

## Plasticization Effect of Hydrogenated Transgenic Soybean Oil on Nitrile-Butadiene Rubber

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**ABSTRACT:** Nitrile-butadiene rubber (NBR) compounds were prepared with different amounts of hydrogenated transgenic soybean oil (HTSO) as renewable plasticizers. For comparison, similar compounds were prepared with petroleum-based dioctyl-phthalate (DOP), one of the most common plasticizers for NBR. Four HTSOs with different degree of hydrogenation were used, of which three HTSOs are prepared by hydrogenation reaction at different reaction conditions and one is commercial available. The plasticization effects of HTSO and of DOP were studied by Mooney viscometry, capillary rheometry, differential scanning calorimetry (DSC), and rubber processing analysis (RPA). The results showed that all the HTSOs had better plasticization effect than DOP on NBR. The swelling index result showed that the highly-hydrogenated-HTSO plasticized NBR vulcanizate have higher crosslinking density than the low-hydrogenated ones. It is worthy to mention that, the introduction of high-hydrogenated-HTSO greatly improved both the processability of the NBR compounds and the mechanical performance of the final products, which is hard to achieve for most of the plasticizers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40643.

**KEYWORDS:** applications; composites; elastomers

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### INTRODUCTION

Nitrile butadiene rubber (NBR) is one of the most important synthetic rubbers because of its large production, excellent oil-resistant performance, and good air tightness.<sup>1–3</sup> However, most of the NBR raw rubbers are hard to be processed due to the high viscosity. Thus, plasticizer is usually added during the mixing procedure to reduce its viscosity and improve its machinability.<sup>4,5</sup> One of the most common plasticizer for NBR is phthalate esters, which are derived from fossil resources and have adverse effects on our health.<sup>6,7</sup> Recently, most of the phthalate ester plasticizers were forbidden in the European Union Countries. Therefore, it is very important and urgent to explore alternative renewable plasticizers for NBR.

Soybean oil (SO) has become one of the biggest plant oils since transgenic soybean was successfully developed, which ensured a low price of SO about \$750/ton. SO, containing 23.4% of oleic, 53.3% of linoleic, 7.8% of linolenic, and around 15% of palmitic and stearic acids, has been used since

the early nineties in many products like soaps, paints, coatings, lubricants, plastics, and elastomers.<sup>8</sup> The major application of SO is as food; however, TSO with the same structure of SO, was controversial if TSO is suitable for human consumption because the ingestion of transgenic corn was found lead to cancer.<sup>9</sup> Therefore, reconsideration of the application of TSO was needed. Our group has recently used TSO as a renewable plasticizer to plasticize ethylene-propylene-diene monomer (EPDM), and we found TSO has better plasticization effect than that of paraffin oil.<sup>10</sup> It was also found that, during the crosslinking process, TSO consumed the curing agents and finally decrease the crosslinking density because of the large amount of double bonds in TSO.

As a derivative of TSO, hydrogenated transgenic soybean oil (HTSO) is also commercially available with a price around 1000\$/ton. By adjusting the hydrogenation degree, different HTSO with different amounts of double bonds could be obtained. The HTSO with small amount of double bonds will have little influence on the crosslinking density of the rubbers.

When compared with the phthalate esters, HTSO is not only a kind of ester but also renewable and nontoxic. Thus, HTSO would be an excellent plasticizer for NBR as a potential replacement of the phthalate esters. However, there is no report about using HTSO as plasticizer for rubbers.

Diocetyl-phthalate (DOP), one of the few available phthalate esters, is the most commonly used plasticizer for NBR. However, this petroleum-based plasticizer is also harmful to our health. In this study, we first use the commercial HTSO and DOP to plasticize NBR in order to explore the possibility of replacing DOP with HTSO as the plasticizer. Then three HTSOs with different degrees of hydrogenation were prepared with a new catalyst from our lab, and the plasticization effects of these HTSOs along with the commercial one on NBR were studied.

## EXPERIMENTAL

### Materials and Formulation

Transgenic soybean oil (TSO) with an iodine value (the weight of absorbent iodine per 100 g of TSO) of 141.7 was a gift from Shandong Wandefu industrial group, Ltd. The catalysis Pd/Rh is made in our lab. Carbon black N330 was purchased from Tianjin Dolphin Carbon Black Development Co. NBR 230S, with 28% AN as the comonomer was purchased from Jilin chemical factory. The Mooney viscosity (Z100°C 1 + 4) of NBR 230S is 50. The commercial available HTSO is a gift from Shandong Liaocheng essence of medicinal materials. Other chemicals and rubber curing additives were all analytically pure and were purchased from HWRK Chemical, China.

### Preparation of Hydrogenated Transgenic Soybean Oil

The hydrogenation reaction of TSO was carried out in a 500 mL reaction vessel. Hundred grams TSO was first added in the reaction vessel, then 0.5 wt % catalysis Pd/Rh was added. Three conditions were used to get HTSO with different degree of hydrogenation: 60°C and 1 Mpa, 100°C and 3 MPa, and 160°C and 3 MPa. The reaction time is 3 h. These obtained HTSOs were named HTSO-1 (60°C and 1 Mpa), HTSO-2 (100°C and 3 Mpa) and HTSO-3 (160°C and 3 Mpa), respectively.

### Mixing and Curing of NBR Compounds

The blending of NBR 230S with carbon black (N330, 50 phr) was carried out on a two-roll mill ( $\Phi$  160 mm, Zhanjiang Machinery Factory, Guangdong Province, China) with a roller spacing of 0.5 mm. HTSO/DOP, zinc oxide (ZnO), stearic acid (SA), accelerators, and Sulfur (S) were added in turn according to the formulation given in Table I. The ingredients were processed on the mill for about 40 min in order to obtain homogeneous NBR compounds. The NBR compounds with different contents of DOP or HTSO were named NBR-DOP/HTSO-*n* (*n* = 5, 10, 15, and 20). The NBR compounds with different type of HTSO were named NBR-HTSO-1–15, NBR-HTSO-2–15, and NBR-HTSO-3–15, respectively. The rubber compounds were then vulcanized by using a compression molding press (Shanghai Rubber Machinery Factory, Shanghai, China) for the curing time of  $T_{90}$  (as determined by a disc rheometer, P355B2, Beijing Huanfeng Chemical Technology and Experimental Machine Plant, Beijing, China) at a pressure of 15 MPa and a temperature of 160°C.

**Table I.** Formulation for NBR Composites

Ingredient	Grams per hundred grams of rubber (phr)
NBR 230S	100
Plasticizer (DOP and HTSO)	Variable (5, 10, 15, and 20)
Carbon black (N 330)	50
ZnO	5
Stearic acid	1.5
Accelerator M	0.8
Sulfur	1.5

### Characterization

**Mooney Viscosity.** The Mooney viscosity was measured by using a Mooney Viscometer (M3810C, Beijing Huanfeng Chemical Industry, China) according to ASTM D 2084 and ASTM D 1646 [Z100°C (1 + 4) min].

**Shear Viscosity.** The shear viscosity was obtained by an Instron 3211 Capillary Rheometer (Instron, UK) at 60°C after the sample was heated for 5 min. The diameter of the capillary was 0.0628 inch.

**Rubber Machinability.** The rubber machinability was measured by using a Rubber Process Analyzer (RPA2000, Alpha Technologies Services LLC, USA) at 60°C and a scanning frequency of 1 Hz.

**Glass Transition Temperature ( $T_g$ ).** The  $T_g$  of the vulcanizate was determined by a STARE system DSC1 Instruments (Mettler-Toledo International, Switzerland). The samples in the form of small rectangles about 0.2 mm thick were accurately weighed and sealed in aluminum crucibles. The temperature was first raised to 100°C at 10°C/min, allowed to stay there for 5 min to eliminate any thermal history and moisture from the sample, and then lowered to -100°C at 10°C/min. Data were recorded in the temperature range -100 to 50°C at a heating rate of 10°C/min. The nitrogen flow was 150 mL/min.

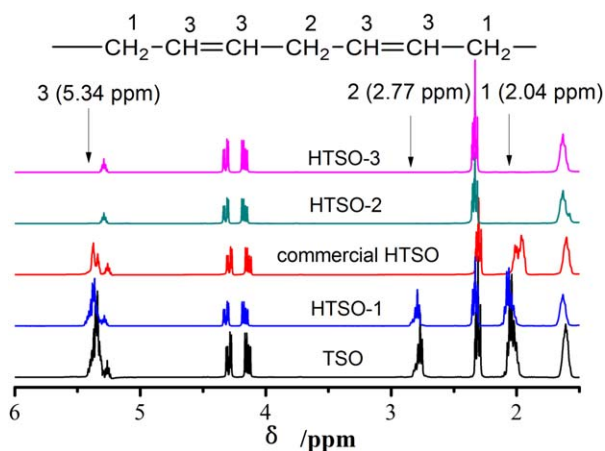
**Cure Characteristics.** The cure characteristics were measured on a Disc Rheometer (P355B2, Beijing Huanfeng Chemical Industry, China) at 160°C.

**Mechanical Properties.** The mechanical properties of all vulcanizates were measured at 25°C according to ASTM D638 with a CMT4104 electronic tensile tester (SANS, China) at a cross-head speed of 500 mm/min. The dumbbell-shaped samples (25 × 6 × 2 mm<sup>3</sup>) were prepared according to ISO/DIS 37–1990.

**<sup>1</sup>H NMR.** <sup>1</sup>H NMR spectra were recorded by using a Bruker AV400 NMR spectrometer (Bruker, Germany) at a frequency of 400 MHz with CDCl<sub>3</sub> as solvent.

**Swelling Index.** The swelling index data were tested by standard GB/T 7763-87. Cyclohexanone was used as solvent. The constant temperature is 30 ± 0.5°C.

**Iodine Value.** The Iodine values of the HTSOs with different hydrogenation degrees were tested by standard GB/T 1676–1981.



**Figure 1.**  $^1\text{H}$  NMR spectra of the HTSOs with different degree of hydrogenation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## RESULTS AND DISCUSSION

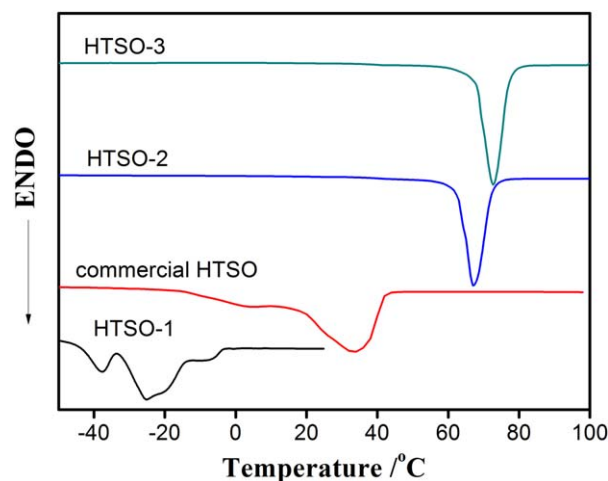
### Preparation and Characterization of Hydrogenated Transgenic Soybean Oil with Different Degrees of Hydrogenation

It is already confirmed that TSO is an excellent plasticizer for EPDM from our previous work<sup>10</sup>; however, it was also found that the introduction of TSO reduced the crosslinking density because the double bonds of TSO could react with the crosslinker. Petrović synthesized polymerized soybean oil by cationic method and successfully reduced the influence of soybean oil on crosslinking density.<sup>11</sup> In this study, three HTSOs with different degrees of hydrogenation were prepared by hydrogenation of TSO to reduce the amounts of double bonds. In addition, a commercial available HTSO was also studied here. Figure 1 shows the  $^1\text{H}$  NMR spectra of these HTSOs. The signals at  $\delta$  5.34 ppm,  $\delta$  2.77 ppm, and  $\delta$  2.04 ppm are attributed by the protons of  $-\text{HC}=\text{CH}-$ ,  $=\text{CH}_2-\text{CH}_2-\text{CH}=\text{}$ , and  $-\text{CH}_2-\text{CH}_2-\text{CH}=\text{}$ , respectively. With high temperature and pressure, the signals attributed by the protons of the double bonds are weak and even disappeared, indicating a high degree of hydrogenation. The degrees of hydrogenation of these HTSOs were also confirmed by the iodine value results. The iodine values of the four HTSOs are 133.7 (HTSO-1), 65.9 (commercial HTSO), 3.8 (HTSO-2) and 2.8 (HTSO-3), which were tested by GB/T 1676–2008 standard. There are only 0.1 double bonds in one HTSO-3 molecular, which means HTSO-3 is nearly saturated.

From the DSC thermograph (Figure 2) we can see that, with increasing degree of hydrogenation, the melting points of the HTSOs largely increases. The multiple broad melting points of HTSO-1 are all below  $0^\circ\text{C}$  due to the amorphousness of the unsaturated oil components. Hydrogenation makes the oil more crystalline and hence sharp melting peak appears. At the room temperature, HTSO-1 is liquid and the other three HTSOs are all solid.

### Comparison of Plasticization Effects of DOP and the Commercial HTSO on NBR

The commercial HTSO is easy to get; thus, we first use this HTSO as plasticizer for NBR. Since DOP has proved an

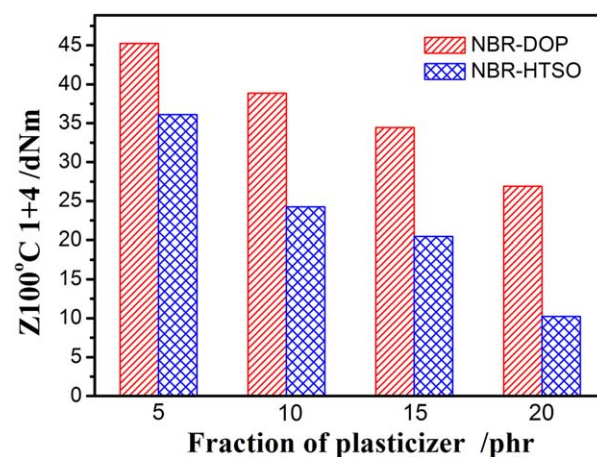


**Figure 2.** DSC curves of the HTSOs with different degree of hydrogenation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

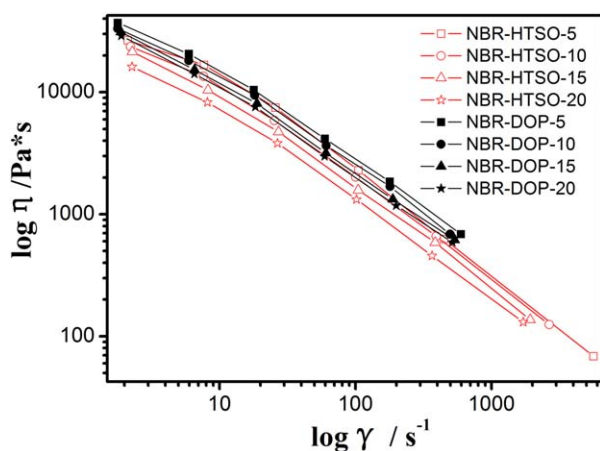
excellent plasticizer for NBR, the plasticization effect of HTSO with that of DOP on NBR were compared at the same plasticizer content and same processing conditions. During the process of the NBR blends, it was found that the solid HTSO was easier to mix with the NBR blends than the liquid DOP. The plasticization effects were determined by Mooney viscometry and capillary rheometry.

**Mooney Viscosity.** The Mooney viscosities of the HTSO- and DOP-plasticized NBR compounds are compared in Figure 3. At the same plasticizer content, the Mooney viscosity of the NBR compound plasticized by HTSO is much lower than that of the compound plasticized by DOP. This result indicates that HTSO can better improve the machinability of NBR than DOP. The Mooney viscosity of NBR-HTSO-10 is even lower than that of NBR-DOP-20.

**Shear Viscosity.** The shear viscosities of the NBR compounds were measured by a capillary rheometer to further demonstrate the plasticization effects of DOP and HTSO on NBR. Figure 4



**Figure 3.** Mooney viscosity of NBR compounds plasticized by different fractions of HTSO and DOP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

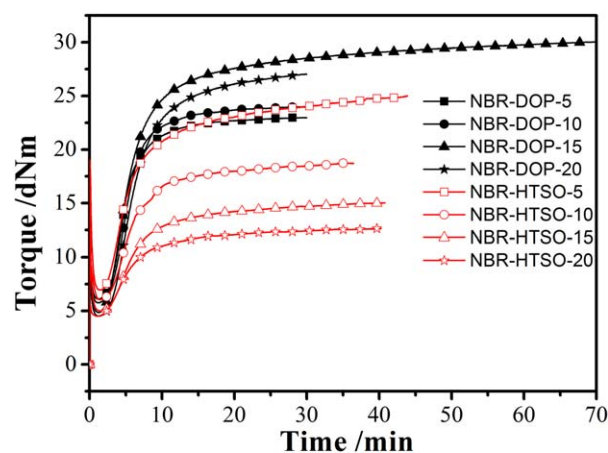


**Figure 4.** Capillary rheological curves of NBR compounds plasticized by different fractions of HTSO and DOP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

shows that the shear viscosity of all the NBR compounds decrease with increasing shear rate, a typical non-Newtonian behavior. With the same plasticizer content, the shear viscosity of NBR-HTSO is much lower than that of NBR-DOP. The appearances of the NBR-HTSO extrudates were smoother than that of the NBR-DOP extrudates, which also indicates better processability of NBR-HTSO compounds than NBR-DOP compounds.

The Mooney viscosity and shear viscosity results both showed that HTSO has a better plasticization effect on NBR than DOP does. To further explore the possibility of replacing DOP with HTSO, the effects of DOP and HTSO on the cure characteristics and mechanical properties of the end-products were studied.

**Cure Characteristics.** The cure characteristics were determined by a curometer, and the vulcanization curves of the HTSO- and DOP-plasticized NBR compounds are shown in Figure 5. It can be seen that with increasing plasticizer content, the



**Figure 5.** Cure behavior of NBR compounds plasticized by different amounts of HTSO and DOP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

maximum torque of the DOP plasticized NBR rubber slightly decreases, while the maximum torque of the HTSO plasticized NBR rubber significantly decreases. This phenomenon indicated that the remaining double bonds in the commercial HTSO could still influence the crosslinking density of the final products. To solve this problem, increase the amount of crosslinker and increase the hydrogenation degree are two effective ways.

**Mechanical Properties.** The mechanical data of the vulcanized NBR plasticized by different amounts of DOP and HTSO are shown in Table II. It shows that at the same plasticizer content, the tensile modulus at 100% elongation and the Shore A hardness of the HTSO-plasticized NBR is lower than that of the DOP-plasticized NBR, because the HTSO-plasticized NBR has lower crosslink density than that of the DOP-plasticized NBR. The low crosslinking density of the HTSO-plasticized NBR rubber are harmful for the mechanical properties, thus, at the same

**Table II.** Mechanical Properties of Vulcanized NBR Plasticized with Different Fractions of HTSO and DOP

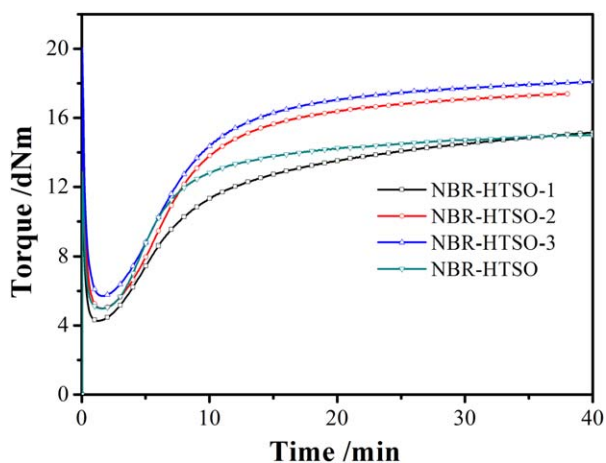
Sample	NBR-DOP-5	NBR-DOP-10	NBR-DOP-15	NBR-DOP-20	NBR-HTSO-5	NBR-HTSO-10	NBR-HTSO-15	NBR-HTSO-20
Shore A Hardness	72	68	65	56	70	65	63	53
Tensile strength/MPa	20.4 ± 0.6	17.1 ± 0.5	16.7 ± 0.4	16.1 ± 0.4	17.2 ± 0.6	12.8 ± 0.6	11.1 ± 0.3	8.8 ± 0.3
Tear strength /kN m <sup>-1</sup>	65.4 ± 0.6	59.0 ± 0.5	50.0 ± 0.4	48.9 ± 0.5	60.1 ± 0.6	50.3 ± 0.8	40.8 ± 0.3	36.9 ± 0.4
Modulus at 100% elongation (MPa)	2.6 ± 0.2	1.9 ± 0.1	1.7 ± 0.1	1.6 ± 0.1	1.8 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	1.3 ± 0.1
Modulus at 300% elongation (MPa)	13.5 ± 0.3	8.7 ± 0.2	7.7 ± 0.2	7.3 ± 0.2	8.2 ± 0.2	6.4 ± 0.2	6.0 ± 0.1	4.7 ± 0.1
Elongation at break (%)	432 ± 13	492 ± 11	506 ± 15	530 ± 15	484 ± 21	474 ± 27	420 ± 31	365 ± 42

**Table III.** Mooney Viscosity Data of the NBR Compounds Plasticized by Different HTSO

	NBR-HTSO-1-15	NBR-HTSO-2-15	NBR-HTSO-3-15	NBR-HTSO-15	NBR-DOP-15
Z100°C 1 + 4 (dNm)	13.97	15.41	17.37	14.61	34.14

**Table IV.** Mechanical Properties of Vulcanized NBR Plasticized with Different HTSO

Sample	NBR-HTSO-1-15	NBR-HTSO-2-15	NBR-HTSO-3-15	NBR-HTSO-15	NBR-DOP-15
Shore A hardness	58	65	67	63	65
Tensile strength (MPa)	13.9 ± 0.5	18.2 ± 0.4	22.8 ± 0.5	11.1 ± 0.3	16.7 ± 0.4
Tear strength (kN m <sup>-1</sup> )	42.0 ± 0.6	50.0 ± 0.4	50.7 ± 0.7	40.8 ± 0.3	50.0 ± 0.4
Modulus at 100% elongation (MPa)	1.6 ± 0.1	2.6 ± 0.1	2.8 ± 0.2	1.5 ± 0.1	1.7 ± 0.1
Modulus at 300% elongation (MPa)	4.3 ± 0.2	8.7 ± 0.2	11.0 ± 0.2	6.0 ± 0.1	7.7 ± 0.2
Elongation at break (%)	695 ± 11	525 ± 14	514 ± 15	420 ± 31	506 ± 15

**Figure 6.** Vulcanization curves of the NBR compounds plasticized by different HTSO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

plasticizer content the HTSO-plasticized NBR rubber has lower tensile strength and tearing strength than that of DOP-plasticized NBR.

In summary, the commercial HTSO exhibits better plasticization effect on NBR compounds than DOP, and HTSO could greatly improve the machinability of the NBR compounds. Though the mechanical properties of HTSO-plasticized NBR rubber is lower than that of DOP-plasticized NBR rubber, we can improve the mechanical properties of the HTSO-plasticized NBR rubber by increase the amount of crosslinker, which was already confirmed by our previous works.<sup>10</sup>

#### Comparison of Plasticization Effects of the HTSOs with Different Degree of Hydrogenation on NBR

To improve the mechanical properties and avoid the influence of HTSO on crosslinking density, we also studied the plasticization effect of the highly hydrogenated transgenic soybean oil (HTSO-2 and HTSO-3) on NBR rubbers, along with the low-hydrogenated transgenic soybean oil (HTSO-1). The amount of

the HTSOs was fixed at 15 phr. The plasticization effect of different HTSO on NBR compounds and the mechanical properties of the final products were compared. Table III shows the Mooney viscosity data of the NBR compounds plasticized by different HTSO. It can be seen that the NBR compound plasticized by the HTSO with higher hydrogenation degree has higher Mooney Viscosity. All the HTSO-plasticized NBR compounds have lower Mooney viscosities than that of DOP-plasticized NBR compound, indicating all the HTSOs can better improve the machinability of NBR than DOP.

The mechanical data of the vulcanized NBR plasticized by different HTSO are shown in Table IV. It shows that with increasing hydrogenation degrees of HTSO, the tensile strength, tearing strength, Shore A hardness, modulus at 100% elongation, and modulus at 300% elongation of the vulcanized NBR rubber increase while the elongation at break slightly decrease. The high hydrogenation degree of HTSO is not good for the plasticization effect on NBR, but it can significantly improve the mechanical properties of NBR. The tensile strength of NBR-HTSO-3-15 is even as high as 22.8 ± 0.5 MPa, and the elongation at break is comparable with NBR-DOP-15. The good crystallization property of HTSO-3 from the DSC result may be one of the reasons of the excellent mechanical properties. Moreover, the weak influence of the highly-hydrogenated transgenic soybean oil (HTSO-3) on crosslinking process of NBR could be another reason.

**The Influence of Hydrogenation Degree of HTSO on Cross-Linking Process.** The influence of HTSOs with different hydrogenation degrees on the crosslinking process was studied by the crosslinking dynamics method and swelling index testing. It can be seen from the vulcanization curves (Figure 6) that, with increasing hydrogenation degree of HTSO, the maximum torque of the NBR compounds increase, indicating an increasing crosslinking density. The increase of the crosslinking density can also be further confirmed by the swelling index data (Table V). Low swelling index value means high crosslinking density. From Table V we can see that, with increasing hydrogenation degree of HTSO, the swelling index value indeed decrease.

**Table V.** Swelling Index Data of Vulcanized NBR Plasticized with Different HTSO

Sample	NBR-HTSO-1-15	NBR-HTSO-2-15	NBR-HTSO-3-15	NBR-HTSO-15
Swelling index	4.11 ± 0.05	3.41 ± 0.04	3.38 ± 0.04	4.02 ± 0.04

## CONCLUSIONS

When compared with DOP, the commercial HTSO also exhibited excellent plasticization effect on NBR. At the same plasticizer content, the HTSO-plasticized NBR showed lower Mooney viscosity and shear viscosity than DOP-plasticized NBR, indicating that the addition of HTSO can lead to better machinability than that of DOP. The mechanical properties of the HTSO-plasticized NBR, such as tensile strength, tear strength, and elongation at break, are not as good as those of the DOP-plasticized NBR because of the decrease of crosslinking density. To improve the mechanical properties and avoid the influence of crosslinking density on NBR, two highly-hydrogenated transgenic soybean oils (HTSO-2 and HTSO-3) were prepared along with one low-hydrogenated transgenic soybean oil (HTSO-1) for comparison. The structures of these HTSOs were characterized by  $^1\text{H}$  NMR method, and the remaining amounts of double bonds in these HTSOs were confirmed by both  $^1\text{H}$  NMR results and iodine value results. After hydrogenation, the mechanical properties of the HTSO-plasticized NBR were greatly improved. At the plasticizer content of 15 phr, the tensile strength of NBR-HTSO-3 (22.8 MPa) is much higher than that of DOP-plasticized NBR (16.7 MPa).

## ACKNOWLEDGMENTS

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