

## 에폭시화 천연고무의 물성 향상을 위한 전분과 이황화몰리브덴 첨가에 관한 연구

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### Study on Improvement of Properties for Epoxidized Natural Rubber by Addition of Starch and Molybdenum Disulfide

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**초록:** Epoxidized natural rubber(ENR)에 전분과 이황화몰리브덴이 다양한 비율로 혼합되었다. 제조된 복합체의 경화 물성과 동적점탄성은 고무 가공 분석기로 측정되었고, 시료의 형태학적 구조는 SEM으로 확인되었다. 기계적 물성, 열분해성, 인장강도, 경도, 마찰계수, 내마모성, 팽윤율도 물성 향상을 확인하기 위하여 조사되었다. 모든 실험 결과에서, 충전제-충전제 상호작용은 전분 함량이 증가함에 따라 향상되었음을 알 수 있었다. 그리고 기계적 물성도 따라 향상되었다. 그 원인은 전분과 ENR 고무 사이에 수소 결합이라는 더 나은 결합의 형성이었다. 또한 이황화몰리브덴의 첨가에 따라, 고무복합체의 윤활성이 증가되어 마찰계수와 내마모성이 개선됨을 알 수 있었다.

**Abstract:** Epoxidized natural rubber (ENR) was filled with starch and molybdenum disulfide ( $\text{MoS}_2$ ) on different ratios. The curing properties and viscoelastic behavior of the composites was tested by rubber processing analyzer, and the morphological structure of the composites samples were characterized by SEM. The mechanical properties, the thermal decomposition behavior, tensile strength, hardness value, friction coefficient, abrasion resistance and swelling ratio were investigated to verify the property improvement of the ENR composites. From the results of all the tests, it can be found that the intermolecular interaction increased with increasing starch content. And the mechanical properties also increased. The possible reason may be the starch could provide the better combination with ENR rubber matrix due to the hydrogen bonding. And with the addition of molybdenum disulfide, the friction coefficient and abrasion resistance properties were improved due to the lubrication of molybdenum disulfide.

**Keywords:** epoxidized natural rubber, starch, molybdenum disulfide, mechanical properties.

### Introduction

Epoxidized natural rubber (ENR) has been introduced as a modified form of natural rubber (NR). As the natural rubber is epoxidized, its chemical and physical properties change according to the extent to which the mole% of modification is introduced.<sup>1</sup> For instance, the glass transition temperature,  $T_g$ , is raised, room temperature resilience is reduced, the rubber becomes increasingly more oil resistance and im-pervious to

gases, polymer viscosity is increased and the polymer becomes more polar as the degree of epoxidation is increased. Some of these properties are more akin to those of synthetic rubber than NR.<sup>2</sup> Filled ENR has been a popular research subject due to the versatility of the ENR to accept numerous types of fillers and reinforcement.<sup>3</sup> Baker and Gelling<sup>4</sup> have found that high loading of silica can be incorporated into ENR and significant reinforcements were observed even without the addition of coupling agent. In another study, Nasir *et al.*,<sup>5</sup> observed that incorporation of  $\gamma$ -mercaptopropyl-trimethoxysilane (A-189) coupling agent into silica filled ENR has resulted in a significant improvement in the tensile and tear strength of the vulcanizates, due to the form of hydrogen bonding and high

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hydrophilicity.

It is known that in the case of filled vulcanizates, the efficiency of reinforcement depends on a complex interaction of several fillers related parameters, such as particle size, particle shape, particle dispersion, surface area, surface reactivity, structure of the filler and the bonding quality between the fillers and rubber matrix.<sup>6</sup>

In this research, the –OH groups in starch and the –S groups in molybdenum disulfide provide the polar bonding combination with the ENR, due to the hydrogen bonding effect and other interaction force, the new physical crosslinking had been formed, which could provide the mechanical properties reinforcement for ENR.<sup>7</sup> After filling with fillers in difference ratio, the vulcanizates were vulcanized during the curing process. Finally, the surface state, TGA, tensile strength, hardness, friction coefficient, abrasion resistance and swelling ratio had been characterized.

## Experimental

**Materials.** Epoxidized natural rubber 50 (EKOPRENA-50, epoxidation 50%), sulfur (S, powder, Daejung, 99%), stearic acid (SA, Samchun chemical, 95% EP), *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS, Tokyo Chemical Industry Company, Japan, 95%), 2,2'-dibenzothiazolyl disulfide (DD, Tokyo Chemical Industry Company, Japan, 95%), zinc oxide (ZnO, Samchun chemical, 99%), starch (Duksan Pure Chemical), molybdenum disulfide (MoS<sub>2</sub>, China).

**Compounding.** The formulation of this research was shown in Table 1. The compounding process was conducted on a two-

roll mill. Note the sulfur and vulcanization promoters were added at the last step for avoiding the pre-vulcanization. After that, samples were vulcanized under 10 MPa for  $t_{90}$  at 160 °C in a heating press machine. The thickness of the samples was set as 1 mm.

**Characterization.** The morphology of the samples after the tensile test was carried out on a FE-SEM (JSM-7500F, JEOL Ltd. Japan). The cure/vulcanization characteristic of as-prepared samples were measured by a rubber process analyzer (RPA-V1, UCAN DYNATEX INC.). The minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), scorch time ( $t_{s2}$ ), and optimum cure time ( $t_{90}$ ) were determined by the above RPA. The cure rate index (CRI) was used to evaluate the cure rate of the rubber, and it was calculated by the following eq. (1):

$$\text{CRI} = 100/(t_{90} - t_{s2}) \quad (1)^8$$

Tensile strength was performed on a Tinius Olsen H5KT-0401 testing machine at a speed of 500 mm min<sup>-1</sup> according to ASTM D412 with the average of three measurements. Specimens on standard dumb-bell shape were cut from the vulcanizate sheets with dimensions 25 mm×6 mm×1 mm (length×width×thickness). Shore A hardness of the specimens was obtained with Shore Durometer Type A according to ASTM D22-40. Friction factor test was performed at room temperature by friction test machine. Abrasion resistance test was performed by Taber Abrasion tester 5135 with a rotate speed of 80 rpm according to ASTM D1044. And swelling ratio tests were carried out in toluene for 1, 2, 4, 8, 12 and 24 h according to ASTM D71-79.

**Table 1. Formulation of Test Sample Compounds**

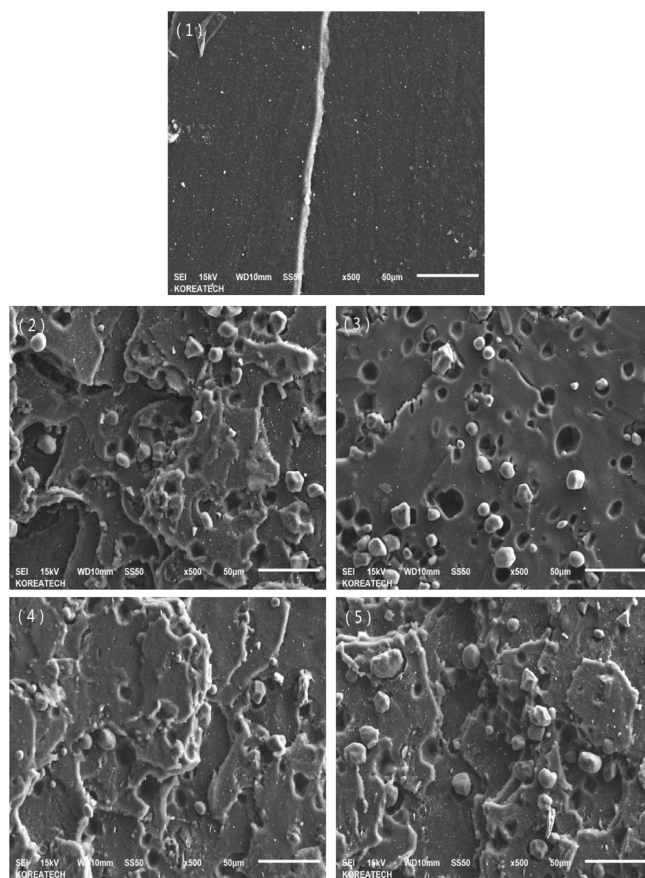
Ingredients	Compound designations				
	Neat (phr <sup>c</sup> )	Starch 10 (phr)	Starch 20 (phr)	Starch 10 MoS <sub>2</sub> 5 (phr)	Starch 10 MoS <sub>2</sub> 10 (phr)
ENR	100	100	100	100	100
Stearic acid	2	2	2	2	2
CBS <sup>a</sup>	1	1	1	1	1
DD <sup>b</sup>	1	1	1	1	1
Zinc oxide	5	5	5	5	5
Starch	0	10	20	10	10
MoS <sub>2</sub>	0	0	0	5	10
Sulfur	1.4	1.4	1.4	1.4	1.4

<sup>a</sup>*N*-Cyclohexyl-2-benzothiazole-sulfonamide. <sup>b</sup>2,2'-Dibenzothiazolyl disulfide. <sup>c</sup>phr: part per hundreds of rubbers.

## Results and Discussion

Curing test results of composites were presented in Table 2. The torque values of all the samples had been increased compared to the neat ENR, due to the strength of fillers, which strongly restricted the deformation and consequently increased the mechanical properties of ENR matrix. With the ratio of starch increasing, the  $M_{th}$ ,  $\Delta M$  and CRI also increased, and starch 20 phr filler provide the biggest  $\Delta M$  and CRI value, which meant this filler not only could improve the mechanical properties of ENR, but also short the vulcanization time of composite. The possible reason is due to the formation of hydrogen bonds between the ENR and starch.<sup>9</sup> And both these two materials have oxygen atom, which would show the polarity, due to the like dissolves like principle, so starch may present a stable state in ENR matrix, and the hydrogen bonds also short the distance of ENR chains, which could reduce the vulcanization time. But as molybdenum disulfide, with the ratio of filling increasing, the  $\Delta M$  reduced. The reason for this phenomenon is due to larger particle size, which could cause the worse combination of phases. Thus, the integrated mechanical properties decreased.<sup>10</sup>

The morphology of samples was observed in Figure 1. From these pictures, it can be found that after the tensile strength, the compounds filled with fillers showed more porous state and the typical starch's ball-like structure, which meant starch could make good combination with ENR matrix, so when broken by tensile tester, they cannot form the smooth section like (1) showed. Compared to (2), the picture (3) presented the largest number of holes and ball-like blocks, just look like lock and ring, which means this filler made the best combination effect with ENR. But from (3), (4) and (5), it can be found the number of ball-like blocks of (4) and (5) had reduced, but the layer structure of matrix increased, it is due to starch will adsorption the  $MoS_2$ , and make the particle size larger, also,



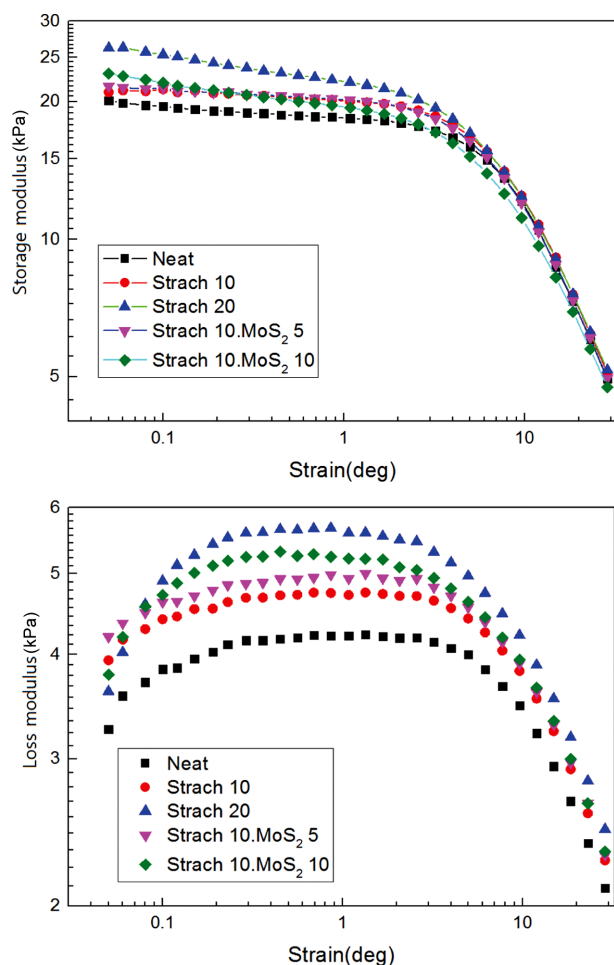
**Figure 1.** SEM pictures of ENR composites: (1) neat ENR; (2) starch 10; (3) starch 20; (4) starch 10,  $MoS_2$  5; (5) starch 10,  $MoS_2$  10.

the interaction formed by  $-S$  is weaker than  $-O$ , which would weak the combination between filler and matrix.<sup>11</sup>

Figure 2 showed the strain sweep results of all the sample. From two figures, it can find that all the storage modulus values were lower than the corresponding values of loss storage, which means all the samples have solid-like behavior. With the ratio of starch-molybdenum disulfide fillers increasing, the

**Table 2. Curing Characteristic Result**

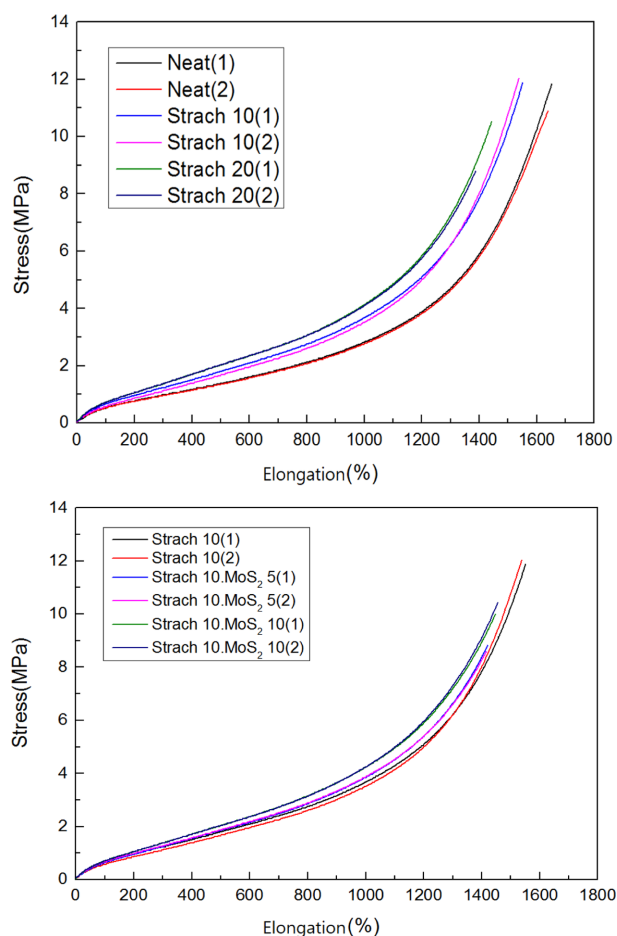
	Maximum torque $M_{th}$ (dNm)	Minimum torque $M_L$ (dNm)	$\Delta M$ (dNm)	Scorch time $t_{s2}$ (min)	Cure time $t_{90}$ (min)	Cure rate index (CRI min <sup>-1</sup> )
Neat	16.40	0.54	15.86	2.38	3.80	70.42
Starch 10	17.11	0.56	16.55	2.17	3.40	81.30
Starch 20	21.59	0.46	21.13	1.98	3.05	93.45
Starch 10 $MoS_2$ 5	18.32	0.44	17.88	1.95	3.18	81.30
Starch 10 $MoS_2$ 10	17.53	0.42	17.11	2.12	3.23	88.49



**Figure 2.** Strain sweep results of the ENR composites.

storage modulus and loss modulus also increasing, which means intermolecular interaction has been increased. It also means that starch and molybdenum disulfide could provide good mechanical properties and viscoelastic effect.

The results of tensile strength were shown in Figure 3. It could be found the modulus of starch 20 phr composite was the largest, and starch-MoS<sub>2</sub> fillers also showed the better tensile strength than starch 10 phr, and with the ratio of MoS<sub>2</sub> increasing, the modulus also increased. The possible reason is the -OH groups in starch and the -S groups in molybdenum disulfide provide the polar bonding combination with the ENR, due to the hydrogen bonding effect and other interaction force, the new physical crosslinking had been formed, which could provide the mechanical properties reinforcement for ENR. Due to the layer structure of molybdenum disulfide, it showed the larger modulus than the rubber matrix, the particle of molybdenum disulfide would combine with the interface of rubber matrix, during the tensile strength test, the part of ten-



**Figure 3.** Tensile strength results of the ENR composites.

**Table 3. Hardness Results of the ENR Composites**

Samples	Hardness (Shore A)
Neat	43
Starch 10	45
Starch 20	46
Starch 10 MoS <sub>2</sub> 5	47
Starch 10 MoS <sub>2</sub> 10	47

sile stress on matrix could reduce by interfacial friction.<sup>12</sup> Also, due to the layer structure of MoS<sub>2</sub>, which hinder the formation of torn grain.

Table 3 showed the hardness results of all the samples. From this figure, it can be found all the composite filled with fillers showed the higher hardness value than neat ENR. Which meant the more compact matrix had formed during the filling process. And starch-molybdenum fillers showed the highest hardness value in this test, with the molybdenum ratio increas-

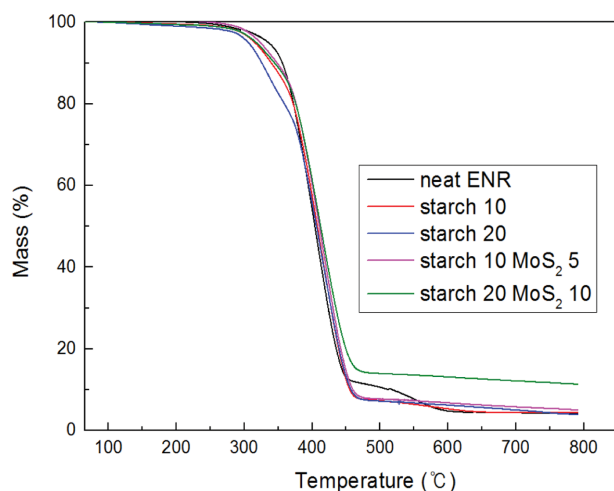


Figure 4. TGA results of the ENR composites.

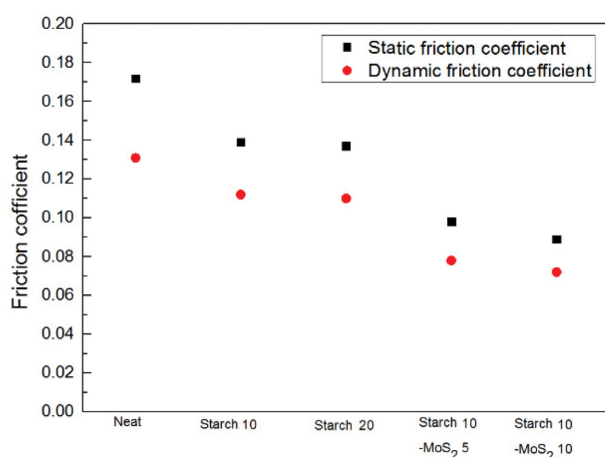


Figure 5. Friction coefficient results of the ENR composites.

ing, the hardness value also increased.

Figure 4 showed the TGA results of all the samples. From these curves, it can be found starch cannot improve the thermal decomposition resistance, due to starch is also organic material, so during the high temperature, it also decomposed, but as  $\text{MoS}_2$ , it is the inorganic material, which cannot decompose, it means the thermal stability had been increased.

Figure 5 showed the friction coefficient results in this research, due to the lubrication effect of  $\text{MoS}_2$ , the composites filled with starch 10  $\text{MoS}_2$  5/10 showed the smallest friction coefficient values. The probable reason can be explained from the frictional behavior: The friction between rubber and solid substance can be considered as two part, like the eq. (2) below<sup>13</sup>:

$$F = F_a + F_h \quad (2)$$

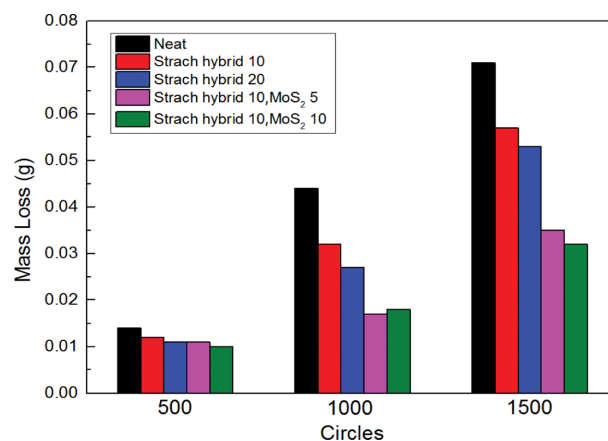


Figure 6. Abrasion resistance results of the ENR composites.

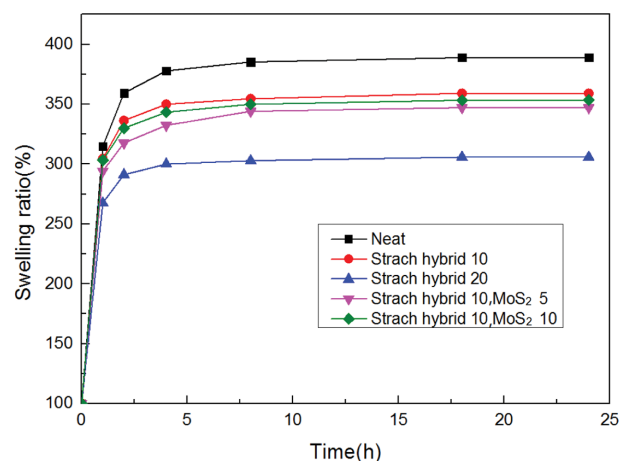


Figure 7. Swelling ratio test results of the ENR composites.

Where  $F_a$  means adhesion force produced by contact, and  $F_h$  means the lag drag force produced by the bulge deformation caused by pressure. Thus, the friction coefficient of vulcanizates depends on the deformation state of the samples, interfacial shear strength and the contact area between the samples and solid substance. In this research, with the ratio of molybdenum disulfide increasing, the hardness value also increased, which could reduce the deformation, so the contact area also reduced, so  $F_h$  reduced. And molybdenum disulfide could reduce the interfacial shear strength,<sup>14</sup> with the ratio of  $\text{MoS}_2$  increasing, so  $F_a$  reduced. In summary, the friction coefficient reduced with the increasing of molybdenum disulfide ratio.

The abrasion resistance test results were shown in Figure 6. Due to the same reason above, starch 10  $\text{MoS}_2$  10 fillers showed the good abrasion resistance in this research, compared to the neat ENR, composite filled with starch 10  $\text{MoS}_2$  10 showed about 2 times abrasion resistance than neat, which

would apply in the conveyor belt and rubber roll filed with longer service life.

The swelling ratio test results were displayed in Figure 7. The swelling ratio ( $Q$ ) was calculated by the following eq. (3):

$$Q(\%) = 100 \times (W_s - W_u)/W_u \quad (3)$$

Where  $W_s$  is weight of the swollen sample and  $W_u$  is weight of the unswollen sample (extracted sample).<sup>15</sup> From the curves, it can be found the neat ENR showed the highest swelling ratio, due to the like dissolves like principle, the neat ENR showed the weakest polarity, so when swelling in toluene which showed non-polarity, it showed the largest swelling degree.<sup>16</sup> But when filled with starch and molybdenum disulfide, due to the increasing of polarity, the swelling degree also decreased. Also, the filler would increase the crosslinking density of matrix, the more crosslinking density, the more compact matrix, and the better swelling resistance.

## Conclusions

Epoxidized natural rubber (ENR) had been filled with starch and molybdenum disulfide ( $\text{MoS}_2$ ) on different ratio. The results of curing characterization showed starch-molybdenum disulfide fillers could improve mechanical properties, and short the vulcanization time. The result of strain sweep showed starch-molybdenum disulfide fillers could strengthen intermolecular interaction and contribute to viscoelastic behaviors of the ENR rubber materials. From the results of SEM, it can be found the layer structure of matrix when filled with starch-molybdenum disulfide fillers, which could provide smaller friction coefficient and better abrasion resistance.<sup>17</sup> And the

results of friction coefficient and abrasion resistance also prove this viewpoint. Tensile strength and hardness results also showed starch-molybdenum disulfide fillers could make better reinforcement with ENR matrix. The swelling ratio and TGA results showed after filled with starch-molybdenum disulfide fillers, the composites would have better swelling resistance and thermal stability.

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