Effect Of The Nitrile Content On Nitrile Rubber Cure In Wide Temperature Range.

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Abstract— Vulcanization of NBR rubber with different nitrile content was studied. Enthalpy of vulcanization drops from 6.62J/g for 18% nitrile rubber to 1.89J/g for 40% one. The peak of vulcanization shifts to higher temperatures for 12°C with nitrile content increase. No secondary vulcanization process was observed for 18% nitrile rubber. The other rubbers possess thermal polymerization at 285°C in neat rubbers accelerated by nitrile groups. This process is additionally accelerated when vulcanization additives are present in rubber. Thus the post-vulcanization peak shifts up to 20°C to lower temperatures for 40% nitrile rubber with increase in enthalpy in 5 times compared to neat rubber. When heated at 250°C for 6 hours no significant change in rubber hardness is occurred for 18% nitrile rubber and 2 times increase for 40% nitrile rubber is measured indicating dramatic role of nitrile content for rubber properties. No considerable effect of nitrile groups cross link on rubber hardness is observed.

Index Terms— cross-link, cure, DSC, hardness, NBR, nitrile, properties, rubber, vulcanization

1 Introduction

Acrylonitrile–butadiene rubber (NBR), commonly known as nitrile rubber, has been commercially available for more than 50 years. NBR has great potential in industry because of its moderate cost, excellent resistance to oils, fuels and greases, easy processibility and very good resistance to swelling by aliphatic hydrocarbons. About 80% of NBR produced is used for machinery and automobile industry [1]. One of the applications of NBR is production of gasket material working in hard conditions including high temperature [2]. The investigation of thermal resistance [3-6] as well as vulcanization [7, 8] of nitrile rubber and its composites has a great scientific and industrial importance.

In this paper the influence of nitrile content on vulcanization and post-vulcanization processes and resultant properties is studied.

2 Experimental

2.1. Material and methods

NBR rubber in thin powder state with 18%, 33% and 40% nitrile content (technical grade) and EPDM was provided by SIBUR and used without purification.

Sulphur, MBT, stearic acid, TMTD, ZnO, toluene were provided by FlukaTM and used without purification

DSC curves of the samples were measured on Netzsch DSC 211 Polyma instrument in nitrogen flow at heating rate of 10 Kpm.

Hardness of rubbers was measured on shore durometer.

2.2. Samples preparation

Nitrile rubber (powder) was gradually added at constant stirring to the solution of sulphur, MBT, stearic acid and TMTD in toluene until homogeneous viscous solution is obtained. ZnO was added to the mixture at constant stirring. No sedimentation of ZnO particles occurred due to viscosity of the rubber solution. The resulted mixture is poured into silicon paper box and rest for night for primary solvent evaporation. After that the resulted film was dried at 50°C in vacuum to a constant weight.

Several layers of the resulted film were molded at 150°C and 7.5MPa load for 30 minutes to obtain vulcanized rubber samples of 8mm thickness.

Heat treatment of the rubber samples was carried out in the same mold form at 200°C and 250°C for 6 hours at 0.25MPa load.

All the information about samples preparation is summarized in Table 1.

3 Results and Discussions

3.1. Rubber cure

The DSC curves for vulcanization process of rubbers with various nitrile content are shown on Fig. 1. The onset temperature as well as peak temperature is affected by nitrile content. One can see that both temperatures shift to higher values with increase of nitrile content. The possible reason of this effect is the influence of nitrile group on electron density distribution in the rubber molecule (see Fig. 2). Nitrile group being an electron acceptor (negative induction effect) reduces the electron density on the double bond in butadiene part which causes decrease of activity of rubber in vulcanization process since sulfphur vulcanization process has radical nature [9]. The same effect of nitrile groups is supposed to result in decrease of heat of vulcanization.

The summarized data for the influence of nitrile content on cure parameters of nitrile rubbers are shown in Table 2.

3.2. Rubber post-cure

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