Study on Mechanical Properties Modification of Styrene Butadiene Rubber Composites Filling with Graphene and Molybdenum Disulfide

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ABSTRACT

Styrene-butadiene rubber (SBR) composites, incorporated with graphene, molybdenum disulfide and their hybrid in different filling ratio, were fabricated by a two roll-mill. The dispersion states of all the samples' matrix were employed by carbon black dispersion tester. The curing properties of the pre-vulcanized rubber composites were investigated, after molding by heating press machine, the tensile strength, storage modulus, friction coefficient, the swelling property had also been tested according to ASTM. The composite G1M10 (filling with 1 phr graphene and 10 phr molybdenum) showed the best mechanical properties and viscoelastic properties in this research with a better filler dispersion state and more compact matrix structure.

Key Words : SBR, Graphene, Molybdenum Disulfide, Composite

1. Introduction

Molybdenum disulfide (MoS_2), a two-dimensional layered transition-metal dichalcogenide, has attracted extensive interest due to its potential in various applications ranging from electronic devices and sensors to catalysts [1]. Recent studies show that single-layered MoS_2 is a flexible and strong sheet with a high Young's modulus of 270–330 GPa and breaking strength of 16–30 GPa [2]. These excellent mechanical properties of MoS_2 make it a promising reinforcing filler for polymeric composites [3]. Recently, it has been demonstrated that, with appropriate surface functionalization, single-layered MoS_2 exhibited high reinforcing efficiency for rubber, which is comparable to that possessed by graphene [4].

Graphene (GE), one-atom-thick nanosheet comprised of sp^2 hybridized carbon atoms, has exceptional mechanical properties, thermal conductivity, mobility of charge carriers and gas impermeability [5]. Thus, GE may be an ideal nanofiller to impart prominent mechanical and multifunctional properties to rubbers, provided that fine dispersion and strong interfacial interaction can be achieved.

Styrene-butadiene rubber (SBR) is one of the most widely used materials in the rubber industry. In order to broaden its application areas, GE can be used as a multifunctional nanofiller for SBR [6]. Given the fact that SBR mainly exists in the form of latex, the present work used a scalable modified latex compounding method to fabricate GE/SBR nanocomposites. A molecular-level dispersion of GE and strong interfacial interaction between GE and SBR were achieved, which were very efficient in increasing the mechanical property of SBR [7]. Moreover, the resulting GE/SBR nanocomposites have low heat buildup, remarkable gas barrier property, high thermal stability, and

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electrical conductivity.

In this research, the nanofiller: graphene, molybdenum disulfide and their hybrid in the different filling ratio were used as the reinforcement agent for SBR, after the filling process, the dispersion states of all the samples' matrix were employed by carbon black dispersion tester. The curing properties of the pre-vulcanized rubber composites were investigated, after molding by heating press machine, the tensile strength, storage modulus, friction coefficient, the swelling property had been also characterized.

2. Experimental

2.1 Materials

Solution styrene butadiene rubber SOL-5130H (styrene content 16 wt%, vinyl content 30% wt, Kuhom Chem.), 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'-di-benzothiazolyl Table 2. Curing Results of all the Samples disulfide (DD, Tokyo Chemical Industry Company, Japan, 95%), zinc oxide (ZnO, Samchun chemical, 99%), molybdenum disulfide (Sigma-Aldrich Co. 5~10nm, 99%), and graphene nanoplatelets (≥99.50%, particle size<5nm, SMX Nanotech, China).

2.2 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 1mm.

2.3 Characterization

The chemical structure of the obtained bio-based polyester polyol and thermoplastic polyurethanes was investigated through Fourier transform infrared spectroscopy (FTIR). The infrared spectra were recorded with a Perkin Elmer Spectrum 100®, with 64 scans and a resolution of 4 cm^{-1}. The spectra had been registered at room temperature for the wavenumbers between 650 and 4000 cm^{-1}. The cure/ vulcanization and viscoelastic properties characterization of as-prepared samples were measured by a rubber process analyzer (RPA) (RPA-V1, U-CAN DYNATEX INC.). The viscoelastic properties were determined with a rubber process analyzer (RPA-V1, U-Can Dynatex Inc., Taiwan. The strain sweep test from 0.01 degree to 20 degrees was operated at 60 °C and 1 Hz according to ASTM D 6204-97. 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 equation [8]:

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

Table 1. Formulation for Test Sample Blends

Ingredient	SSBR (phr[c])	Graphene (phr)	MoS_2 (phr)	Stearic acid (phr)	Zinc oxide (phr)	Sulfur (phr)	CBS[a] (phr)	D.D[b] (phr)
G0.5 M0	50	0.5	0	1	3	1.5	1.5	1
G1 M0	50	1	0	1	3	1.5	1.5	1
G1 M5	50	1	5	1	3	1.5	1.5	1
G1 M10	50	1	10	1	3	1.5	1.5	1
Neat	50	0	0	1	3	1.5	1.5	1

[a]N-Cyclohexyl-2-benzothiazole-sulfonamide,
[b]2,2-Dibenzothiazolyl disulfide,
[c]phr, part per hundreds of rubbers.

Table 2. Curing Results of all the Samples

Samples	Maximum torque, M_H (dNm)	Minimum torque, M_L (dNm)	ΔM (dNm)	Scorch time, t_{s2} (min)	Cure time, t_{90} (min)	Cure Rate Index (CRI min^{-1})
G0.5 M0	53.24	3.48	49.76	4:45	7:53	31.95
G1 M0	56.50	4.19	52.31	2:30	5:16	36.10
G1 M5	58.03	4.65	53.38	2:45	4:48	48.78
G1 M10	60.57	4.95	55.62	2:28	4:12	57.80
Neat	51.06	3.83	47.23	5:25	8:49	29.41

The hardness of samples was obtained by a shore durometer type A according to the ASTM D 22-40.

The tensile strength test was measured three times on a Tinius Olsen H5KT-0401 testing machine at a speed of 500 mm/min according to ASTM D412. The samples were made of a dumb-bell shape with the dimensions of 25 mm × 6 mm × 1 mm after the vulcanization on the heating press machine. The resilience test was performed by Ball Rebound machine which according to the ASTM D3574-17 and ISO 8307. Friction factor test was performed at room temperature by friction testing machine TO-100-IC according to ASTM 1894. And swelling tests were carried out in toluene for 1, 2, 4, 8, 16 and 24 h according to ASTM D71-79.

3. Results and Discussion

Curing results were shown in Table 2 and Fig. 1. From these results, it could be seen after the filling process, the torque value difference and CRI of filled composites increased higher compared to the neat SBR, which meant all the fillers in this research could provide reinforcement effect for SBR rubber, and with the amount of filler increasing, the reinforcing effect also increased. The probable reason would be due to the nanosize fillers (graphene and MoS_2) could provide more crosslinking points than micro size fillers when filling into the rubber matrix, which would improve the combined effect between fillers and rubber materials. Also, due to the same reason, more crosslinking points in the matrix could shorten the distance between rubber chains, thus, the CRI value, which could show the rate of vulcanization, also increased with the increasing of nanosize fillers ratio.

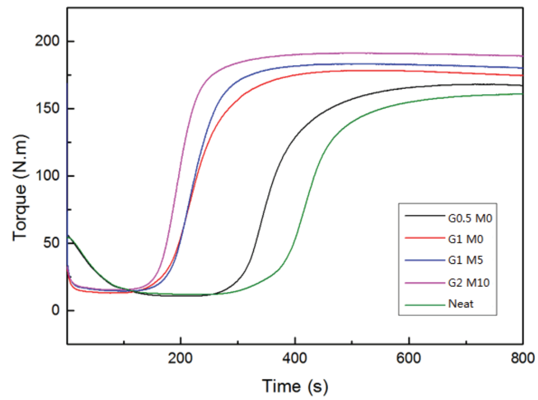

Fig. 1. Curing curves of all the samples.

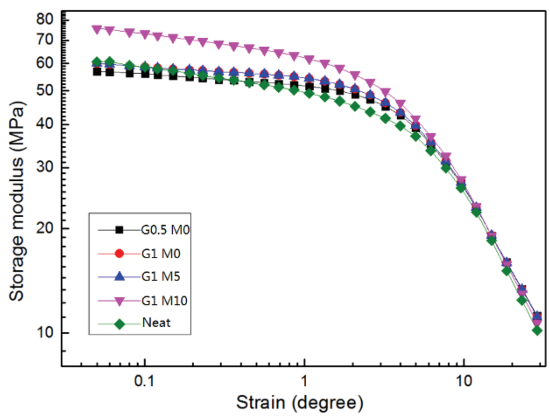

Fig. 2. Storage modulus results of all the samples.

The storage modulus and loss modulus results were shown in Fig. 2 and Fig. 3, from these curves, it could be seen fillers filled composites showed better test values than neat SBR, which meant fillers could improve the combination of filler and matrix. And the composite G1

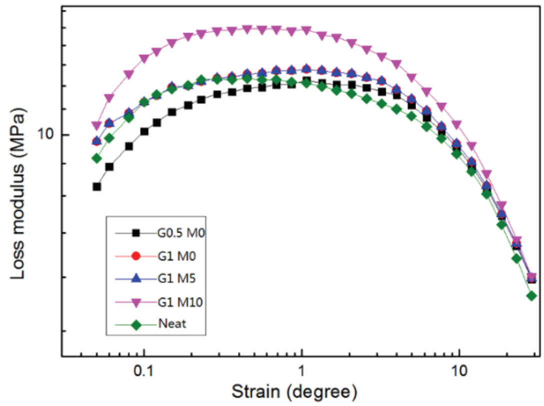

Fig. 3. Loss modulus results of all the samples.

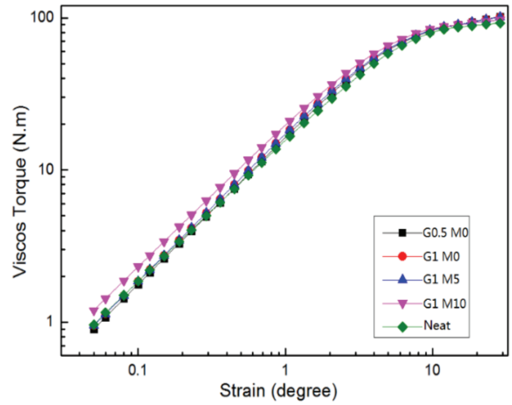

Fig. 5. Viscous torque results of all the samples.

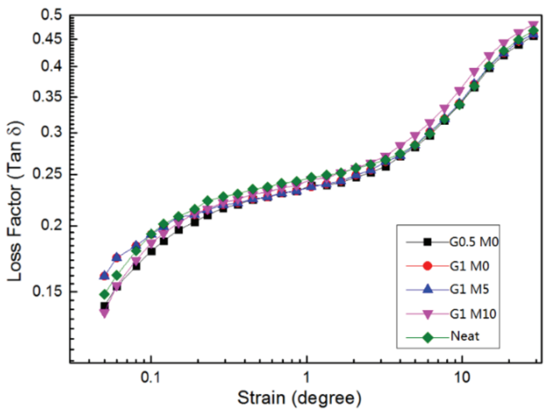

Fig. 4. Loss factor results of all the samples.

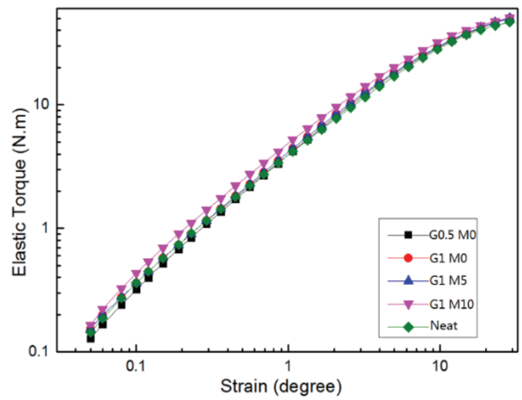

Fig. 6. Elastic torque results of all the samples.

M10 showed the most significant modulus values in this test, but other 3 filler filled composites presented the similar trends and values, which meant G1 M10 was the best filling ratio in this research, due to the low density of graphene, the filling volume of graphene was more than MoS_2, but the influence of MoS_2 was more than graphene. Which meant the weight of fillers materials provide more significant influence than volume in rubber filed.

The loss factor results were shown in Fig. 4, all the curves showed similar trends and values. The loss factor is calculated by the equation following:

$$\text{Tan } \delta = \text{loss modulus (G'')} / \text{storage modulus (G')} \times 100\%$$

due to the filling ratio in this research is so little, which could not make a more significant difference compared to the neat SBR in the filling process, thus, loss factor also could not show a significant difference in this test.

Fig. 5 and 6 showed the viscous and elastic torque of all the samples during the strain sweep mode test, from these curves, it could be found the curves of G1 M10 were always on the top, which meant this material had the best viscous and elastic torque in this research, and the best viscoelastic properties in this research.

Fig. 7 showed the results of the tensile strength of all the samples. From this figure, it could be found with the filler filled into the SBR rubber, the tensile stress had been increased compared to the neat composite, the composite G1 M10 showed the most considerable tensile stress result in this test, which meant this ratio of fillers could provide the best tensile strength reinforcement effect in this research. The probable reason was due to the nanoparticle size of graphene and MoS_2, which could reduce the dislocation effect of fillers when filling into the rubber matrix [9]. Moreover, the larger specific surface area could provide more crosslinking points. It could make better reinforcement

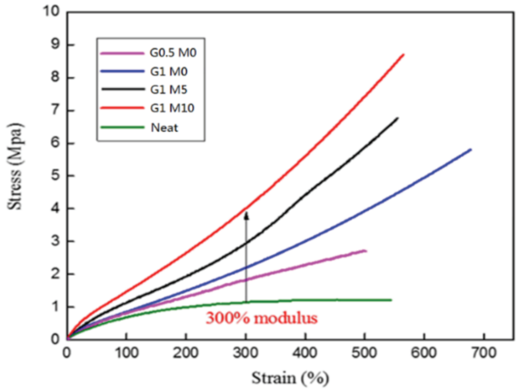

Fig. 7. Tensile results of all the samples.

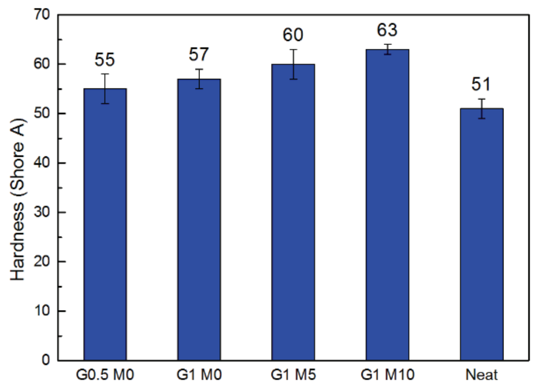

Fig. 8. Hardness results of all the samples.

and combination, then, presented a better tensile strength.

Fig. 8 showed the results of hardness test, from the figure, it could be seen that with the filling ratio increased, the hardness value also had been increasing, and G1 M10 showed the most significant value in this test.

Fig. 9 showed the results of resilience, which were characterized by the ball-rebound tester, the neat composite presented the most significant value, but with the filling ratio increased, the rebound value decreased. The probable reason would be: the fillers in this research had a small particle size when filled into the rubber matrix, they provided crosslinking points. Due to the small particle size of fillers, the crosslinking distance between rubber chain could be shortened [10], and make the matrix more compact, which could not provide enough space to get better rebound property, thus, the more filling ratio of fillers, the fewer rebound values.

Due to the larger specific surface area, smaller particle

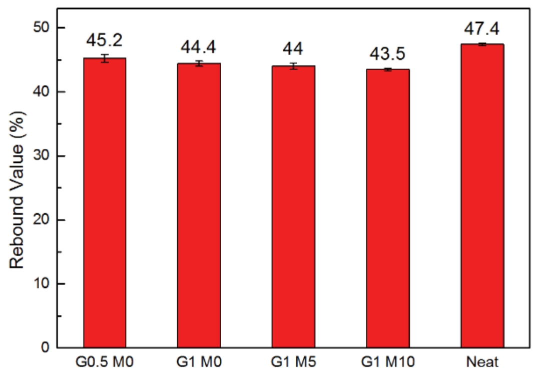

Fig. 9. Resilience results of all the samples.

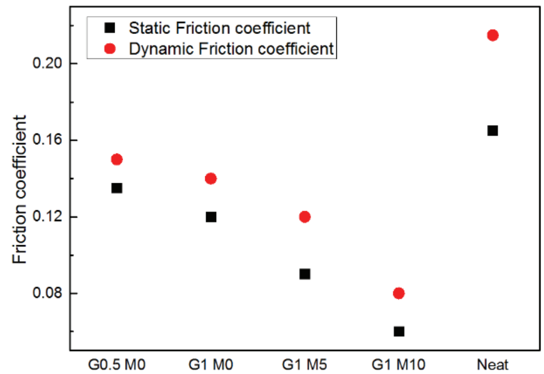

Fig. 10. Friction coefficient results of all the samples.

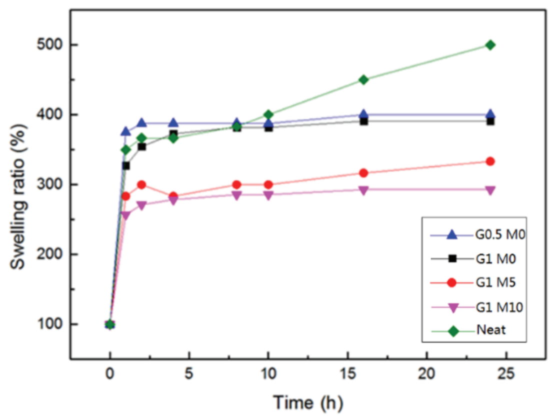

Fig. 11. Swelling test results of all the samples.

size and less layer structure, graphene and MoS_2 had become great friction-reducing agent for rubber research, from Fig. 10, it could be seen that compared to the neat composite, all the composite samples filled with fillers showed lower static/dynamic friction coefficients in this test.

Table 3. Dispersion Test Results of Filled Samples

Sample	Max Particle Diameter	Agglomerations	Ave. Particle Diameter	Particle Rate%	Dispersion%
G0.5 M0	6.012	5	1.17	2.343	83.10
G1 M0	4.343	3	1.295	2.803	82.00
G1 M5	3.934	0	1.065	4.372	58.45
G1 M10	3.561	0	0.941	2.456	70.08

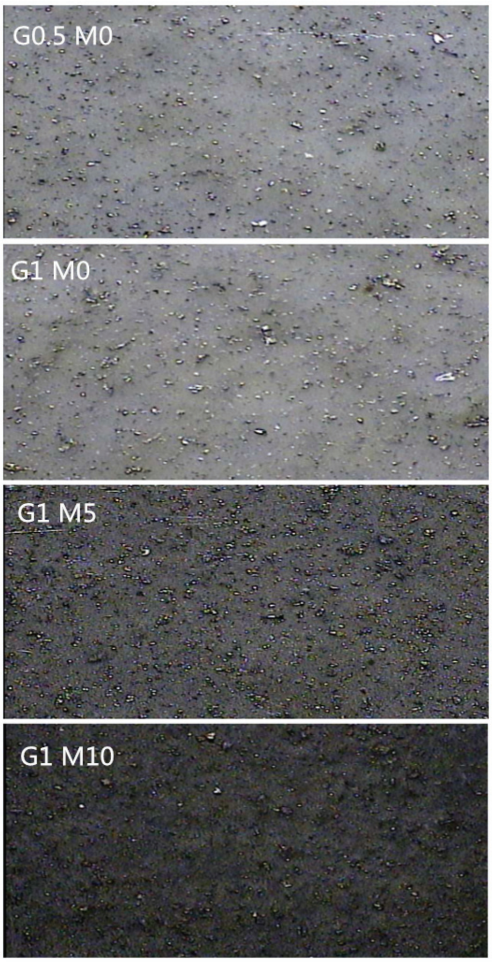

Fig. 12. The dispersion state of filled samples.

However, from the results of G0.5 M0 and G1 M0, G1 M0, G1 M5, and G1 M10, it could be found with the ratio of graphene increasing, the friction coefficients decreased not apparently. On the contrary, with the ratio of MoS_2 increased, the friction coefficients reduced sharply, which meant MoS_2 was better friction reducing agent, and G1 M10 showed the best friction reducing the effect in this test [11].

The results of the swelling test were shown in Fig. 11, from these curves, it could be found with the ratio of fillers increasing, the swelling ratio of samples had been decreased. However, also, MoS_2 showed better swelling resistance reinforcement effect than graphene. The reason could be due to the polarity of MoS_2, which could provide excellent swelling resistance for rubber from the swelling agent toluene [12].

The results of the dispersion state were shown in Table 3 and Fig. 12, from the results, it could be found that pure graphene showed a larger particle size than hybrid filler. It was due to the agglomeration effect of graphene layers, caused the block effect [13], which could increase the size of filler, however, due to the lower polarity compared to the MoS_2, pure graphene showed better dispersion rate than hybrid filler filled composites [14, 15]. However, as the hybrid fillers, due to the lack of functional groups compared with pure graphene, the agglomeration effect was less than pure graphene [16, 17, 18]. Thus, the particle size also was less than pure graphene. However, from the data of G1 M5 and G1 M10, it could be found the considerable difference of particle rate and dispersion rate, the probable reason should be due to the ratio of hybrid fillers, the more ratio of MoS_2, the less agglomeration effect from graphene, and the better dispersion effect [19-24].

4. Conclusion

Nano filler: graphene, molybdenum disulfide and their hybrid in the different filling ratio were used as the reinforcement agent for SBR, after the filling process, the dispersion states of all the samples' matrix were employed by carbon black dispersion tester. The curing properties of the pre-vulcanized rubber composites were investigated, after molding by heating press machine, the tensile strength, storage modulus, friction coefficient, the swelling property had also been characterized. From the results of all the test, it could be found the nanofillers could provide significant mechanical and viscoelastic properties reinforcement effect for SBR rubber, and with the ratio increased, MoS_2 showed the more substantial influence of reinforcement effect compared with graphene. The probable reason might be due to the low density of graphene, which could not provide more shear force to the rubber matrix. The composite G1 M10 presented the best mechanical and viscoelastic properties, and great dispersion data in this research, which meant this filler should provide the best reinforcement effect, and also, it was proved that pure nano-graphene could not provide good reinforcement effect.

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접수일: 2019년 9월 2일, 심사일: 2019년 9월 18일,
게재확정일: 2019년 9월 23일