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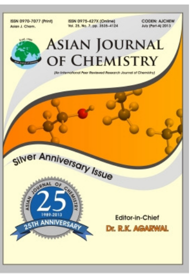

Study on Properties of Natural Rubber Compound Using Starch as Filler†

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Natural rubber (NR) compounds were produced using an eco-friendly material, starch (St), as a filler. Natural rubber and starch (at different concentrations) were mixed with a coupling agent, resorcinol-formaldehyde. The natural rubber/starch mixture was coagulated in a $CaCl_2$ solution using methanol and dried in a dry oven. The starch that dispersed in the natural rubber latex was measured by particle size analysis and field emission scanning electron microscopy. After co-coagulation and drying, the curing agent, vulcanization-accelerator and antioxidant were added to the mixture. The rubber was then vulcanized at the optimal temperature and time. The effect of the starch concentration on the curing characteristics and mechanical properties of the natural rubber/resorcinol-formaldehyde/starch compounds was investigated.

Key Words: Natural rubber, Starch, Resorcinol-formaldehyde, Vulcanization.

INTRODUCTION

Technology innovation is very important in the rubber industry due to the rapid development of new materials and the strengthened international environmental regulations. The recent trends of technology innovation in the rubber industries can be summarized as follows: (1) the development of a novel elastomer with novel functional, high performance and superior durable properties; and (2) the development of novel "green" elastomer. A "green" elastomer not only reduces energy consumption, but is also very friendly to the environment due to the renewable and biodegradable properties. Therefore, the preparation of an environmental friendly elastomer has attracted considerable attention worldwide. With the surge in oil price, the cost of petroleum products, such as carbon black, has increased significantly. Starch is a natural resource that can be derived from plant sources. Therefore, the application of renewable starch in elastomer compounds instead of carbon black can reduce the consumption of non-renewable petroleum. In addition, starch is abundant on earth and is inexpensive. Therefore, the use of starch as a reinforcing filler in elastomer compounds is a promising way of producing "green" elastomers.

Based on the molecular structure, starch can be divided into (a) amylose and (b) amylopectin. Amylose is a linear structure and amylopectin is a branched structure with a higher molecular weight. The weight ratio of amylose and amylopectin is different, which is dependent on the original resource. For example, the amylose content in corn starch and rice starch is approximately 25 % and 23 %, respectively. Starch consists of a larger number of glucose units and possesses many hydroxyl groups in the backbone. Therefore, the interfacial interaction between the hydrophilic starch and hydrophobic rubber matrix is quite poor. The surface modification of starch is needed to enhance the interfacial interaction with rubber. Surface grafting of vinyl monomers, such as methyl methylacrylate, butyl acrylate or styrene, is an effective way of modifying the surface properties of starch[1-5]. The surface grafting of poly (butyl acrylate) onto starch backbones was reported to improve the compatibility between natural rubber and starch[6]. Another way of improving the interaction is to use a coupling agent. The addition of a coupling agent, such as N-b(aminoethyl)-g-aminopropyl trimethoxy silane[7] and resorcinol-formaldehyde[8], improved the starch/styrene butadiene rubber interfacial interaction.

In the present study, starch was used as a reinforcing filler in natural rubber compounds. The coupling agent, resorcinol-formaldehyde (RF), was used to improve the interfacial interaction between starch and natural rubber. The concentration of resorcinol-formaldehyde-modified starch on the performance of natural rubber, such as the tensile strength, tear strength, hardness and compression set, was investigated.

EXPERIMENTAL

Corn starch (Gencoat, Samyang Genex Company, South Korea) with a particle size 5-23 μm was used for compounding

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with natural rubber. Natural rubber (NR) latex with a solid content of 60 % was purchased from JungWoo Trade Company. The coupling agent resorcinol formaldehyde (RF) was prepared in our laboratory. Resorcinol (98 %) was supplied by DaeJung Chemistry Company. Formaldehyde (35 %) was supplied by SamChun Company. The other elastomer additives, such as curing agent, accelerator and antioxidant, were used as received.

Gelatinization of starch: Starch was dispersed into deionized water in a 2000 mL beaker. The weight ratio of starch/deionized water was 15/80. The starch dispersion was heated to 90 ºC with mechanical stirring at 120 rpm. Gelatinized starch was obtained after 1 h of gelatinization. Finally, the starch paste was cooled to room temperature for 30 min.

Preparation of natural rubber/resorcinol-formaldehyde/starch compounds: A fixed amount of 8 phr coupling agent resorcinol-formaldehyde was titrated slowly into the natural rubber latex in a 2 L Pyrex reactor with rapid stirring at room temperature for approximately 10 min. The obtained starch paste (10, 20, 30, 40 and 50 phr) was added to the NR/RF latex with vigorously stirring and the temperature was then increased to 90 ºC to initiate the cross-linking reaction. Fig. 1 presents the proposed reaction mechanism among NR/RF/

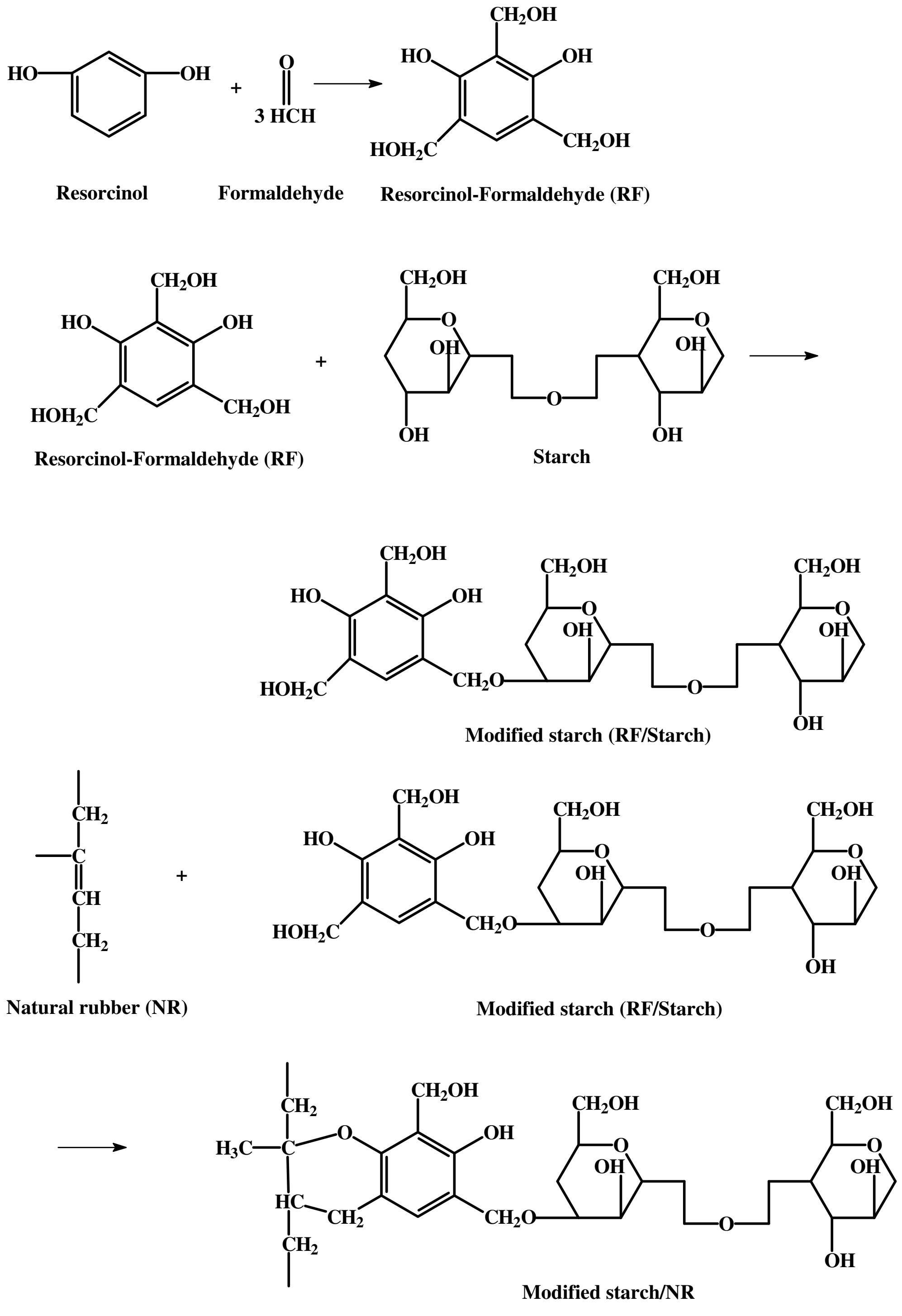

Fig. 1. Reaction mechanism of NR/RF/starch

starch. Firstly, the hydroxyl groups of resorcinol-formaldehyde could interact significantly with starch through hydrogen bonding. Secondly, the methylene quinone intermediate generated by the resorcinol-formaldehyde system could also react with the active allylic hydrogen of the isoprene unit in the natural rubber macromolecular chain[9]. Therefore, resorcinol formaldehyde acted as a "bridge" linking the natural rubber and starch. In particular, a high density NR/RF/St crosslinking structure could be formed easily after drying the compounds in an oven and curing in a hot press.

Approximately 4 g of $CaCl_2$ was dissolved in a 2000 mL methanol solution to prepare the coagulation solution, which was then used to coagulate the NR/RF/starch mixture. The coagulate was washed with water and dried in an oven at 60 ºC for 2 days.

The NR/RF/starch compounds were mixed with various elastomeric additives, such as sulfur, stearic acid, zinc oxide, accelerator tetramethyl thiuram disulfide (TT), dibenzothiazole disulfide (MBTs), diphenyl guanidine (D) and antioxidant [2,2,3-trimethyl-1,2-dihydroquinoline (RD)] on a two-roll mill at 50-60 ºC. Table-1 presents the composition of the compounds used in this study. The compounds were vulcanized for the optimum curing time t_{90} under 10 Mpa at 160 ºC. The samples were cut into a dumbbell-shape to measure the mechanical properties.

TABLE-1
COMPOUND FORMULATIONS

Compounds phr	NR	NR/RF/ St10	NR/RF/ St20	NR/RF/ St30	NR/RF/ St40	NR/RF/ St50
Natural rubber	100	100	100	100	100	100
Starch	0	10	20	30	40	50
RF	8	8	8	8	8	8
Sulfur	1	1	1	1	1	1
ZnO	5	5	5	5	5	5
Accelerator TT	0.5	0.5	0.5	0.5	0.5	0.5
Accelerator D	0.5	0.5	0.5	0.5	0.5	0.5
Accelerator MBTs	1	1	1	1	1	1
Stearic acid	1	1	1	1	1	1
Antioxidant RD	1	1	1	1	1	1

FT-IR analysis: Fourier transform infrared (FT-IR, spectrum 100, Perkin Elmer) spectroscopy was used to examine the structure of the NR/RF/St compounds. The frequency range and resolution was 4000-400 cm^{-1} and 4.0 cm^{-1}, respectively.

Average particle size analysis: A particle size analyzer (Zeta Sizer 3000HSA, Malvern instruments) was used to determine the particle size of starch dispersed in the NR/RF mixtures.

Morphology: Field emission scanning electron microscopy (FE-SEM, JSM-7500F) was performed to observe the starch particle dispersion in the NR/RF Latex. The samples were coated with a thin layer of golden before the observations.

Mooney viscosity test: The Mooney viscosity of all the samples was measured according to ASTM1646 using a Mooney Viscometer (MV, Myungji Tech, TH-200). Three different samples were measured and the mean was used for further analysis.

Vulcanization properties test: Vulcanization characteristics were measured on the Rheometer (RM, Myungji Tech, DMR 200). The test temperature was 160 ºC. Various vulcanization characteristics, such as the scorch time (t_{s2}), optimum cure time (t_{90}), minimum torque (M_L) and maximum torque (MH), were determined.

Mechanical properties test: Mechanical testing was performed on a universal testing machine (United Calibration, SFE-1) at a speed of 500 mm/min according to ASTM D412. The hardness of the compounds was measured using a Shore Durometer type A (TIME, TH200) according to ASTM D2240. The tear strength was also measured on an universal testing machine (united calibration, SFE-1) at a speed of 50 mm/min. The testing specimen was cut to a KS B-type shape for testing. A compression set test was performed according to ASTM D395. The specimens were cylindrical in shape with a diameter of 30 mm and height of 13 mm. The specimens were compressed in the compression device at 100 ºC for 22 h. The compression set value was calculated using the following equation:

$$Cs = \frac{t_0 - t_1}{t_0 - t_2} \times 100\% \qquad (1)$$

where Cs : compression set (%); t_0 : Original thickness of the specimen; t_1 : Final thickness of the specimen; t_2 : Thickness of the space bars used.

The values reported were an average of five measurements.

RESULTS AND DISCUSSION

Dispersion of starch in the natural rubber/resorcinol-formaldehyde (NR/RF) latex: The particle size of the starch dispersed in the NR/RF latex was measured by particle size analysis. As shown in Fig. 2, the mean particle size of pure natural rubber latex was approximately 600 nm. The presence of gelatinized starch from 10 to 50 phr caused a successive increase in mean particle size from 725 to 1200 nm. As the starch concentration increased, the dispersion of starch in the NR/RF latex became difficult and starch aggregates formed easily due to the strong hydrogen bonding among starch particles. Another reason for this phenomenon was the formation of a NR/RF/starch oligomer. As shown in Fig. 1, the particle size of starch increased once the coupling agent resorcinol formaldehyde and natural rubber were grafted onto the starch backbones.

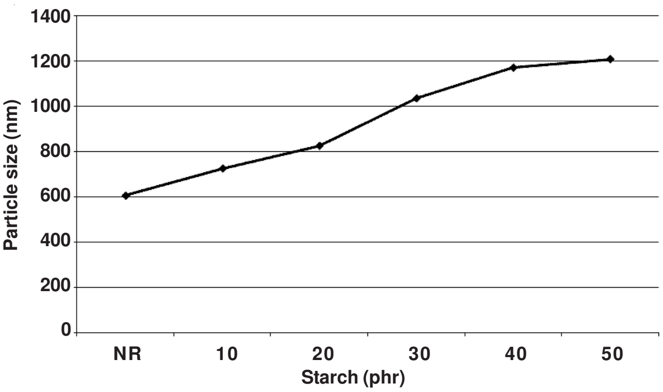

Fig. 2. Effect of the starch concentration on the mean particle size of starch dispersion in the NR/RF latex

The dispersion of starch in the natural rubber or NR/RF latex was observed by FESEM. Some starch aggregates appeared on the surface of NR/starch compounds, as shown in Fig. 3(a). The starch aggregates disappeared after adding the coupling agent (RF), as shown in Fig. 3(b). This suggests that resorcinol formaldehyde was grafted onto the starch backbone and effectively prevented the starch from aggregation.

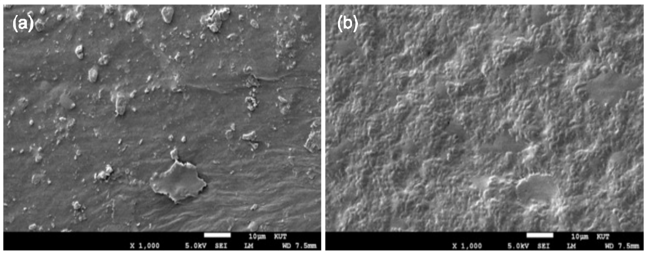

Fig. 3. FE-SEM images of (a) NR/St 50 phr; (b) NR/RF/starch 50 phr (×1000)

Structure of NR/RF/St compounds: Fig. 4 shows FT-IR spectra of natural rubber, starch and NR/RF/St compounds. The absorption peak at 1500 cm^{-1} was assigned to the C=C bond in the natural rubber macromolecular chains. For natural rubber/resorcinol-formaldehyde/starch compounds, the density of the C=C peaks at 1500 cm^{-1} decreased compared to pure natural rubber. This shows that resorcinol formaldehyde and starch were grafted successfully onto the C=C double bond of natural rubber.

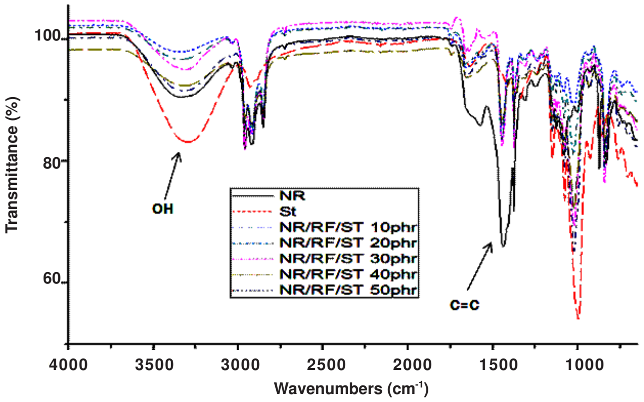

Fig. 4. FT-IR spectra of NR, pure starch and NR/RF/starch

Curing characteristics of the NR/RF/Starch compounds: The viscosity of the rubber compounds is very important for manufacturing rubber products. Therefore, the viscosity of NR/RF/St compounds was examined, as shown in Fig. 5. The viscosity of the NR/RF/St compounds increased linearly with increasing starch concentration. This is because that the incorporation of rigid starch strongly restricts the movement of soft natural rubber chains. In addition, at higher starch loadings, *e.g.* 50 phr, the strong filler-filler interaction of starch could also increase the viscosity of the NR/RF/St compounds.

Table-2 lists the curing characteristics of the natural rubber and NR/RF/St compounds. The scorch time t_{S2} and curing time t_{90} of NR/RF/St were shorter than those of natural rubber. This suggests that the incorporation of starch accelerates the curing rate of natural rubber compounds. The maximum torque (T_{max}), minimum torque (T_{min}) and T_{max}-T_{min} increased successively with increasing starch concentration from 10 to 50 phr. The increase in Tmin was attributed to the increase in viscosity. The increase in Tmax indicated the strong reinforcement of starch on the natural rubber matrix. T_{max} - T_{min} can be considered the crosslinking density of rubber compounds. Therefore, a NR/RF/St crosslinking structure formed, which influenced the crosslinking density of natural rubber compounds.

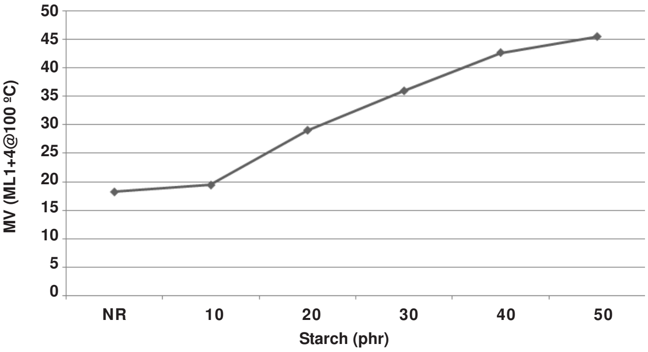

Fig. 5. Effect of the starch concentration on the Mooney viscosity of NR/RF/starch compounds

TABLE-2
CURING CHARACTERISTICS OF THE NR/RF/st COMPOUNDS

Compounds	t Point 10 (min)	t Point 90 (min)	T torque MAX	T torque Min	TM-Tm
NR	0:50	1:21	11.8	0.6	11.2
NR/RF/St10	0:41	1:08	13.5	0.9	12.6
NR/RF/St20	0:46	1:11	17.8	1.4	13.8
NR/RF/St30	0:46	1:11	23.7	2.0	21.7
NR/RF/St40	0:41	1:08	29.8	2.8	27.0
NR/RF/St50	0:41	1:10	33.3	3.1	30.2

Mechanical properties of NR/RF/St compounds: Fig. 6 shows the tensile strength and elongation at break of natural rubber and NR/RF/St compounds. The tensile strength of pure natural rubber was approximately 18 MPa, which increased to 23.6 MPa when 20 phr starch was added. On the other hand, the tensile strength deteriorated with further additions of starch. The elongation at break was decreased with the addition of starch from 10 to 50 phr. The improvement in tensile strength from 18 to 23.6 MPa was attributed to the formation of a NR/RF/starch crosslinking structure. When the starch concentration was >20 phr, the starch dispersion in the natural rubber matrix became worse. At this time, the filler-filler interaction was predominant in the NR/RF/St compounds and fracture occurred easily on or near the boundary of the starch aggregates.

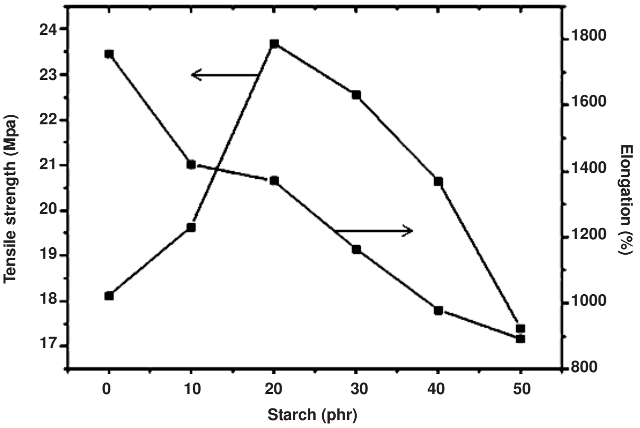

Fig. 6. Tensile strength and elongation of the NR/RF/starch compounds

Figs. 7-9 shows the tear strength, hardness and compression set of the NR/RF/St compounds, respectively. The tear strength was improved significantly in the presence of starch. The tear strength of NR/RF/St50 was approximately 2 times that of natural rubber. The hardness was also increased remarkably when starch was added. On the other hand, the compression set value of the NR/RF/St compounds decreased when starch was added. This is because the addition of rigid starch reduces the elasticity of natural rubber compounds. This observation is in agreement with the viscosity data.

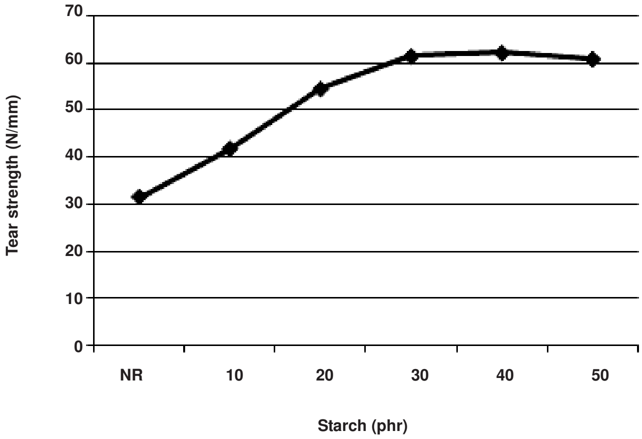

Fig. 7. Tear strength of the NR/RF/starch compounds

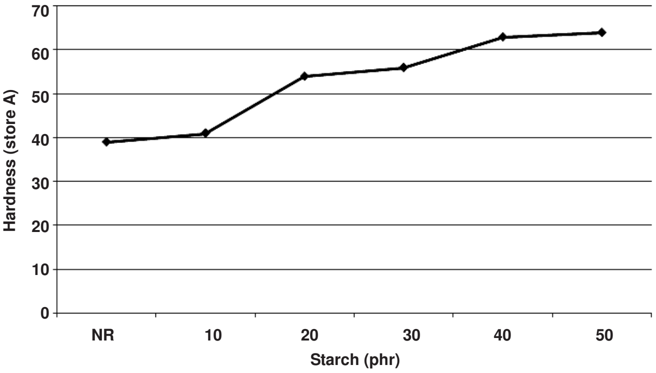

Fig. 8. Hardness of the NR/RF/starch compounds

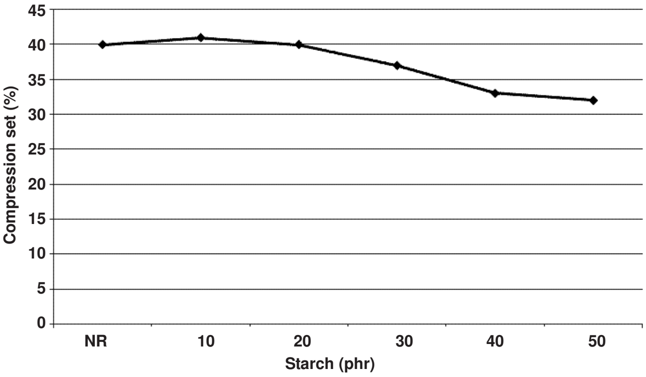

Fig. 9. Compression set of the NR/RF/starch compounds

Conclusion

Natural rubber/resorcinol-formaldehyde/starch compounds were prepared using the latex compounding method. The coupling agent (resorcinol-formaldehyde) not only effectively improved the dispersion of starch, as observed by FE-SEM, but also improved the interfacial interaction between natural rubber and starch. As a result, the tensile strength could be improved by adding 20 phr starch. Further addition of starch deteriorated the tensile strength due to the poor starch dispersion.

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