Effects of *Trans*-Polyoctenylene on the Mechanical Properties of NBR

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Synopsis

Trans-polyoctenylene (TOR), a high-polymer polymerization product of cyclooctene, has found use as a processing aid in high-viscosity rubber stocks. We have compared some physical and mechanical properties of a NBR-compound with TOR with those of the same compound without TOR. Mooney viscosity was lower for the compound with TOR. Cylinders with a height and diameter of 20 mm were molded. It was found that stress–relaxation measured in the common static way was almost the same for the two compounds. Dynamic stress–relaxation occurred much more rapidly for the compound with TOR. The compound with TOR increased in hardness more rapidly when aged in air, and showed a higher swelling in oil. The DSC results imply that TOR is incorporated as a separate phase in the parent rubber. The sealing properties are affected detrimentally when TOR is used as a processing aid in NBR.

INTRODUCTION

Trans-polyoctenylene (TOR) is a polymerization product of cyclooctene. It was originally synthesized by Natta et al.[1] using methathesis, a metal-ion catalyzed rearrangement reaction. TOR has one double bond on every eighth carbon, and is a semicrystalline polymer.

The TOR used in this study was made by Hüls in FRG and commercialized as Vestenamer 8012. The producer claims[2] that, in this product, about 80% of the double bonds are in the trans position. The mean molecular weight is between 50,000 and 60,000. For the pure material, the melting point is at about 55°C and the glass transition temperature at about −75°C. Crystallinity is evaluated to 33%.

TOR is proposed as a processing aid especially in very hard and highly filled rubber stocks. Descriptions of the function of processing aids are to be found in almost any book in rubber technology.[3] There are two main groups of processing aids: those having a physical effect on the properties and those that work in a chemical manner. An example of the latter group is the peptizers. Processing aids having a physical influence on the properties of the rubber are, for example, petroleum oils, petroleum jelly, and ester plasticizers. These additives make processing easier, but they can have a detrimental effect on long-term properties, staining, and color stability, and they can also affect adhesion to other rubbers and metals. Methacrylate esters used as polymerizable plasticizers in peroxide-vulcanized rubbers are said to ease the processing and thereafter contribute to an increase in hardness, stiffness, and state of cure in the vulcanizate by participating in the crosslinking reaction.

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Obviously a compound incorporating TOR has a lower viscosity at the melting temperature of TOR, 55°C. The manufacturer says[2] that the addition of TOR facilitates the processing of a rubber compound by:

—lowering internal heating and diminishing energy consumption during blending,

—making incorporation of fillers faster and making the dispersion of them better,

—lowering viscosity so that extrusion, injection molding, and calendering are more easily accomplished,

—increasing green strength,

—facilitating the mixing of two rubber materials of different polarity.

It is said that vulcanisates with TOR have improved cocrosslinking properties[4]; TOR is not blooming or otherwise evaporating[2] and is rather insensitive to leaching.[2]

EXPERIMENTAL

The aim of the study was to find out whether this product is preferable to other processing aids. For this reason two NBR compounds were made having the compositions shown in Table I. In the compound TOR–NBR, 15% of the parent rubber was replaced by TOR. The Mooney viscosity was measured on the uncured compounds. After curing, some mechanical and physical properties were measured.

Weight gain in oil 3 according to ASTM D 471 was measured at 85°C. Heat capacity as a function of the temperature was studied with a DSC apparatus

TABLE I
Compositions of the Rubber Compounds

Ingredients	Weight (g)	
	NBR	TOR–NBR
Perbunan N 2807[a]	100	85
Vestenamer 8012[b]	—	15
ZnO	5	5
Stearic acid	2	2
Koresin[c]	3	3
Dioctylftalate[d]	5	5
Vulcanox HS[e]	1	1
FEF N550[f]	70	70
Tionex[g]	1.5	1.5
Vulkacit I[h]	1.5	1.5
Structol SU135[i]	2	2

[a] Nitrile rubber.
[b] *Trans*-polyoctenylene.
[c] A tackifier.
[d] A plasticizer.
[e] Polymerized trimethyldihydroquinoline, an antioxidant.
[f] Carbon black.
[g] *Tetra*-methyl-thiuram monosulfide.
[h] Dimethyl-diphenyl-thiuram-disulfide.
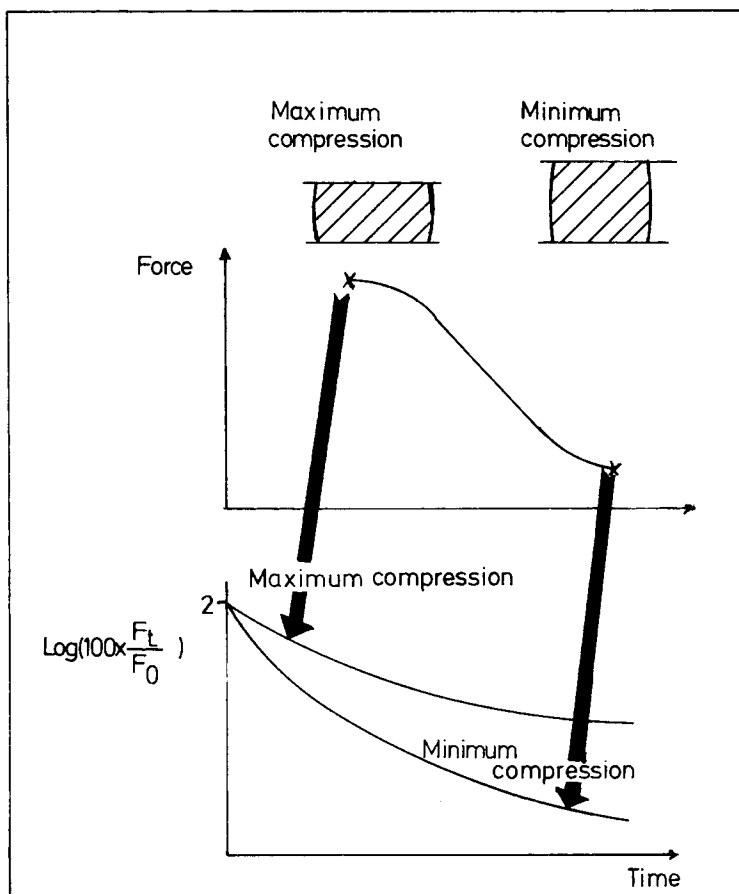[i] Sulfur (a 75% Masterbatch).

Fig. 1.   Principle for measurement and data presentation of dynamic stress–relaxation.

(Perkin-Elmer DSC 2) both on the two compounds and also on pure TOR. The heating rate was 10 K/min. Cylindrical specimens were molded, with both height and diameter equal to 20 mm. On these specimens hardness change during aging in air at 85 and 100°C was recorded. Weight gain in oil 3 (ASTM 471) was measured at 85 and 100°C. Permanent set after 168 h in 85°C air was measured, the specimens were compressed to 80% of their original height. After thermal aging the specimens were left to recover for 1 h at room temperature. Permanent set was calculated as $100 \times (H_0 - H_R)/H_0 - H_C)$, where H_0 is uncompressed height, H_C is compressed height (here $0.8 \times H_0$), and H_R is recovered height.

Weight change during extraction in *p*-xylene was also studied. Static compression relaxation was measured as described in Ref. 5. Dynamic stress–relaxation was also measured. Dynamic stress–relaxation is a measurement method that offers information about how a rubber material relaxes when deformation is not constant. The apparatus in described in Ref. 6, and the principle shown in Figure 1. The dynamic compression is built up of a prestrain on which a sinusoidally varying compression is superimposed. Here the prestrain was 4 mm, which is 20% of the original height, and the

amplitude of the sinusoidally varying strain was 1 mm, which is 5% of the original height. The difference between maximum compression and minimum compression was twice the amplitude, i.e., 2 mm. The force is recorded at maximum compression and at minimum compression. This means that the force was recorded when the specimen was 15% compressed (minimum compression), and 25% compressed (maximal compression). The force reaches its maximum at maximum compression, and its minimum at minimum compression. Since the compression varied sinusoidally, the force varied in the same manner. A dynamically loaded sealing gives its poorest tightening effect at minimum compression, when the restoring force has its smallest value.

The results are presented in diagrams as the common logarithm of 100 times the force at time t divided by the force at time zero plotted as a function of the time. When the results are presented in this way, two curves are obtained that start at the same point at zero time. In earlier studies, made on natural rubber,[6] it was found that the curve for stress–relaxation at minimum compression decreases faster than the curve for maximum compression. This behavior is quite alarming because the restoring force at minimum compression governs the difference in pressure which the sealing can maintain. The force at minimum compression is smallest from the beginning and has the fastest relaxation.

RESULTS AND DISCUSSION

The Mooney viscosity of the uncured NBR was lowered from 88 to 80 by the addition of TOR. After leaching in p-xylene, the weight change was about the same for the two NBR compounds, indicating that it seems to be impossible to leach out the TOR from the cured TOR–NBR compound. This is in good agreement with the supplier's claims. Swelling in oil 3 (ASTM 471) reached equilibrium at 13% weight gain for the NBR compound and at 20% weight gain for the TOR–NBR compound. The permanent set was the same
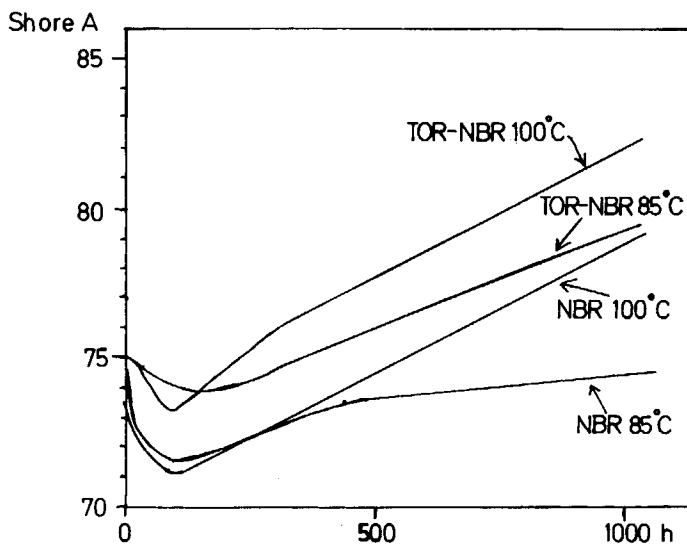

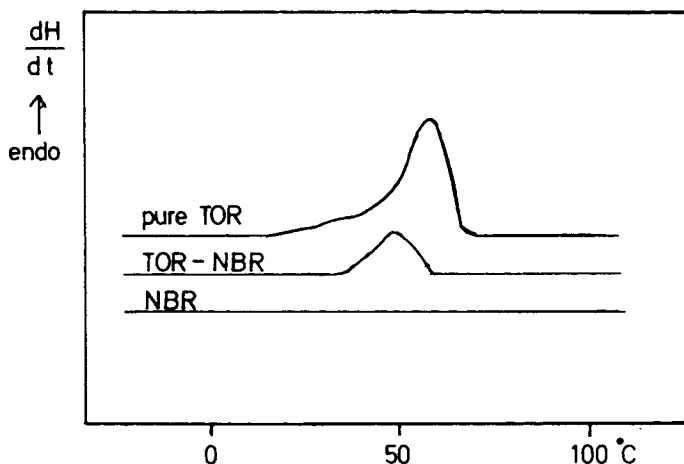Fig. 2.   Results for hardness measurements.

Fig. 3.   Results from DSC studies of pure TOR, NBR, and TOR-NBR.

for the two compounds, about 13%. The hardness change in air at 85 and 100°C is shown in Figure 2. At both temperatures, the TOR–NBR compound shows the fastest increase in hardness. Thermograms from the DSC study of pure TOR and the NBR compounds with and without TOR (Fig. 3) show that the parent NBR compound has no melting peak, TOR–NBR has a melting peak at a temperature slightly under that where melting of pure TOR occurs. It is obvious that TOR in this TOR–NBR compound melts. This implies that TOR is dispersed as a separate phase in the parent polymer, as has also been reported by other researchers.[4] Thus the material properties are probably influenced when the temperature is raised above 55°C.
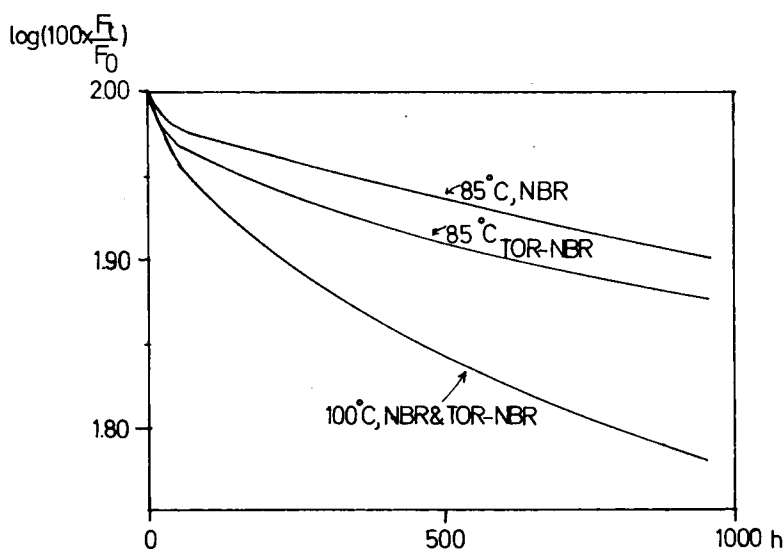

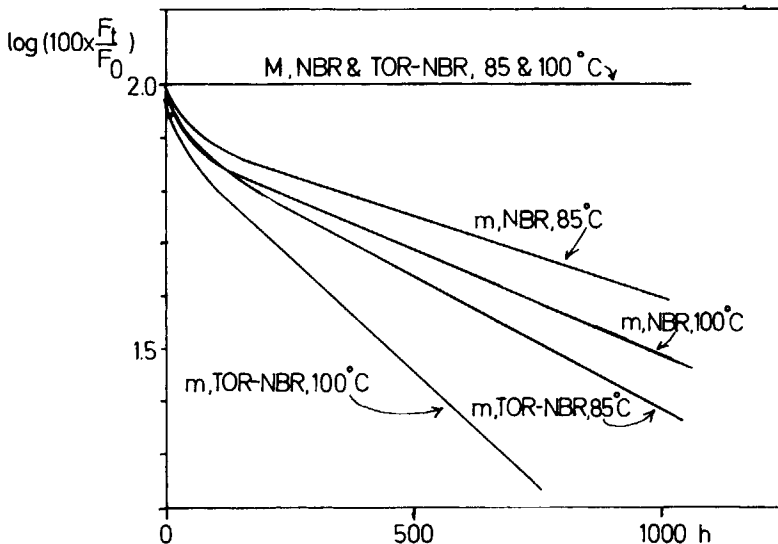Fig. 4.   Results from measurement of stress relaxation in air at 85 and 100°C.

Fig. 5. Results from dynamic stress relaxation in air at 85 and 100°C. Curves for relaxation at minimum compression is denoted by m and relaxation at maximum compression is denoted by M.

Stress–Relaxation Measurements

Stress–relaxation measurements were made at 85 and 100°C with air as surrounding medium. Results from static stress relaxation studies (Fig. 4) show a small difference between the NBR and the TOR–NBR vulcanizate at 85°C, and no difference at 100°C. For dynamic stress–relaxation (Fig. 5), the results are, however, quite different. The relaxation curves for minimum compression, which provides information about the sealing capacity of the material, decreases much faster for TOR–NBR than for the parent NBR compound. An explanation of the higher relaxation rate in the TOR–NBR compound could be that the TOR phase in the TOR–NBR compound is easy to deform irreversibly. Even if there is some cocrosslinking between the parent rubber and the TOR, the TOR phase itself is perhaps not crosslinked, and thus not truly rubbery. It is probably very difficult to disperse the crosslinking agent into the low-viscosity zones of TOR inside the TOR–NBR compound. When the material is deformed, these liquid zones are irreversibly deformed. Dynamic stress–relaxation, but not static stress–relaxation, reveals this deterioration in the mechanical properties. In this study the measurements were made at temperatures higher than the melting point of TOR. It is possible that measurements at temperatures lower than +55°C would not show this very fast dynamic stress–relaxation. Sealings made from a TOR–NBR compound can probably not be recommended for use at temperatures above +55°C.

CONCLUSIONS

The TOR–NBR compound has a lower Mooney viscosity than pure NBR. The DSC study implies that TOR is incorporated as a separate phase in the parent rubber. When the TOR–NBR vulcanizate is leached in boiling p-xylene,

no TOR is removed from the material. TOR–NBR absorbs more oil 3 (ASTM 471) than NBR. Incorporation of TOR in NBR has some influence on the mechanical properties of the material: e.g., hardness increases in hot air more rapidly, and the relaxation rate for minimum compression under dynamic stress is much faster. These effects on the mechanical properties are not revealed by the measurement of static stress–relaxation and permanent set. It is obvious that the incorporation of TOR leads to a deterioration in the sealing properties of NBR.

References

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