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Original Article

Preparation and Investigation of the Mechanical and Thermal Properties of Styrene Butadiene Rubber using Dicumyl Peroxide as Curing Agent

Nguyen Thanh Liem*, Nguyen Huy Tung, Nguyen Pham Duy Linh, Bach Trong Phuc, Nguyen Thi Thuy, Bui Chuong

Hanoi University of Science and Technology, No. 1, Dai Co Viet Street, Hai Ba Trung Distric, Hanoi, Viet Nam

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Abstract: This paper investigates the mechanical and thermal properties of styrene butadiene rubber (SBR) using dicumyl peroxide as curing agent. The results showed that the tear strength of SBR with 2 phr DCP as curing agent increased sharply from 31,7 N/mm to 73,2 N/mm compared to SBR cured with sulfur. The other mechanical properties like tensile strength, elongation at break are unchanged. The accelerators DM/TMTD used by curing of SBR have not only influence on mechanical properties but also on the curing time. Using 0.5-phr trimethylolpropane trimethacrylate (EM 331) also increases the thermal stability of SBR, thermal aging ratio reaches 0.79 from 0.66 comparing with sample without EM 331. Nano silica have good effec for thermal conductivity coefficient of SBR . At the nano silica content of 3% the thermal conductivity coefficient increases by more than 20.68%, from 0.672 W / m * K of SBR to 0.811 W / m * K of SBR/nano silica composite. This will probably have a good effect on properties of finished product when blending SBR rubber with other types of synthetic rubber which have different vulcanizing properties.

Keywords: Styrene butadiene rubbers, dicumyl peroxide, nano silica, thermal conductivity coefficient.

1. Introduction

The vulcanization of rubber with peroxides has been known for a long time instead of traditional crosslinking agent such as sulfur [1]. Rubber can be saturated or contain very few carbon- carbon double bond, for instance, Ethylene Propylene Diene Monomer (EPDM).

The peroxide curing agents can be used independent or combination with co- agents in order to achieve the appropriate mechanical properties of finished products. Peroxide tends to

* Corresponding author.
Email address: liem.nguyenthanh@hust.edu.vn

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increase the mechanical properties but also increase the thermal stability, reduce the retention level of compression strength. It's very important for many products that are working under the high temperature environment such as conveyor belt, O-ring or rubber seal etc. [1,2].

Styrene Butadiene Rubber (SBR) is one of the most popular synthesis rubbers because of the great mechanical properties like low abrasion loss, high resistance to chemical medium such as some weak acid, base.

However, the disadvantages of SBR is poor resistant to oxygen, ozone, weathering, UV and especially at high temperature when exposed to heat over 100^{o}C due to the double bond in rubber chain backbone. Therefore, blend SBR of compound with other rubbers for improve the drawbacks is popular used. Due to the presence of high polar group, SBR is common blended with other heat-resistance rubbers such as silicon rubber, EPDM in order to increase the degree of adhesive with steel or polyester conveyor belt [3].

The SBR is often vulcanized with sulfur because of containing numerous of double bonds in rubber chain. Nevertheless, when the sulfur cross-linking agent was introduced to vulcanize the heat-resistance rubber products, the thermal stability often dramatically reduced because of devulcanization, intra chain cyclic of sulfide or other phenomenon under high temperature. Consequently, this leads to the rapid decrease of product properties as well as product life.

The purpose of this study is preparation and characterization of SBR by peroxide cure system in order to improve the mechanical l and thermal properties of vulcanizate through the optimization the ratio of ingredients in rubber formulation.

2. Materials and Methods

2.1. Material

The SBR used in this study is SE 1500 was supplied by Lanxess (Germany). The product information of SBR were also given by manufacturer such as Mooney viscosity ML (1+4) 52 MU; Styrene content 23,5 %; Mass and loss drying ≤ 0,5%. Accelerator MBT (2-Mercaptobenzothiazole); accelerator DM (Dibenzothiazole disulfide); accelerator TMTD (Tetramethyl thiuram disulphide); antioxidant 4020 N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (Vulkanox 4020) were purchase from Lanxess (Germany). Carbon black HAF N330, zinc oxide, dicumyl peroxide (DCP), co-agent EM 331 (*Trimethylopropane trimethacrylate*) and parafinic oil were of commercial grade.

2.2. Testing and processing

2.2.1. Characterization methods

The curing is assessed by using a rotor less rheometer RLR-4 (Japan), at 160^{0}C ±1 C, according to ASTM D2084-95. The mixing energy of each compound is recorded. The cure characteristics: Ml (minimum torque), Mh (maximum torque), t_{c90} (optimum cure time), t_{s2} (scorch time) is registrated

The tensile tests dumbbell-shaped samples are cut from the molded rubber sheets according to TCVN 4509-2006. Both tensile strength and elongation at break are determined on an Instron 5582 Universal Testing Machine with a crosshead speed of 300 mm/min. Tear strength is determined on an Instron 5582 Universal Testing Machine with a crosshead speed of 300 mm/min according to TCVN 1592-1987. The hardness test is carried according to TCVN 1959-88 on TECHLOCKTGS 709N equipment. Abrasion test is carried according to DIN 35588 on GOTECH (Taiwan). Thermal aging test is carried in 150^{0}C for 168 hours according to ISO 4195:2012.

2.2.2. Formulation and preparation procedures

Because SBR was vulcanized using DCP curing agent, the cure system has much influence on the machining conditions of rubber. In order to studies the effect of various accelerators on curing process, formulations were developed and listed in Table 1.

Table 1. Basic formulation for curative studies

Sample	A	B	C
SBR, phr	100	100	100
Stearic acid, phr	1.5	1.5	1.5
Vulkanox 4020, phr	1.5	1.5	1.5
Zinc oxide, phr	5	5	5
HAF N330, phr	40	40	40
MBT, phr	-	1.5	
DM/TMTD, phr	-	-	1.5
EM 331, phr	2	2	2
Paraffinic Oil, phr	5	5	5
DCP, phr	2	2	2

The mixing process is described in Figure 1. Compound is carried out in the Toyoseiky internal mixer with banbury rotor blade. The rotor speed is set at 50 rpm in 70^{0}C. Firstly, SBR is put in the mixing chamber for mastication in 10 mins. After that, the additives are stepwise added to the mixture according to the diagram in Figure 1. In the end of the mixing step, the compound is kept stable in room temperature and vulcanized at 160^{o}C with the suitable time.

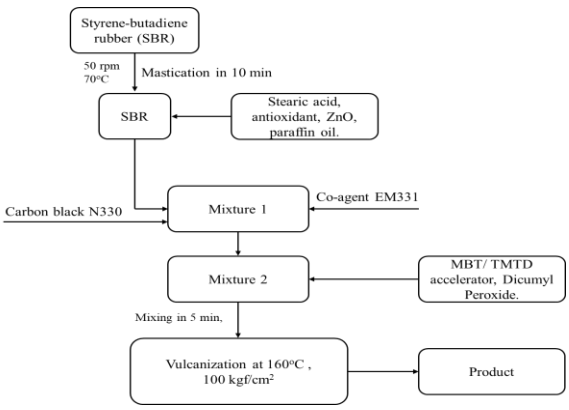

Figure 1. Processing of mixing SBR.

3. Results and Discussions

3.1. Effect of accelerator to curing behavior and physical properties of SBR

By using rotor less rheometer, the cure characteristics are showed in Table 2:

Table 2. Vulcanization characteristic of SBR with different accelerators

Sample	MH, dN.m	ML, dN.m	t_{10}, min	t_{90}, min
A	31.98	2.87	2.37	23.83
B	25.77	2.89	2.28	23.16
C	22.72	2.97	2.07	18.80

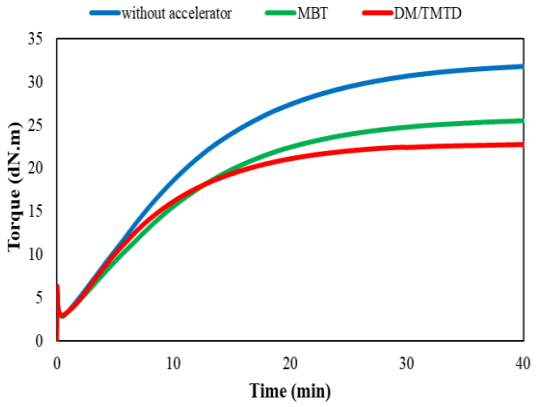

Figure 2. Curing curve of SBR with different accelerators.

As the results showed in Table 2 and Fig 2, the initial viscosity of mixture (ML) and the scorch time (t_{10}) were quite similar for all samples. However, the maximum torque which is attributed to the optimal vulcanization time (t_{90}) slightly decrease when accelerator were introduced.

The induction time of sample using co-accelerator DM/TMTD was shorter than sample using MBT in a comparison. It could be explained that the combination of DM and TMTD is fast accelerator system with cure rate higher than MBT. Moreover, it also contain amount of sulfur in the structure. During vulcanization process, sulfur was released and contributed to the cross-linking reaction, leaded to reduce the vulcanization time.

This is very important in industry because of it could be decrease the processing time, save the energy during vulcanizing process and save the production costs.

Figure 3 and 4 illustrate the results of mechanical properties of SBR with various accelerators.

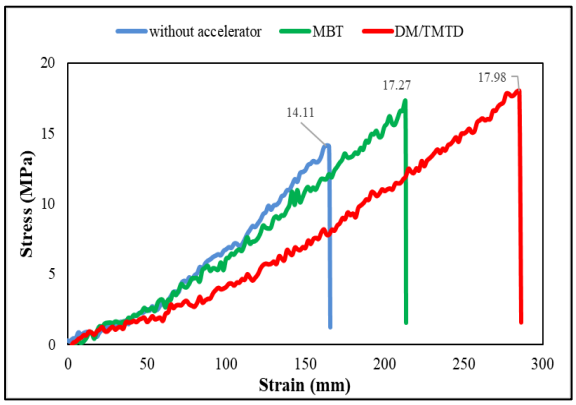

Figure 3. Stress-strain curve of SBR with various accelerators.

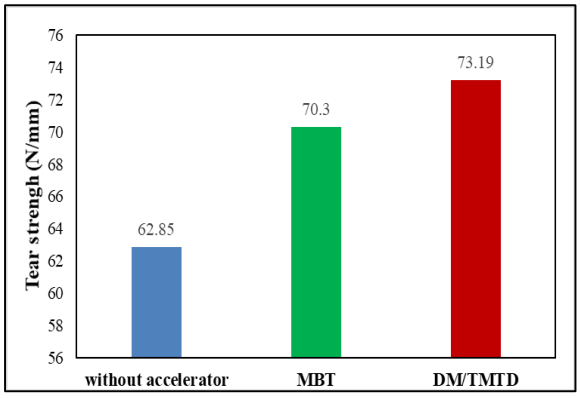

Figure 4. Tear strengh of SBR with various accelerators

It can be seen that the using of DM/TMTD given the highest values of physical properties in the rubber. The tensile strength increases 27.4% (from 14.11 MPa to 17.98 MPa). The tear strength increases 16.5 % (from 62.85 N/mm to 73.19 N/mm). This was probably due to the fact that the increase of cross-link density because of the presence of disulfide compound in the structure of DM and TMTD. Based on the curatives experimental studies, the DM/TMTD co-accelerators have been selected and used in the followed steps.

3.2. Effect of DCP content to physical properties of SBR

A various SBR samples with different DCP dosage from 1 to 5 phr were prepared. The results are shown in Figure 5, 6, 7 and 8.

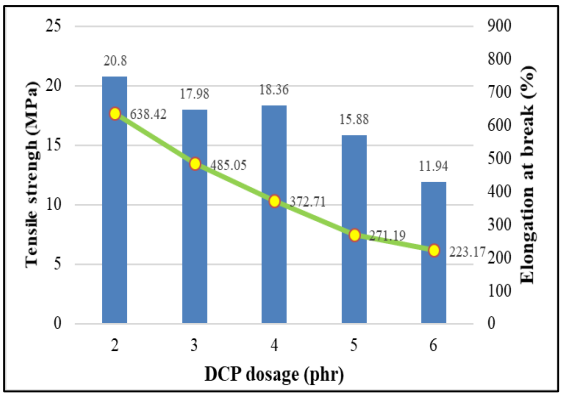

Figure 5. Effect of DCP dosage to the tensile strength and elongation at break of SBR.

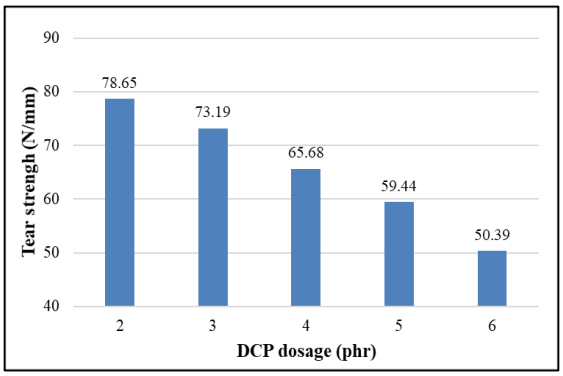

Figure 6. Effect of DCP dosage to the tear strengh.

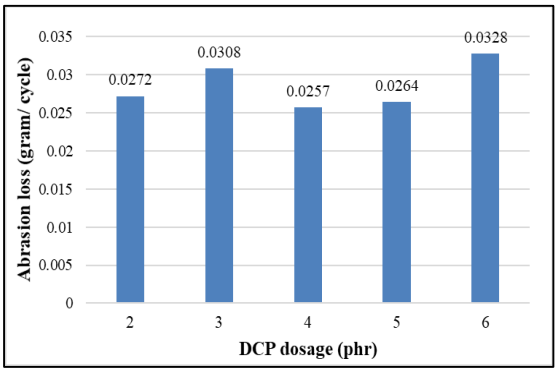

Figure 7. Effect of DCP dosage to the abrasion resistance.

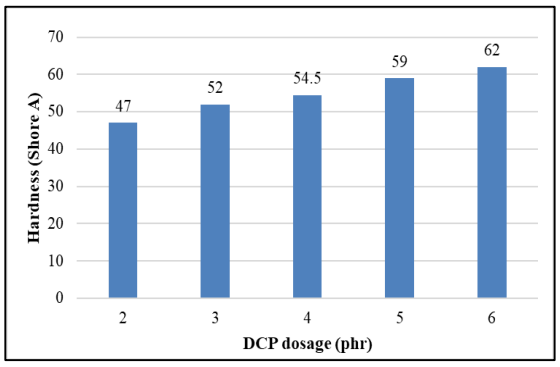

Figure 8. Effect of DCP dosage to the hardness.

According to the results, when the DCP dosage increase to 2 phr, the physical properties tend to increase and slightly decrease after reaches the highest values. In the case of the compounds containing high dosage of DCP, the residual free radicals are generated during vulcanization process may participated to the chain scission reaction, lead to the reduction of properties [4]. As depicted in Figure 7, the abrasion loss of SBR samples is fluctuated around 0.02 gram/ cycle. It can be said that the DCP proportion doesn't much impact to the abrasion resistance of SBR compound. Regarding the hardness, the chain scission contributed to the increase of crosslink density as well as increases the hardness of SBR. In this study, the SBR was also vulcanized by sulfur in order to make a comparison with the samples, which are vulcanized by DCP curing agent. The tensile strength, elongation at break and tear strength are show in Table 3.

Table 3. Effect of curing agent to mechanical properties of SBR.

Sample	Tensile strength, MPa	Elongation at break, %	Tear strength, N/mm
D1	15.7	179	55.0
S1	15.7	244	30.0
D2	**17.9**	**285**	**73.2**
S2	**17.5**	**280**	**31.7**
D3	17.3	272	65.6
S3	14.8	165	30.2
D4	15.9	248	59.4
S4	13.8	163	25.9

Note:

The sample name D1-D4 and S1-S4 are the sample used different curing agents, DCP and Sulfur, respectively; with the dosage correspond to 1-4 phr.

It can be seen that when the curing agent are not higher than 2 phr, with the both DCP and sulfur cure system, the tensile strength are similar. However, the tear strength of sample using DCP is much more higher. When the curing agent dosage increases up to 3 and 4 phr, the physical properties of rubber compound always higher for vulcanizing system used DCP. Therefore, it is possible that DCP is the appropriate curing agent for SBR vulcanization.

3.3. Effect of EM-331 on thermal aging properties of SBR

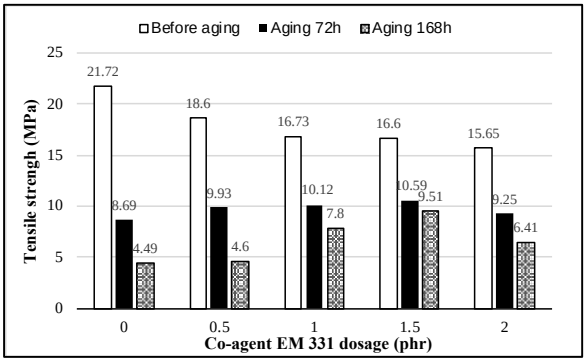

Figure 9. Effect of co-agent EM331 dosage to the tensile strength of SBR before and after thermal aging.

With the purpose manufacturing the rubber material with good thermal resistance, low thermal aging factor, trimethylolpropane trimethacrylate (EM 331) was added in the SBR compound. Based on the results in Figure 9, when EM 331 was introduced to SBR formulation, the tensile strength after thermal aging is slightly increase then decrease. It is well known that the using of functional co-agent contributed to increase the total linking in SBR during vulcanization process [5]. Furthermore, the polymerized co-agent could play an important role like a transfer-load factor upon external

strain [6]. However, with 2 phr of DCP given the optimal crosslink density, the residual EM 331 may cause to polymerization and generate the internal polyacrylate between rubber chains. This leads to reduce the effectiveness interaction of SBR chains as well as reduce the tensile strength.

Figure 9 also showed the results of thermal aging at 150^0C, after exposed 168 hours in high temperature, the SBR without EM 331 show the higher retention level of tensile strength compare with SBR used EM 331. Thus, the addition of trimethylolpropane trimethacrylate EM 331 in the SBR compound provides the great heat resistance and decrease the thermal aging.

3.4. Effect of nano silica to thermal properties of SBR

Due to the low thermal conductivity of rubber (usually has a coefficient of thermal conductivity less than 0.6 W/m*K), additives can be used to improve the thermal conductivity is also one of the methods to get higher properties. The effect of nano silica content to thermal conductivity of SBR is shown in Table 4.

Table 4. Effect of nano silica content to thermal conductivity of SBR

Nano silica content, %	Lambda, W/(m*K)
0	0.672
1	0.731
3	0.811
5	0.729

The results in Table 4 shows that the coefficient of thermal conductivity (Lambda) of SBR compounds increase by adding nano silica. The coefficient thermal conductivity increases from 0.672 W/m*K (sample without nano silica) to 0.811 W/m*K (sample of 3% nano silca). However, the coefficient of thermal conductivity tends to decrease when 5% nano silca is added (0.729 W/m*K).

This can be explained by nano-sized silica, which has functional groups on the surface capable of binding to rubber molecules and has made the material block become tighter. However, when the amount of silica nano introduced is large (in this case, it is greater than 5%), the silica nanoparticles have the phenomenon of agglomeration in the mixing process, which leads to breaking the homogeneous structure of the polymer. However, the introduction of nano silica with content below 5 phr, the decrease in thermal conductivity is negligible.

4. Conclusion

Dicumyl peroxide DCP is well used as a curing agent for SBR. The results show that the physical properties of SBR compound vulcanized by peroxide system were similar with SBR compound vulcanized by sulfur when the DCP proportion was 2 phr. Additionally, the studies also demonstrate that the functional co-agent EM 331 plays a significant role in peroxide vulcanization of SBR. The addition of 2 phr of co-agent dosage is not only increasing the physical properties but also the heat resistance of SBR rubber.

Nano silica gives good effect for thermal conductivity coefficient of SBR and the best nano silica content was 3%. The thermal conductivity coefficient increases by more than 20.68%, from 0.672 W/m*K by SBR to 0.811 W/m*K by SBR/nano silica (3%) composites. This will probably have a good effect on finished product properties when blending SBR rubber with other types of synthetic rubber, which have different vulcanizing properties.

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