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Crosslink Density Study on Rubber Vulcanizates Using a Dynamic Mechanical Analyzer

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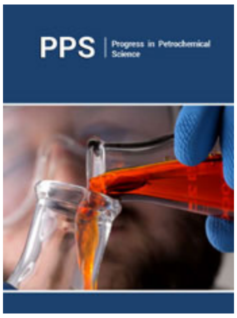

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Abstract

A quantitative method of measuring crosslink density by using a Dynamic Mechanical Analyzer (DMA) is described here in this study. This method is based on the measurement of storage modulus on cured vulcanizate samples through a simple temperature sweep. The Molecular weight between crosslinks and the crosslink density obtained by DMA was further compared with the solvent method using the Flory-Rehner approach. The selected rubber matrix was Natural Rubber (NR) and the study was carried out by the conventional vulcanization system. The cure time varied proportionately below and above the tC90 obtained through rheometric study at wide intervals.

Keywords: Modulus; Vulcanizate; Temperature; Molecular weight; Natural rubber

Abbreviations: DMA: Dynamic Mechanical Analyzer; NR: Natural Rubber; CV: Conventional Vulcanization

Introduction

The Crosslink density is an important requirement for understanding the functional properties of rubber vulcanizates. During crosslinking, polymer segments from different polymer chains get interconnected by covalent/ionic linkages. Conventional Vulcanization (CV) is the most common curing approach in industries. The change in crosslink density will have a direct influence on the Mechanical properties, which are the governing parameters for the performance of the final products like tyres. There are different techniques available to detect the crosslink density like Mooney Rivlin, Thiol-amine method, Dynamical flocculation model, Temperature Scanning Stress Relaxation, NMR method, etc. [1]. The conventional method of determination of cross-link density by the Flory-Rehner Equation is the most common approach [2]. Flory-Rehner described the mixing of polymer and liquid molecules as predicted by the equilibrium swelling theory. This process is time-consuming and needs interaction parameters in which most cases are not available. In this study, the mixing of rubber compounds was carried out in two stages (Master and Final) in a 1.5L volume Laboratory Banbury mixer (Stewart Bowling, USA) having a two-wing tangential rotor with a temperature control unit. Initially, the natural rubber along with the peptiser (DBD) was added into the mixer and masticated for the 30s. Followed by, the carbon black, process oil, zinc oxide, stearic acid, and process aids, were added to the mixer. The master batch was dumped after a total of 300s. The dump temperature (display) of the master batch compounds was found to be between 140 and 145 °C. The master batch compound along with the curative package, viz, sulfur, TBBS, and DPG was added into the mixer at 0s and dumped after 180s. The observed display dumb temperature of the final batch compound was found to be between 90-95 °C. The tensile slabs were compression moulded at different cure rate by using Hydraulic curing press (Hind Hydraulics, India). Based on the tc90’ (min.) value from the rheometric study, slabs were cured at 20% to 200% (at an interval of 20%) and 300% of tc90’ (min.) respectively for this study. Crosslink density measurements through the swelling method are performed and calculated by using Flory-Rehner Equation[1] for comparison with Dynamic Mechanical Analyzer measurements. Crosslink density measurements by Dynamic Mechanical Analyzer are performed through a Temperature Sweep. The Molecular weight between the crosslinks was calculated by using the following equation [3].

$$M_e = 2\left(1+v\right)\rho RT / E \quad \text{(Equation 1)}$$

Where, M_e is Molecular weight between the crosslinks (g/mol) by using Dynamic Mechanical Analyser, v is the Poisson ratio (0.5), is the Polymer density in (g/cc), R is the gas constant, T is the absolute temperature and E' is Storage Modulus (MPa) from Dynamic Mechanical Analyzer.

$$V_e = \frac{\rho}{M_e} \quad \text{(Equation 2)}$$

Where V_e is crosslink density per unit volume in mol/cc by Dynamic Mechanical Analyzer Method and M_e obtained from Equation 1. Temperature sweep of cured rubber vulcanizates was performed by using a Dynamic Mechanical analyzer from ACOEM, France. Cured test pieces were subjected to a Temperature from 60 °C to 120 °C at the constant dynamic strain of 0.2% and at a frequency of 1Hz. The tests were carried out in tension mode. The specimen for tension mode was punched out from the slabs. The specimen dimension was a strip of 25mm in length, 10mm in width, and 2.0mm ± 0.2mm in thickness. The test length was 10mm ± 1.0mm with the remainder of the strip in the grips. Table 1. Crosslink Density by Swelling is always lesser compared to DMA studies. However, the trend remains the same. There is an increase in the crosslink density upon increasing the cure rate in both studies Figure 1. Chemical crosslinks are studied in Swelling Method whereas both the Physical and Chemical crosslinks have been measured in the DMA Study Figure 2 [4].

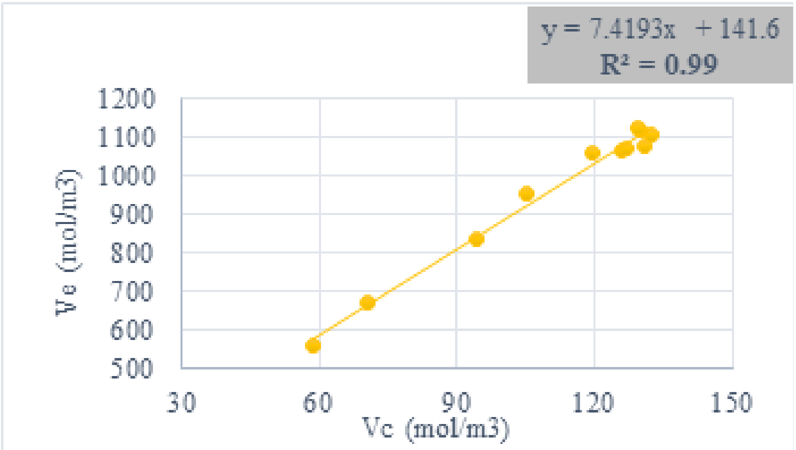

Figure 1: Cross Link Density Study DMA vs Swelling Study.

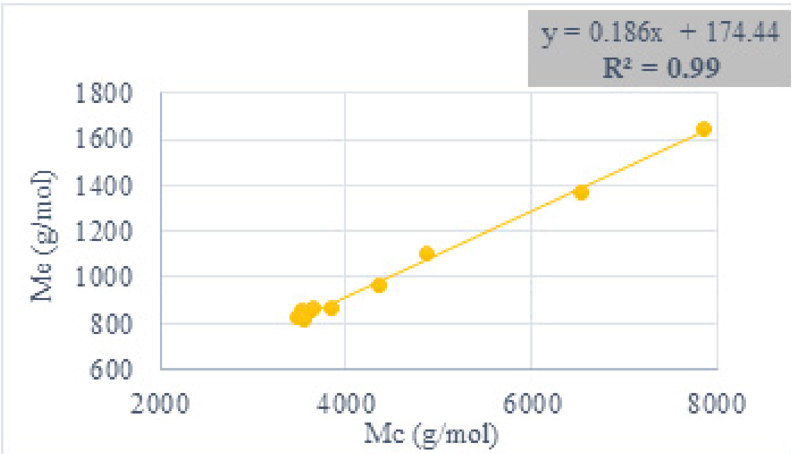

Figure 2: Molecular Weight Between Crosslinks DMA vs Swelling Study.

Table 1: NR CV study.

Percent Cure Time	E' at 90 °C (MPa)	V_e by DMA (mol/m^3)	V_c (mol/m^3)	M_e by DMA (g/mol)	M_c (g/mol)
20% tC90	5.07	559	59	1645	7842
40% tC90	6.08	671	71	1371	6517
60% tC90	7.58	837	94	1099	4871
80% tC90	8.65	955	105	963	4362
tC90	9.58	1058	120	869	3845
120%tC90	9.63	1065	126	865	3647
140%tC90	9.68	1069	127	860	3629
160%tC90	9.77	1079	131	853	3521
180%tC90	10.03	1107	132	831	3476
200%tC90	10.13	1118	130	823	3535
300%tC90	10.17	1123	129	819	3556

Conclusion

The results show a good correlation between the Crosslink density measurement study using Dynamic Mechanical Analyzer and the conventional Flory-Rehner approach. In addition to the crosslink density measurements, understanding the molecular weight between the crosslinks is also possible by using DMA Method. The test method is less time-consuming and involves very few assumptions compared to the swelling method.

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