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Test Method

Viscoelastic behaviour of silica filled natural rubber composites – Correlation of shear with elongational testing

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ABSTRACT

Dynamic mechanical behaviour of natural rubber-silica composites was studied by a frequency sweep method at different temperatures (40 °C,70 °C and 100 °C) using a dynamic mechanical analyzer and a rotorless rheometer, RPA, in an attempt to establish a correlation between the two. The composites with silica content up to 40 phr were studied. It was found that the dependence of dynamic modulus on the frequency as obtained from both the instruments followed a similar trend. This suggests that the dynamic mechanical properties of rubber compounds can be determined even during curing. A correlation could be arrived at between the two sets of data, making it possible to predict one set knowing the other. The impact of silane coupling agent, bis (3-triethoxysilylpropyl tetrasulphide), TESPT, on viscoelasticity was also investigated. The mechanical properties were improved in the presence of TESPT. Additionally, an increase in thermal stability was also observed in the presence of TESPT. Scanning electron micrographs showed the better filler dispersion in the case of silane-coupled silica composites.

1. Introduction

The dynamic mechanical properties of vulcanized elastomer play a major role in the performance of many rubber products such as tyres. The dynamic mechanical and thermal behaviour are significantly dependent on temperature and test frequency. The complete account of the viscoelastic properties can be obtained by performing dynamic experiments over a range of time, temperature or frequency. Dynamic mechanical analyzers are designed to measure the response of a material to controlled sinusoidal deformation. The test is typically done in tensile mode. The Rubber Process Analyzer (RPA) is another powerful instrument which can provide the response of cured as well as uncured rubber compounds to sinusoidal deformation, particularly in shear mode [1]. It is possible to measure the viscoelastic properties of rubber by varying strain and frequency in one test. The single test provides data of rubber compounds before, during and after cure. RPA measures the storage modulus G′, loss modulus G″, the loss factor tan δ, complex viscosity, η^* etc.

Dynamic mechanical properties of polymer composites have been extensively studied [2–10]. Most of these works deal with the study of time, temperature and strain dependent dynamic properties of materials. Thomas et al. reported that the dynamic mechanical properties of polymer composites were improved to a greater extent by the incorporation of natural fibre as filler [3,4]. The dynamic mechanical response of carbon black (N330) and modified carbon black filled vulcanizates to a wide range of temperatures and strains was investigated by J. J. Han et al. [5]. In their study, it was concluded that the improved matrix-filler interaction enhanced the dynamic mechanical properties of the vulcanizates.

Ramorino et al. developed a method to characterise the dynamic behaviour of rubbers by electro-dynamic shaker and compared with the data obtained from DMA [6], finding that the data were consistent. Konecny and co workers compared the complex modulus, E* measured by DMA in tensile mode and complex modulus, G* measured by RPA in shear mode over a range of strain amplitude using various types of carbon black and clay filled SBR rubber composites [7]. They observed that these amplitude dependent dynamic mechanical characteristics derived from two instruments had a linear relationship with high correlation coefficient.

In a dynamic mechanical test, the applied frequency play a vital role to the materials' mechanical response. The material becomes viscous or liquid behaviour predominates at low frequency range and the response is more elastic or behave as a solid at relatively high frequencies. Thus, the response of a viscoelastic material to a forced deformation is time dependent. Since time and frequency

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are inversely related, high frequencies are analogous to short times and long times corresponding to low frequencies. This behaviour is also similar to what happens with temperature changes. The change caused by increase of frequency is equivalent to that caused by decrease of temperature [8].

Frequency sweep experiments can provide a fingerprint of a material. It provides an effective method to study the molecular weight and molecular weight distribution. The modulus at frequencies below one reciprocal second showed marked changes in the storage modulus as the molecular weight distribution is broadened for a polymer melt. In view of these changes, subsequent product improvements could be made through adjustments in molecular weight distribution. The tack and peel performances of adhesives can be investigated by the frequency sweep tests [8]. Frequency scan studies at different temperatures can help to construct master curves to show the behaviour of material over several decades of time, and hence it is possible to predict the long term performance in specific operating conditions.

The viscoelastic properties of epoxidised trans 1,4-polyisoprene by frequency sweep studies were investigated by Huafeng Shao et al. [9]. Jean l. Leblanc et al. performed frequency sweep studies within the linear range at different temperatures of silica and carbon black filled SBR composites [10]. Master curves were created through time temperature superposition at a reference temperature of 100 °C.

Clearly, frequency dependent dynamic mechanical properties of different materials have been widely investigated. However, a systematic study on the frequency dependency of analogous dynamic mechanical characteristics from two different devices have not been reported. In this article, we report the dynamic mechanical properties of silica filled natural rubber composites as determined by the frequency scanning tests on a DMA and an RPA in an effort to identify probable correlation between the two test methods. The effect of filler loading and coupling agent on the dynamic mechanical properties are presented. The mechanical properties and thermogravimetric analysis of the composites are also studied.

2. Experimental

2.1. Materials

The natural rubber, ISNR-5, was procured from Rubber Research institute of India, Kottayam. The filler used was commercial silica. The coupling agent used was Si 69, imported from Degussa, Germany. Chemically, Si 69 is bis(triethoxysilylpropyl)tetrasulphide, TESPT. Zinc oxide, stearic acid, TMTD (tetramethylthiuramdisulfide), sulfur, CBS (cyclohexylbenzthiazylsulfenamide), TMQ (1,2-dihydro2,2,4-trimethylquinoline), DEG (diethylene glycol), naphthenic oil, used were of commercial grade.

2.2. Processing

The compounding was done on a two roll mixing mill (150 × 330 mm) as per ISO 2393. The rubber formulations are given in Table 1.

Table 1
Formulation and Compound Designation for NR composites.

Formulation[a]	S0	S10	S20	S30	S40	SS10	SS20	SS30	SS40
NR	100	100	100	100	100	100	100	100	100
Silica	0	10	20	30	40	10	20	30	40
TESPT	0	0	0	0	0	1	2	3	4
DEG	0	1	2	3	4	1	2	3	4
Naphthenic oil	0	1	2	3	4	1	2	3	4

[a] All weights are in parts per 100 g of rubber (phr). ZnO 5, stearic acid 2, TMQ 1, CBS - 0.8, TMTD 0.2, and sulfur 2.5 are common to all mixes.

2.3. Measurement of dynamic mechanical properties

2.3.1. Dynamic mechanical analyzer

A DMA Q800 (TA instruments) was used to measure the dynamic mechanical characteristics of rubber composites in tension mode. Measurements of storage modulus G′, loss modulus G″, and the loss factor tan δ were carried out as a function of frequency. Initially strain sweep experiments were done at a constant temperature of 100 °C to find the linear viscoelastic region. Frequency sweep experiments were then conducted over a frequency range of 0.01–33 Hz at 40 °C,70 °C and 100 °C within the linear viscoelastic region at a strain amplitude of 15 μm.

2.3.2. Rubber Process Analyzer

Dynamic rheological measurements were done in the cured state using a Rubber Process Analyzer (RPA 2000), Alpha Technologies). Strain amplitude corresponding to the linear viscoelastic region was determined and kept constant. The uncured samples were first cured to their respective cure times at 150 °C and the temperature was then reduced to the test temperature. The selected temperatures were 40 °C,70 °C and 100 °C. The sample was kept for a pre heating time of 4 min at each test temperature. The sample was then subjected to a frequency sweep from 0.03 to 33 Hz in a single sweep at a constant strain amplitude of 0.5° (7%).

2.4. Thermogravimetric analysis (TGA)

The thermal data of the samples was obtained by heating about 5–8 mg of dried sample from room temperature to 800 °C under nitrogen atmosphere at a rate of 20 °C/min in a TGA Q 50 Thermal Analyzer (TA Instruments).

2.5. Mechanical properties

Test pieces were cut from the compression moulded sheets. Tensile properties were measured using a Shimadzu Universal Testing Machine Model AG-I 10 KN as per ISO 37 using type 1 dumbbells cut along the grain direction. The gauge length was set at 40 mm and the testing speed was set as 500 mm/min at room temperature. The tear strength was determined by ISO 34–1 using crescent test pieces. The hardness of the sample was measured using a Shore A hardness tester according to ISO 7619.

2.6. Morphological studies

Examination of the tensile fracture surfaces of NR and silica filled NR and NR/Si/TESPT composites was carried out using JEOL Model JSM.6390 LV scanning electron microscope. The samples were gold plated to prevent specimen charging.

3. Results & discussion

3.1. Dynamic mechanical analysis by DMA & RPA

3.1.1a. Effect of strain

Fig. 1 shows the dependence of storage modulus at 100 °C on strain of the composites containing different filler loading. The modulus is found to be independent of strain at low strain levels. At higher strain levels, all the moduli tend to converge to a common point. The onset of non-linear behaviour occurs at lower strain amplitude on addition of filler, which is similar to the Payne effect [11]. The figure shows that the Payne effect is more prominent for 40phr silica composites. This is due to higher filler-filler networking. The decrease in modulus by increasing strain is due to the breaking down of filler-filler networking.