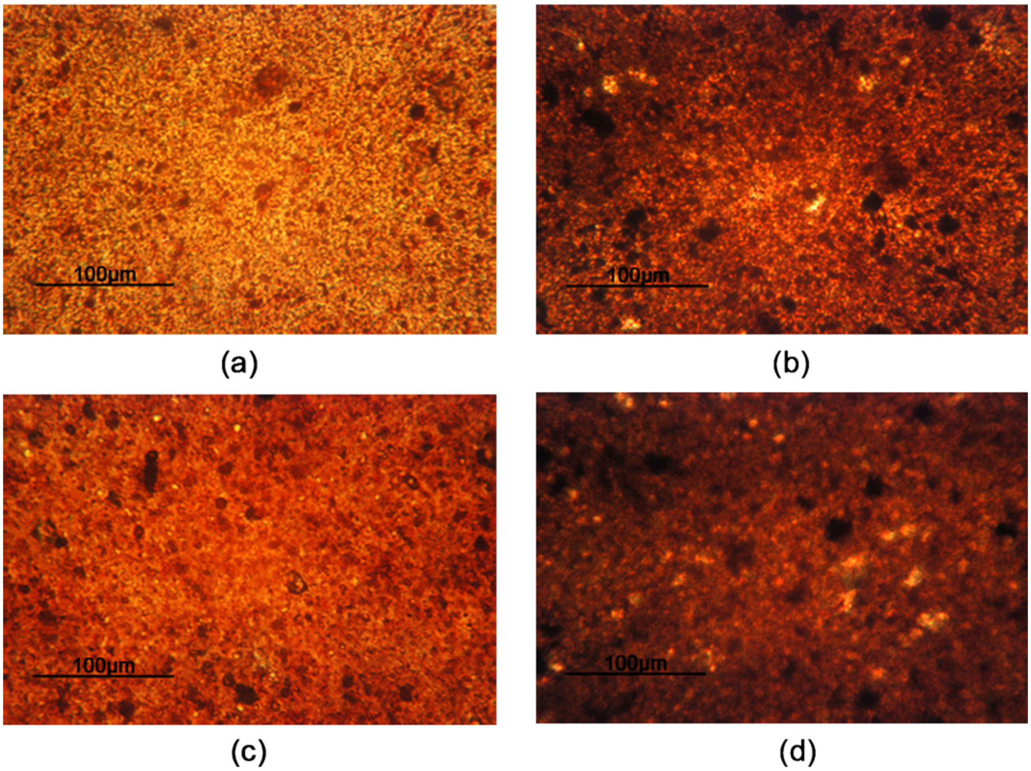

Fig. 7. OTM micrographs of CR/starch/NaAA composites with varied DCP amounts before and after water immersion: (a) and (b) 0 phr DCP, and (c) and (d) 2.25 phr DCP. (a) and (c) are before immersion, and (b) and (d) are after immersion.

4. Conclusions

In the present WSRs, an increase in DCP amount led to a large increase in water swelling ratio and meanwhile a decrease in the mass loss ratio, which may help to prolong the life time of the WSRs. Further the composites were uniformly swollen in water and kept their original shapes well. The hardness and stresses at 100% and 300% also increased with the increase in DCP amount.

The addition of DCP facilitated the homopolymerization of NaAA while decreased the reaction between NaAA and CR. The starch was homogenously dispersed in the composites via the latex compounding technique, which will facilitate the applications of starch in the WSRs.

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