Natural Rubber/Butadiene Rubber/Ethylene-Propylene-Diene-Monomer blends by Various Approaches and therefore Improves the Final Mechanical Properties

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Abstract - Ethylene-Propylene-Diene rubber (EPDM) possesses excellent ozone, heatand ageing resistance due to its highly saturated chemical structure. It is well known that incorporation of saturated EPDM rubber into high-diene rubbers, such as natural rubber (NR) and (butadiene rubber) BR, is a way to achieve non-staining ozone resistance for tyre sidewall applications instead of using conventional antiozonants, such as N-1,3-dimethylbutyl,-N'-phenyl-para-phenylenediamine (6PPD), which have staining effects and leach out via migration. For reason of the difference in molar concentrations of double bonds and the difference in polarity, blending of EPDM with high-diene rubbers generally gives the following problems: thermodynamicincompatibility of these types of rubber, cure incompatibility and heterogeneous reinforcing filler distribution in each of the rubber phases.

Keywords – EPDM, High-diene rubber,N-1,3-dimethylbutyl,-N'-phenyl-para-phenylenediamine (6PPD)

I. INTRODUCTION

Rubber is a fantastic material and is widely used in our normal lives due to itsspecial characteristic: visco-elasticity. Use of a single rubber is rarely adequate formanufacturing of rubber products. Therefore, blends of rubbers are achieving moreand more technological and commercial interest since they provide an acceptabletechnological process for accessing properties not available in a single elastomer.The potentially improved properties include chemical, physical and processing benefits. Changing intra-molecular composition, such as making block copolymers, isa way to achieve tunable properties as well. However, this is limited by availablesynthesis processes. Intermolecular changes, such as adjusting composition ordistribution of components in blends, are not limited by such synthetic limitations andare commercially preferred.

II. STUDIES ON EPDM MODIFICATION BY N-CHLOROTHIO-N-BUTYL-BENZENESULPHONAMIDE

Ethylene propylene diene rubber (EPDM) is a highly saturated elastomer, which is widely used in applications that require good ozone resistance. It has long been known that the ozone resistance of high-diene rubbers such as natural rubber (NR), styrene-butadiene rubber (SBR), nitrile rubber (NBR) and butadiene rubber (BR) can be greatly improved by the incorporation therein of EPDM1. However, the vulcanizes of such elastomer blends are generally poor in both static and dynamic mechnical properties, such as ultimate strength-related properties, fatigue resistance, hysteresis, etc.

2.1. Materials

N-chlorothio-N'-butyl-benzenesulphonamide (CTBBS) was prepared using n-butylamine (99.5%, Aldrich), triethylamine (99.5%, Aldrich), dichloromethane (99.9%, Biosolve), benzenesulphonyl chloride (99.0%, Aldrich), sulphurdichloride (98%, Fluka) and diethyl ether (99.8%, Fluka). The elastomers selected for the blend were natural rubber (SIR20, Standard Indonesian Rubber), butadiene rubber (Kosyn KBR01, Korea Kumho Petrochemical Co.,Ltd) and four types of EPDM rubber: Table 3.1. The other compounding ingredients used were extra pure grade zinc oxide (Merck, Germany), finely divided sulphur (Merck, Germany), 95% pure stearic acid (Aldrich, Germany), poly(2,2,4-trimethyl-1,2-dihydroquinoline) or TMQ (Flexsys B.V., the Netherlands) and N-cyclohexyl-2-benzothiazolesulphenamide (CBS).

2.2. Results and Discussion

2.2.1. Grafting of CTBBS onto different types of EPDM in solution

Grafting of CTBBS onto EPDM was first tried by the solution technique. The reacted EPDM was then characterized by ATR and NMR to check whether grafting occurred.

2.2.2. Comparison of the various EPDMS

It is remarkable that grafting happens for ENB-EPDM and HD-EPDM, but not for DCPD-EPDM. Figure 3.8 shows the structure of the three diene monomer types built into EPDM. The different reactivity of the double bond in their structure is the reason for the different behaviors of those three EPDMs during CTBBS-grafting. Considering the difference in reaction speed, the reactivity of the three EPDMs towards grafting varies in the order ENB-EPDM > HD-EPDM > DCPD-EPDM. Unfortunately, the CTBBS-grafting in the case of ENB-EPDM is accompanied by a strong tendency towards gelation due to cationic side reactions.

3.3. CONCLUSIONS

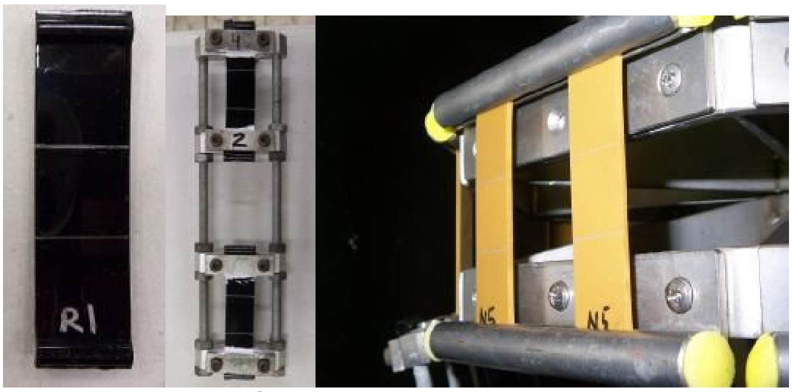
N-chlorothio-N-butyl-benzenesulphonamide (CTBBS) has a different behavior with respect to grafting on various EPDM-types. The highest grafting efficiency can be reached for HD-EPDM. No grafting is observed for DCPD-EPDM. ENB-EPDM has the highest reactivity, however gelation is observed even at low conversions. The highest grafting level achievable for LENB-EPDM is 20% relative to the available unsaturation, and for HENB-EPDM, evens less.

III. MALEIC-ANHYDRIDE GRAFTED EPM AS COMPATIBILISING

There is a great technological interest in the use of blends of various rubbers to achieve tunable enhanced properties. But blending of dissimilar rubbers is severely restricted due to lack of technological compatibility of the component rubbers. Three types of mutual incompatibility can generally exist between dissimilar elastomers: incompatibility due to viscosity mismatch which prevents or greatlydelays the formation of intimate blends1; thermodynamic incompatibility, which prevents mixing on the molecular scale; and incompatibility due to cure rate mismatch2.

3.1. Static and dynamic ozone testing

The ozone resistance of the blends was tested according to ISO 1431-1 in an Argentoxozone test cabinet (Argentox Ozone Technology GmbH, Germany) under ;



(a) (b) (c)

Figure 4.1Test specimen (a) and test configuration in ozone cabinet: static condition (b), dynamic condition (c).

MAH-EPM as compatibilising agent: mechanical properties both static and dynamic conditions. The test specimens were 20mm in width and 2mm in thickness with modified ends, as shown in figure 4.1. For the static ozone test, the specimens were clamped between grips, elongated to 20% and tested under the following conditions: temperature 40±2oC; relative humidity 50±5%; ozone concentration 50±5pphm for the first 96 hours, and100±5pphm for the next 96 hours. The test is normally carried out at an ozone concentration of 50±5pphm. In the present study, after the first dynamic test at 50±5pphm ozone concentration and 20% elongation for 96 hours, no compound showed cracks on the surface. Further test-runs on the same test specimens were then carried out consecutively in order to be able to differentiate between each compound.

3.2 Results and Discussion

3.2.1 Tensile and tear properties

Stress-strain curves for the gum and HAF-filled blends, respectively. It is clear that both the gum- and HAF-filled-Ref-1 compounds show much poorer tensile properties than Ref-0, commonly blamed on viscosity mismatch, thermodynamic incompatibility, cure incompatibility and inhomogeneous filler distribution. EPM-5 shows even worse tensile properties compared to Ref-1, for the gum blend as well as for HAF-filled blend. The addition of MAH-EPM does improve the tensile properties though compared to the straight NR/BR/EPDM Ref-1 blends in both the gum and HAF-filled cases. Again, the addition of NPD-EPM does not improve and even damages the stress-strain properties for the gum blend. Also no significant changes for the filled blend were achieved relative to Ref-1.

3.3 Conclusions

MAH-EPM was added as compatibilising agent to NR/BR/EPDM blends, both gum and HAF-filled. Straight EPM an NPD-EPM were also studied for comparison. The mechanical properties of NR/BR/EPDM rubber blends are clearly improved by the addition of 5phr MAH-EPM. Straight EPM and NPD-EPM do not bring improvement to the blends properties. The tensile strength of the MAH-EPM compatibilised blend is much higher than the straight NR/BR/EPDM blend and is even very close to the NR/BR tyre sidewall compound. Higher modulus, better trouser tear strength and slightly increased elongation at break are also obtained by applying MAH-EPM to the NR/BR/EPDM blends. An improvement of the fatigue-to-failure property is also observed after the addition of MAH-EPM, when the test is carried out at constant strain energy instead of at the same extension. All these improvements suggest that MAH-EPM does improve the compatibility and the carbon black distribution between NR/BR and EPDM, next to some smaller effect of additional ionic crosslinking with ZnO. The ozone resistance under both static and dynamic conditions of all the NR/BR/EPDM and NR/BR/EPDM/EPMs blends with 30phr of EPDM and EPMs is comparable to the NR/BR compounds with 6PPD. The anti-ozonant 6PPD can therefore be omitted from 30phr EPDM-containing tyre sidewall compounds.

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