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Viscoelastic behaviour of filled, and unfilled, EPDM elastomer

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Abstract

The viscoelastic behaviour of gum and a highly filled ethylene-propylene terpolymer (automotive windowseal component) at 138 parts carbon black loading was investigated using a dynamic mechanical analyser over a wide range of time, temperature, strain and frequency. The tensile stress relaxation and recovery results of the gum system show time-dependent but strain-invariant behaviour, whereas the filled system shows both strain and time dependence. The relaxation time spectrum of the filled system reveals nonlinear viscoelastic behaviour. The networks of carbon black formed at such a high loading contribute significantly to the relaxation process. The 3D plot of tensile modulus as a function of time and temperature for both the systems follow a similar trend, and even for short-time testing the highly filled system appears to be time–temperature superposable. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Rheological behaviour; Ethylene–propylene terpolymer; Tensile stress relaxation

1. Introduction

Ethylene–propylene–diene terpolymer (EPDM) is emerging as a dominant elastomer in several engineering applications, particularly in applications that demand excellent chemical and thermal stability. As fillers are added, the systems exhibit quite complex rheological behaviour. The new engineering applications of these systems demand the accurate and reproducible determination of short-term mechanical response behaviour and prediction of long-term properties of gum and their filled compounds (both, in static and dynamic conditions). Thus, the prediction of those properties becomes a challenging task for rubber processors and end-users [1–4].

Elastomers, in general, are complex viscoelastic materials and their mechanical response behaviour depends strongly on the loading procedure, loading history, time (frequency) and temperature [5,6]. White et al. [7] investigated the rheological behaviour of EPDM rubber systems with various levels of carbon black using rotational and capillary instruments. The results of combined studies covered a wide range of shear rates or stresses. Normally, the viscoelastic relaxation of a polymeric material extends over several decades of time or frequency scale at a particular temperature. The instruments normally used to measure the viscoelastic behaviour of polymeric materials have limited time/frequency windows and depending on the experimental window, only a part of the total viscoelastic response is observed from experimental results. However, by using the time–temperature superposition principle it is possible to measure the viscoelastic data of a polymeric system at different temperatures over a limited period of time/frequency

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and construct composite curves that extend the effective time scale/the dynamic frequency range to a large extent. Time–temperature superposition is only possible in the case of linear viscoelastic and thermorheologically simple materials. The thermorheological simplicity demands that all molecular mechanisms present in the molecules have the same temperature dependence. In recent years, thermorheological complexity has been revealed in different polymeric materials, such as polystyrene, polypropylene and even in polyisobutylene [8–10]. They can be considered as different manifestations of the fact that all viscoelastic mechanisms involved (the side group rotation and crank shaft motions, responsible for the secondary relaxations (β, γ, δ, etc.); the co-operative segmental motions, responsible for the glass transition (α relaxation); and the terminal relaxation) have different temperature dependence and, therefore, exhibit different time-scale shift factors [8–10]. In such a case, the use of time–temperature superposition to predict the mechanical response behaviour is not a possibility.

Processability and final properties of most elastomeric products could be best evaluated by appropriate test on gum elastomers over different filler concentrations, temperatures and time. Both gum and filled compounds can provide significant insight into the microstructural understanding of the filler–rubber interaction of a highly filled system. The automotive windowseal compound, used in this investigation, is a highly filled and oil-extended [11,12] EPDM-based compound. The stress relaxation and dynamic mechanical behaviour of a gum and such highly filled EPDM composite were precisely determined over a wide range of strains, time, and temperatures. The linear viscoelasticity and possibility for the time–temperature superposition of the unfilled, and highly filled, EPDM systems have been examined.

2. Experimental

2.1. Materials

Ethylene–propylene–diene rubber (EPDM): JSR EP1O3AF was supplied by Japan Synthetic Rubber, JSR. The termonomer is ethylene norborene – 4% (ENB), ethylene:propylene ratio of 63:37, molecular weight 6.6×10^5.

Table 1
Formulations of the mix

Compounding ingredient	FILLED (phr)	UNFILLED (phr)
EPDM (JSR EP 103 AF)	100	100
Carbon black (N660)	138	–
ZnO	5	–
Stearic acid	1	–
PE wax	3	–
Aktiplast (zinc salt of fatty acid)	3	–
Hydrocarbon resin	2	–
Polyethylene glycol	1.5	–
Brown Factice (vulcanised vegetable oil)	10	–
Oil	80	–
Polyguard HR	0.5	–
Sulphur	1.55	1.55
Vulcacit DM[a]	0.97	0.97
MBT[b]	0.58	0.58
Butazate[c]	0.40	0.40
ZDC[d]	0.22	0.22
TMTD[e]	0.66	0.66

[a] Dibenzthiazyl disulphide.
[b] 2-Marcaptobenzothiazole.
[c] Zinc di *n*-butyldithiocarbamate.
[d] Zinc diethyldithiocarbamate.
[e] Tetramethylthiuram disulphide

Carbon black (N 660) received from Continental Carbon Black was used for this study.

2.2. Mixing and compounding

Table 1 shows the rubber compound formulation, which represents a typical formulation for automotive windowseal component. Dispersive mixing of the gum and filled systems was carried out in a two-roll mill preheated at 100°C. In the case of carbon black filled system, black masterbatch was prepared first with 138 parts of the filler. The second stage involved addition of curatives, namely sulphur and accelerator (Efficient Vulcanisation-EV system). Samples were then compression moulded at 180°C for 5 min. The samples were allowed to relax over 7 days before testing.

2.3. Viscoelastic measurements

A dynamic mechanical spectrometer (Model DMA 2980, TA Instruments, USA) was used for various viscoelastic measurements of complex properties of gum and filled EPDM in the tension mode. Stress relaxation, strain recovery, strain sweep, temperature sweep measurements were performed for studying the viscoelastic behaviour of both the systems.

3. Results and discussion

3.1. Dynamic properties as a function of temperature

Fig. 1 illustrates the elastic modulus, E', and loss modulus, E'', of both gum and filled systems at 1 Hz over −100 to 100°C for the uncured system. Fig. 2 shows the tan δ values for both the systems over the same temperature region. From the nature of the curves (Fig. 1) for both compositions, the different characteristic regions could be easily observed. They are respectively: (A) the glassy region; (B) the transition region; and, (C) the rubbery region. The major effects of filler loading compared to the gum systems are as follows:

1. Compared to the gum system, the filled system has higher E' and E'' values over the whole range of temperatures throughout all the three regions.
2. Filled system has a lower glass-transition temperature (α) compared to that of the gum system ($E'_{\max}$ at −48°C compared to −44°C for the gum system).
3. In the filled system, the shift of the glass rubber transition (T_g) to the lower temperature occurs concomitant with decrease in the tan δ peak height. The system is a highly filled and oil-extended formulation. Oil shifts the peak to low temperatures by penetrating between molecular chain segments and, thus, increasing the free volume. A second broader tan δ peak (α') centred on −14°C is also observed in the case of filled system.

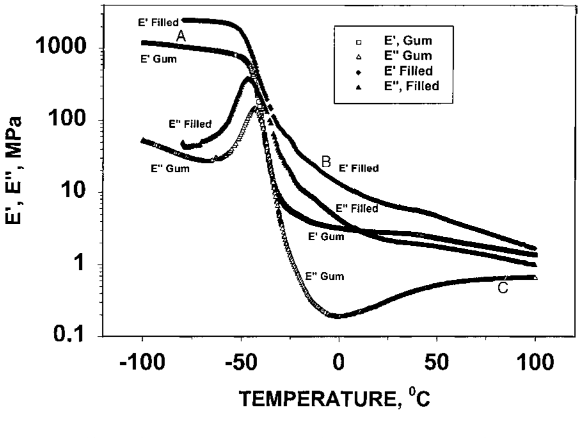

Fig. 1. Effect of temperature on elastic and loss moduli for uncured gum and filled systems.

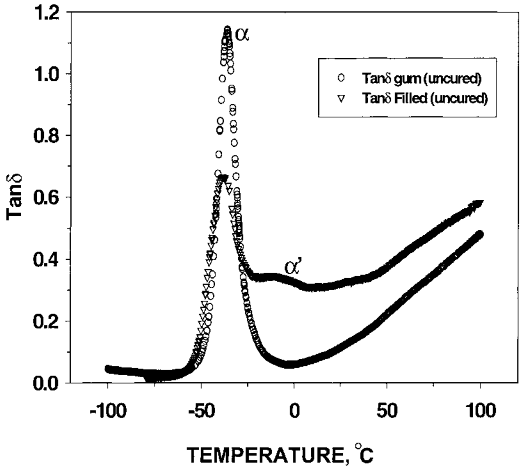

Fig. 2. Effect of filler on the damping behaviour.

4. Filled polymer constitutes a system with a complex structure of at least two components: (a) the adsorbed hard rubber (adsorbed within, and between, the filler aggregates and the hard rubber shell surrounding the carbon black); and (b) the bulk rubber [1–3]. The inclusion in a viscoelastic material not only plays the role of a stress raiser, but also changes the time-dependent behaviour of the bulk material. Thus, the adsorbed hard-immobilised rubber causes a perturbed relaxation response and the segmental dynamics of this layer is restricted. The low-temperature tan δ as observed in Fig. 2 (α, at −39°C for filled and −36°C for gum systems, respectively) may be ascribed to the glass-transition relaxation of the bulk rubber. The mobility of the bulk rubber is unaffected by the filler. Monomeric, highly soluble plasticiser penetrates into the intermolecular space of the elastomer molecules, enhances the segmental mobility and flexibility, and thus decreases the glass-transition temperature of the composites. Thus, the tan δ position shifts towards lower temperature. The higher temperature maximum

in tan δ is due to the adsorbed hard rubber around the carbon black aggregates. Segmental mobility of the interphase layer of the polymer adsorbed on the filler surface is restricted and shifted towards the higher temperature. The diffused nature of the maxima may be attributed to the broader distribution of this relaxation process. Thus, plasticiser increases the mobility of the molecular segment, which is not adsorbed on the filler surface; on the other hand, filler immobilises and reduces the mobility of the polymer segment, which is adsorbed on the filler surface

3.2. Stress relaxation as a function of strain

Fig. 3 shows the tensile stress relaxation behaviour of gum vulcanised EPDM at 25°C for different strains in the range of 1.5 to 10%. At different strain levels, modulus E' decreases with time. Decay of modulus follows the same pattern within the strain range (i.e. it depends on time and not on strain). It appears that the relaxation modulus value for the gum system is time-dependent; however, it is independent of the strain within the experimental range. Therefore, the gum system could be considered as the linear viscoelastic system. Fig. 4 shows the strain recovery curve for the system after the samples were subjected to stress–relaxation test for 30 min. It consists of two parts: the initial instantaneous recovery; and the final slow recovery. It clearly indicates that the material suffers no permanent set and, within a second, recovers 80% of the deformation, and within 30 min it recovers completely.

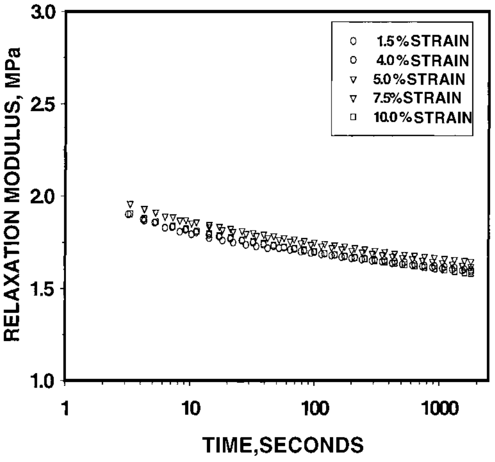

Fig. 3. Effect of strain on the modulus and its relaxation with time for gum vulcanised system.

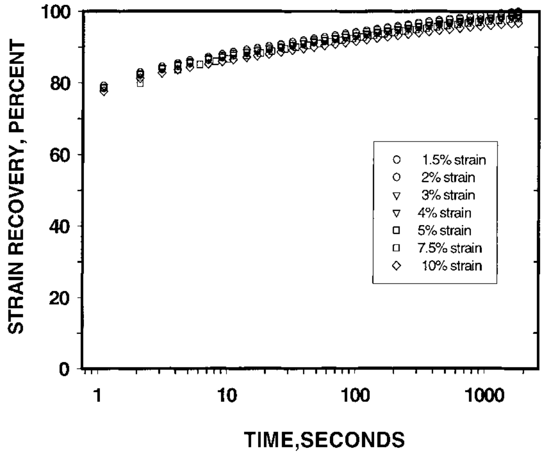

Fig. 4. Strain recovery in gum vulcanised system subjected to stress relaxation experiment for 30 mm.

Fig. 5 shows the tensile stress relaxation behaviour of filled vulcanised EPDM at 25°C for different strains in the range of 0.25 to 10%. A striking difference is observed for the gum and its filled compound. Fig. 5 shows not only time dependence, but also strain dependence. It consists of two parts in the low-strain regions: the initial part of fast decay of modulus and the final part of slow decay of modulus. The rate of relaxation also differs significantly in two cases as evidenced from the nature of the curve.

It is clearly observed that the gum compound is strain invariant, but the linearity principle (the stress relaxation modulus curves are independent of the strain at which they are carried out) does not hold true in a filled system even at very low strains. It also appears that the material does not show even generalised viscoelsatic behaviour, (the effect of changing the strain at which relaxation takes place is merely to multiply the stress decay curve by a strain-dependent factor). While the gum system maintains the plateau over a range of amplitudes, the filled system does not at all exhibit a plateau. There is substantial change in the shape of the decay curve over the ranges of strain and times of investigation. Thus, a highly filled and compounded EPDM rubber vulcanisate shows complex nonlinear viscoelastic behaviour. A similar obser-

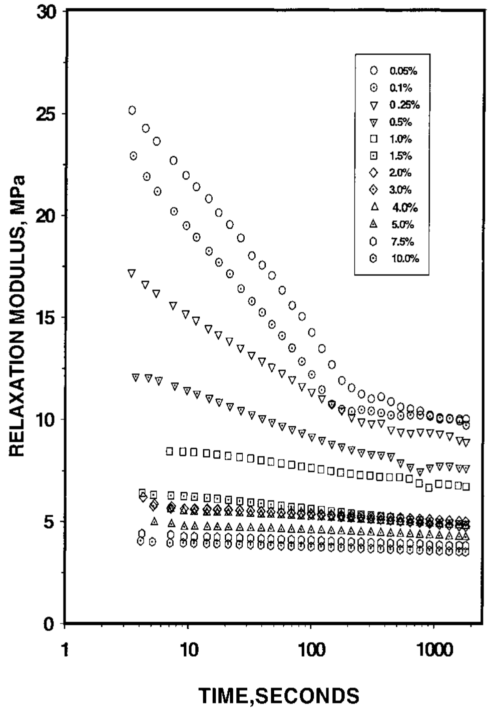

Fig. 5. Effect of strain on the modulus and its relaxation with time for filled system.

vation was made by White et al. [7] from creep and recovery data even at very low stress using a modified version of a sandwich rheometer. The relaxation time spectrum of filled system further reveals that during the relaxation process, i.e. after the sample being deformed, many processes, such as carbon black structure breakdown, permanent set, etc. can occur. The network of carbon black formed at such a high loading contributes significantly to the overall relaxation process.

3.3. Stress relaxation as a function of time and temperature

Fig. 6 shows a 3D plot of tensile modulus as a function of time and temperature for gum vulcanised EPDM. Experiments were carried out at 2% strain over a temperature range of −80°C (193 K) to 100°C (373 K) and for times up to 2000 s. Modulus and time are plotted on log scales and temperature on a linear scale. The modulus decreases with increasing temperature as expected, and the shapes of the curves at various temperatures appear to be superposable to form a single master relaxation curve [6].

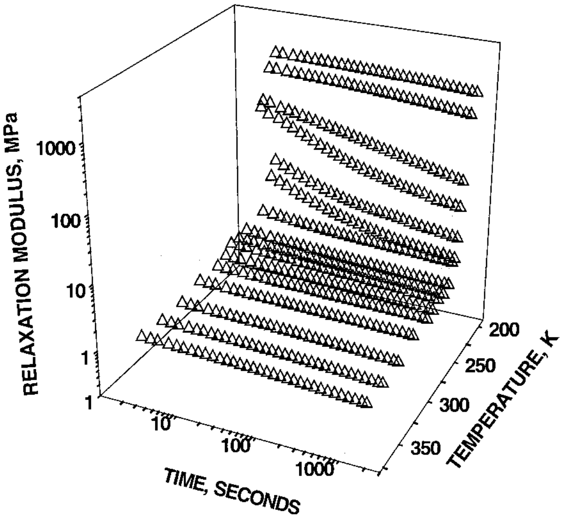

Fig. 6. Plot of modulus as a function of time and temperature for gum system at 2% strain.

Fig. 7 shows the 3D plot of tensile modulus as a function of time and temperature for filled vulcanised EPDM over the same range of time and temperature range as for the gum system. In the filled system, experiments were carried out at 0.25% strain. In the filled system, the modulus value also decreases with temperature as expected; however, the absolute value

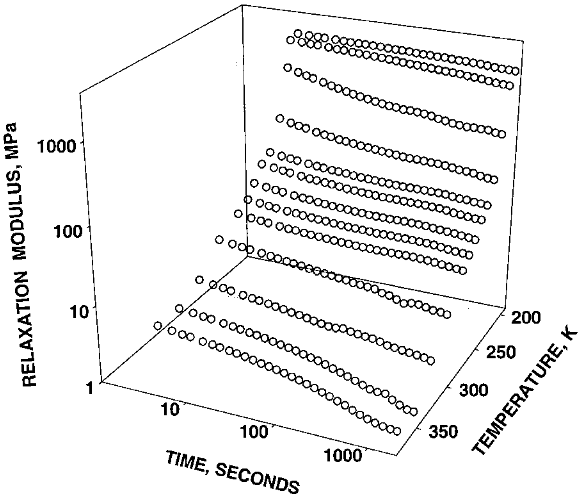

Fig. 7. Plot of modulus as a function of time and temperature for filled system at 0.25% strain.

at any temperature and time considered is higher compared to that of the gum system. It appears that though the filled system is nonlinear and thermorheologically complex, time–temperature superposition is possible for short-period results (3 decades of time scale). It is understood that it is essential to do experiments over prolonged period of time (about five decades of time scale) to understand the failure of superposability in the case of thermorheologically complex materials.

4. Conclusions

The following conclusions have been drawn from the present investigation:

- Gum EPDM elastomer is a linear viscoelastic and thermorheologically simple material; however, when it is highly loaded with filler it appears to be much more complicated showing nonlinear behaviour even at very low strain.
- Filler aggregates adsorb a part of the molecular chain between, and within, the filler aggregate agglomerates and isolate and reduce the mobility of a part of the chain segment.
- In short-time testing, thermorheologically complex materials also appear time–temperature superposable.

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