

# Linear Viscoelastic Behaviour of Highly Crosslinked Silica Reinforced Poly(dimethyl-siloxane) Rubbers

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*The thermo-mechanical behavior of silica-reinforced crosslinked elastomers has been examined by conducting shear thermorheological experiments and microstructural evaluation on two series of randomly crosslinked poly(dimethyl-siloxane) (PDMS). For all the samples studied here it was found that due to the featureless mechanical spectrum, the time temperature superposition (TTS) principle could not be applied to expand the accessible frequency range by the construction of master curves. Characterization of the filler particles before and after their inclusion into the PDMS matrix was conducted by dynamic light scattering (DLS) and transmission electron microscopy (TEM). These observations are discussed with respect to recent evidence that particle clustering may occur in non-crosslinked systems. Finally, short time high temperature aging (up to 30 hrs) experiments were observed not to influence the viscoelastic behaviour.*

*Keywords: highly crosslinked siloxane elastomers, linear viscoelasticity, time-temperature superposition, silica filler*

Most polymers and elastomers used for industrial or commercial applications are composites, which contain solid fillers. The presence of solid particles in uncrosslinked polymers profoundly modifies its rheological behavior and mechanical properties. Although these composites have been extensively studied during the past decades, not all the experimentally observed phenomena, such as yield stress effects are well understood [1,2]. Cross-linked polymer composites have improved mechanical properties, i.e. an increase in modulus, hardness, tensile strength, tear and abrasion resistance, as well as resistance to fatigue and cracking, but reinforcement may also generate increase in hysteresis (and thus of heat buildup) and permanent deformations [3-7]. It is generally assumed that the reinforcement phenomenon is manifested mostly in the rubbery zone of the viscoelastic spectrum, but filler particles may also affect the glass transition and the glassy secondary [6, 7].

There are two types of approach for predicting the behaviour of filled polymer composites: continuum models and molecular models. The first one is generally based on a classical elasticity result, namely Eshelby's theory concerning the calculation of strain energy in systems [8, 9]. Several models were derived in the past for some regular geometrical shape inclusions; however, in practice most filler particles show irregular shapes and often have high dimensional polydispersity. In such cases, because a micro-mechanical description is difficult, variational methods are used to obtain upper and lower bounds, without specification of interface geometry. Although successfully used in few cases [10-12], this approach has the drawback it can not account for the direct polymer-filler interactions, which finally determine the macroscopic behaviour. The second approach is based on the molecular theories of rubber elasticity. The early attempts to describe a crosslinked polymer network have led to James and Guth's "phantom-like" polymer chains model [6] (i.e. no interchain interactions between spatially neighboring chains) and to Wall and Flory's affine network theory [13]

in which network junctions transform affinely under macroscopic strain. In Edwards' and co-workers modern description of rubber elasticity, the network is formed starting with a giant linear molecule that is successively connected onto itself, and, the phantom and affine models are obtained as limiting cases [14, 15]. In the case of composites, the presence of filler particles profoundly modifies the network topology and introduces additional complexity like polymer-filler and filler-filler interactions [16]. Although in the field of physics of unfilled elastomers and rubber composites significant progress has been achieved, a comprehensive molecular theory to explain the reinforcement origin is still unavailable [6].

Silica particles are of great industrial importance since they may be easily compounded with the polymer melt and give reinforcement to rubbers such as silicone rubber. The geometry, architecture and size distribution of the aggregates and the nature of polymer-particle interactions strongly influence the physical properties of the polymer composite. For example, Cohen - Addad and co-workers has shown that the presence of silica particles affects the crystallization process of PDMS adsorbed onto the silica surface [17-20]. Specifically, the extent of crystallization is diminished by the presence of the silica particles but the dimensionality of the crystal growth is not affected. Crystallization kinetics are claimed to vary as follows: at low silica concentrations nucleation effects are dominant and an increase in silica concentration accelerates the crystallization kinetics. But further increase in silica concentration introduces spatially constraints resulting in slowing down of the crystallization kinetics. When silica particles are dispersed into a polymer matrix, they can either disperse or form aggregates and flocculate depending on the nature of inter-particle forces. These aspects were studied by Cabane and co-workers [Lafuma et al (1991) [21]; Wong et al (1992) [22]]. They found that these interactions are influenced by the architecture of the polymer layer adsorbed onto the silica surface. If the silica surface is not saturated with polymer (the thickness of the

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	M <sub>n</sub> , (g/mol)	M <sub>w</sub> , (g/mol)	M <sub>z</sub> , (g/mol)	M <sub>w</sub> /M <sub>n</sub>	x <sup>a</sup> , %(wt.)	y <sup>a</sup> , %(wt.)
PS 424	20600	43200	65900	2.10	7.5	92.5
PS 426	19900	41400	61500	2.08	1.0	99.0

**Table 1**  
MOLECULAR CHARACTERIZATION OF THE PDMS; DATA FURNISHED BY UNITED CHEMICAL TECHNOLOGIES

Sample	Polymer conc., % (wt.)	CabOSil MS7 conc., % (wt.)	HiSil233 conc., % (wt.)	Initiator conc., % (wt.)
PS 424	79.7 and 70.8	10 and 20	-	10.3 and 9.2
PS 426	88.9	10	-	1.1
M 97	67.5	21.6	4.1	6.8

**Table 2**  
FORMULATIONS USED FOR OBTAINING THE CROSSLINKED SAMPLES

adsorbed layer remains small until the surface is almost saturate) the non-adsorbed parts of the polymer chains lie away from the silica surfaces and interact with other similar chain segments forming bridges which keep the particles together. Yet, polymer-saturated silica surfaces will repel each other and no flocculation is observed.

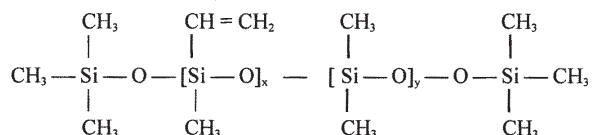
Although the (linear and non-linear) viscoelastic behavior of unfilled melt, filled melt, and filled crosslinked PDMS rubber has been intensively studied in the past [23-35], the thermo-rheological behaviour of reinforced silicone rubber has received less attention. Information concerning the relaxation modulus over a wide time/frequency window is of crucial importance in predicting long term viscoelastic behaviour. It is well known that each technique used to obtain isothermal relaxation data has a limited time/frequency experimental window, which typically does not exceed 4 logarithmic decades. One may extend the accessible range by using the so-called time temperature superposition (TTS) principle or the thermorheological simplicity [4]. This technique was successfully used in the past to obtain relaxation master curves for a wide variety of polymers at temperatures well above the calorimetric glass transition temperature, T<sub>g</sub> [4]. There is increasing experimental evidence for departures from the TTS principle in polymers at temperatures around and below T<sub>g</sub> [36-43]. In a series of fundamental papers, Ngai, Plazek, Roland and their co-workers, explained this phenomenon in the case of linear polymers within the conceptual framework of a coupling model, as due to a difference in temperature dependence of local segmental relaxation from that of the relaxation of the chain modes [44-46]. Yet, it is believed that TTS is applicable to all polymeric systems above T<sub>g</sub>.

It is the purpose of this paper to analyze the influence of the material microstructure on the shear thermo-viscoelastic behaviour for temperatures above T<sub>g</sub>, in a series of unfilled and filled PDMS rubbers, and to evaluate the applicability of TTS for filled, crosslinked systems.

## Experimental part

### Polymer sample preparation

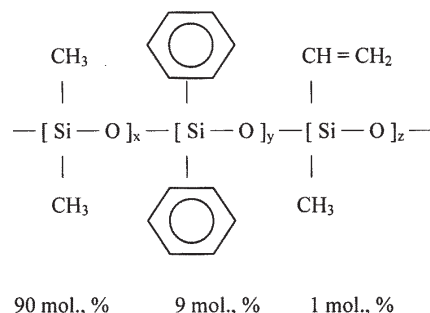
The first series of samples were prepared from trimethylsiloxy terminated - dimethylsiloxane - vinylmethylsiloxane copolymers (supplied by United Chemical Technologies Inc commercially termed PS 424 and PS 426):



The molecular weights of the uncrosslinked polymers were determined by size exclusion chromatography (SEC). The samples were dissolved in toluene and run at 1 mL/min through a four columns (10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup> and 500 Å) GPC system, (Waters, USA), equipped with a refractive index detector. For calibration a series of seven narrow molecular weight PDMS standards (molecular weights between 350 and 3·10<sup>6</sup> g/mol, PSS, Mainz, Germany) were used. In tables 1 and 2 the chain microstructure is presented together with sample formulations by weight. Since M<sub>e</sub>, the molecular weight between entanglements, for PDMS is roughly 11,000 g/mol [Ferry (1980) [4]] the silicones studied here are lightly entangled polymers. The material is crosslinked, primarily at the vinyl sites, through free radical reaction with tert-butyl-peroxy-2-methylbenzoate as initiator. Formulations were composed stoichiometrically, with theoretically, one free radical generated per available vinyl group.

The filler used was a fumed Cab-O-Sil MS7 silica (Cabot USA), whose characterization will be presented in the next section. Processing is accomplished by mixing the two components together first manually, then passed three times through a three rolls paint mill. The mixed material is compression molded for 2 h at 120°C, then postcured out of the mold at 200°C for 24 h. Next, some of these samples have underwent accelerated aging at 200°C for 30 days in a temperature controlled oven.

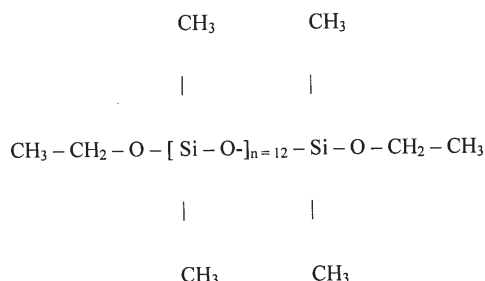
The second series of samples were prepared from dimethyl-, vinylmethyl-, phenylmethyl-siloxane terpolymer (commercially named M97 supplied by Nusil Silicone Technology Inc.):



The molecular weights were not determined. The composite was prepared using a fumed (Cab-O-Sil MS7) and a precipitated silica (HiSil 233, PPG, USA) as fillers, and a processing aid manufactured by Union Carbide Inc., ethoxy end-blocked PDMS Y-1587 (for formulation details see table 2).

The mixture is then processed by intensively mixing on a roll mill. The "rolling" serves to "freshen" the reinforced polymer and to mix in the peroxide initiator. Freshening serves to break down some of the structure formed

between polymer and filler, and to allow easier processing. The material is then compression molded with heat; the part is stripped from the mold and then postcured, in the same conditions as for the first series composites. The composite was cured by free radical reaction using peroxide as initiator, which decomposes when heat is applied. We will refer to these samples, from now on, as “roll only”. Other samples underwent an additional mixing step, in a laboratory scale intensive Banbury mixer to see if additional filler dispersion could be achieved, hence the “roll and mix” terminology.



### Silica filler characterization

The fumed Cab-O-Sil and precipitated HiSil silica particles used for reinforcing the polymer samples are manufactured by Cabot and PPG Industries Inc. respectively. According to the manufacturer data, the fumed and precipitated silica have large surface areas, typically 150 to 200 m<sup>2</sup>/gm, and are chemically inert (pH=7). They are physically reactive when dispersed in many polymers and, by forming physical bonds with the macromolecular chains, a strengthening effect is observed. The fumed Cab-O-Sil MS7 particles are produced by the hydrolysis of silicon tetrachloride vapour in a flame of hydrogen and oxygen, as spheres. These molten spheres may fuse together to form three dimensional fractal chain aggregates, with amorphous structure. Precipitated HiSil 233 silica particles exhibit high absorption properties, chemical stability, and are industrially used as anticaking agent by improving flow properties.

Dynamic light scattering (DLS) experiments were performed to determine the size of amorphous silica samples. The literature supplied by the manufacturer indicates an average individual particle size of about 10 - 20 nm; also, the particles are amorphous in nature and based on supplied micrographs, they appear to be sintered. The value of particle size reported by the manufacturer is based on a value calculated from the surface area measured by BET and on an assumption of spherical morphology. The current method of analysis uses the photon correlation spectroscopy of quasi-elastically scattered light generated by a 670 nm wavelength laser (Zeta-Plus, Brookhaven Instrument Company). The detector records scattered light at 90° with respect to the incident beam. According to the manufacturer, this method supplies precise particle size determination for properly prepared samples of monodisperse near-spherical particles with the mean diameter in the range 2 nm to 2 μm.

Initial DLS measurements were performed on low concentration silica samples dispersed in ultra-pure low-carbon water (Easy-Pure UV, Barnstead). These samples were analyzed both before and after being “sonicated” using an ultrasonic water bath (Cole-Parmer). This procedure has been successfully used in our laboratory in the past to disperse suspensions of colloidal hematite (α-Fe<sub>2</sub>O<sub>3</sub>) for similar analyses. The results of this procedure

did not disperse the samples into 10-20 nm particles. Samples were then filtered using a 200nm-size polycarbonate filter to determine whether a small fraction of completely dispersed particles existed. DLS measurement indicated that all particles were filtered.

It was then decided to attempt to “clean” the fumed and precipitated particle suspensions by placing them in dialysis membrane bags and dialyzing the samples against a dilute perchloric acid solution (0.0001 mol/L of HClO<sub>4</sub>). This procedure consisted of replacing the rinsing solutions on a daily or twice daily basis for 5 days, after which the solutions were changed to Easy-Pure water. The dialysis membranes (Spectra/por 7, Spectrum Laboratory Products) were nominally 1000 daltons, a pore size that is sufficient to retain 10 nm sized particles while allowing dissolved ionic species to pass. The total period of dialysis was 12 days. DLS measurements were performed after the cleaning procedure. The pH of the two samples was measured to be greater than 6. Based on a point of zero charge of silica particles of ~ 3, the particles will have a significant negative surface charge [47]. In a very dilute system it is expected that this negative surface charge would be sufficient to overcome the attractive van der Waals forces and thus if the particles are indeed separate they would be completely dispersed [47]. The measurements were performed as before and resulted in particle sizes around 500 nm. The samples were filtered with a 200 nm polycarbonate filter and subsequently measured. The DLS measurements indicated that no particles were present after the filtration. Thus, the silica samples consist of smaller 10-20 nm particles that are sintered together forming particles of roughly 300-500 nm.

Since dynamic light scattering measurements cannot discern the morphology of the agglomerated particles to determine how they are packed, we have analyzed our filled polymer samples with transmission electron microscopy (TEM). The 80nm to 100nm thickness sections were obtained by ultramicrotomy technique at -156°C, using a Leica microtome. A full voltage setting of the ionizer was needed to allow section detachment from the diamond knife. In order to increase the image contrast, the samples thus obtained were stained using the following procedure: first they were exposed to OsO<sub>4</sub> vapour during 15 min, then successively kept in an uranyl acetate solution for 8min and in a Reynolds lead citrate solution for 3 min. The photographs were obtained using a Philips CM-200 transmission electron microscope, operating with 0.2MV electron gun and 1.2 Å maximum resolution.

### Rheological measurements

The rheological measurements were carried out on a Rheometrics RMS-605 mechanical spectrometer, with experimental frequencies ranging between 0.1 to 100 rad/s using torsional rectangular sample configuration; in this way sample slippage on tools is avoided. In all cases we have ensured the linearity of the stress response with respect to the strain amplitude in order to remain within the linear viscoelastic domain. The range of temperatures was 25° to 110°C. These temperatures are well above the calorimetric glass transition for PDMS (T<sub>g</sub> = -120°C).

### Results and discussions

We present figures 1 and 2 TEM results on the fresh PS 424 and PS 426 (both with 10% by weight filler concentration) chosen as examples. For both fresh samples, particles are seen to form fractal shaped organized clusters of small aggregates of (roughly) 500 nm. Smaller aggregates are also observed, and it is likely

that they originate from greater ones, which were milled during the sample processing. It should be pointed out that since the thickness of the microtomed section is probably smaller than the average cluster size, sample preparation for TEM necessarily introduces changes in cluster orientation and possibly cluster size. Yet, it will not invalidate the general conclusion concerning the qualitative nature of clustering and the estimated typical cluster size.

Macosko and co-workers have studied the long - term behaviour of uncrosslinked PDMS filled with different silica particles [48-50]. They have reported significant particle diffusion especially for higher molecular weight PDMS samples reinforced with chemically untreated filler. Also, shear rheometry performed during aging has revealed that lower molecular weight filled systems soften with time while higher molecular weight gum stocks harden. The model they proposed to explain these phenomena is based on three filler - polymer - filler type interactions: 1) a single chain directly bridging two separate aggregates, 2) primary entanglement: entanglement between two chains adsorbed on separate aggregates and 3) secondary entanglements: entanglement involving non - adsorbed chains. However, for our samples which underwent accelerated aging during 30 days at 200°C, particle clusters geometry seems not be affected by the thermal aging on this time scale. In other words, we did not observe any noticeable filler particle diffusion in these highly crosslinked composites, as opposed to the results obtained for uncrosslinked PDMS. This might lead to the conclusion that in order to achieve particle diffusion, partially or even full polymer chain mobility may be necessary.

We present in figures 3a, 3b, 3c, 3d the results of isothermal  $G'$  and  $G''$  moduli measurements for the samples PS 424 (7.5% vinyl content) and PS 426 (1% vinyl content) for different filler concentrations (by weight). Data for the unfilled crosslinked PS 426 are not presented here, since the measured torque was below the transducer sensitivity. The scatter in  $G''$  data is larger than in  $G'$  as a result of the

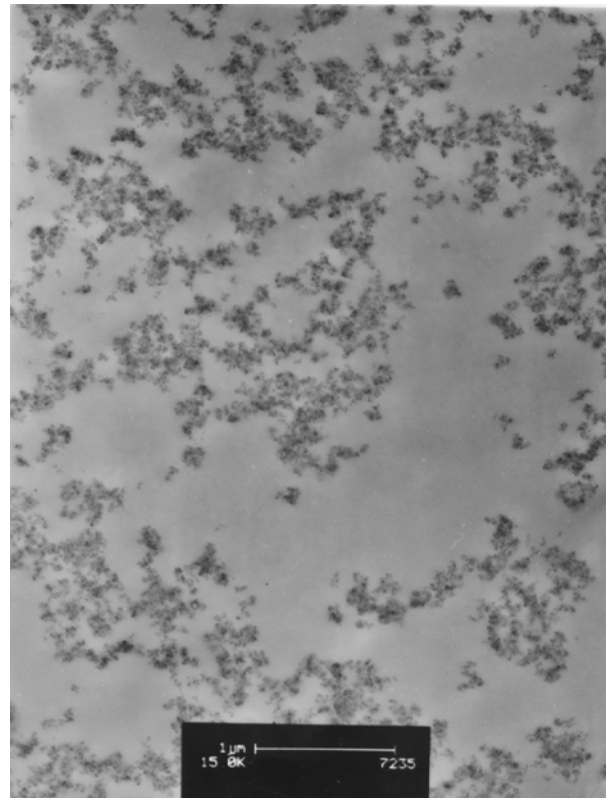


Fig. 2. TEM photograph of the sample PS 426 with 10% filler concentration (by weight).

relatively lower values of  $G''$ . Due to the high crosslinking density (see below), the materials exhibit a behaviour close to that of an ideal elastic body, in which the phase angle between  $G'$  and  $G''$  defined as  $\delta = \tan^{-1}(G''/G')$  is very small, i.e. about  $0.5^\circ$ . Such small angles are at the lower sensitivity (accuracy) limit for the transducer used in the present experiment, and result in scattered data. Although  $G''$  moduli are considerably lower than the corresponding  $G'$ , their values are not negligible; thus it would be inappropriate to interpret the results using the limiting elasticity theory instead of the more general theory of viscoelasticity. Despite the scatter in  $G''$  it is possible to discern specific trends in the data which are beyond the random experimental error. In all four figures and at all tested temperatures  $G'$  has a constant value over three decades of frequency and over a range of about  $80^\circ\text{C}$ . This indicates that the measured value of  $G'$  corresponds to the equilibrium shear elastic modulus of the crosslinked system. The values of this equilibrium modulus increase as expected with filler particle concentration and with amount of crosslinks (fig. 3b vs. 3d). From the modulus value in figure 3a it is possible to estimate the crosslink density of the unfilled rubber by using the James - Guth "phantom network" theory. From this calculation we estimate the molecular weight between crosslinks for PS 424 as 750 daltons. Despite the approximate nature of the calculation, the result is an indication of the high degree of crosslinking obtained in this system.

Figures 3a to 3d reveal that  $G'$  is virtually independent of temperature over the experimental range and  $G''$  increases with temperature at the highest temperatures for some of the systems. A probable explanation is that at higher temperatures, the free volume increases and the polymer chains experience more mobility in these densely crosslinked systems; consequently, the friction dissipation due to interacting relaxing species is increased. Another feature is that  $G''$  data are only weakly frequency dependent. As a result, it is difficult to horizontally superpose

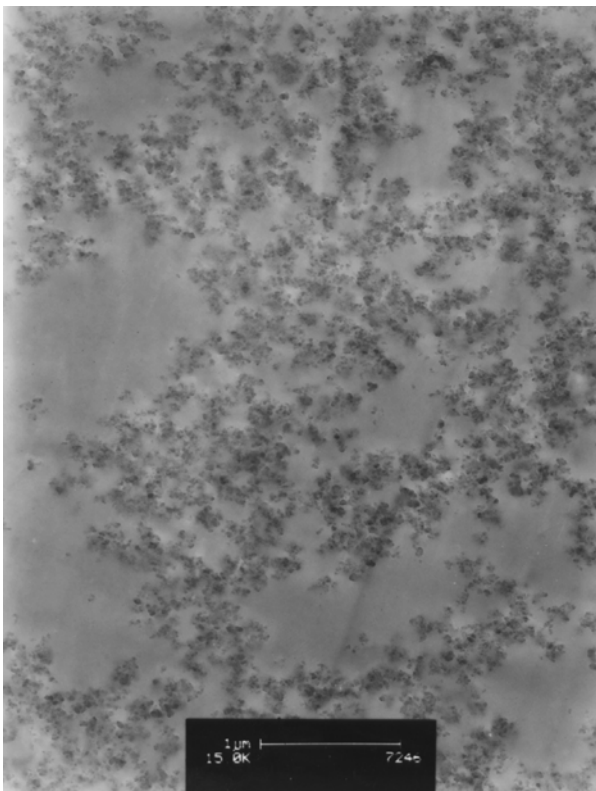


Fig. 1. TEM photograph of the sample PS 424, with 10% filler concentration (by weight).

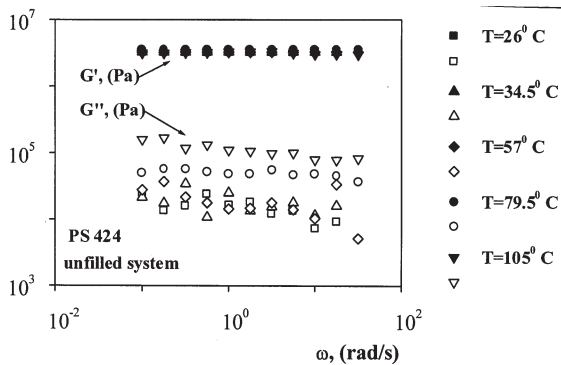


Fig. 3a: Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the unfilled PS 424 sample.

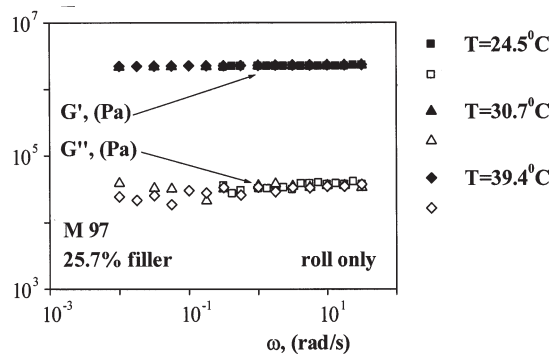


Fig. 4a: Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the 25.7% filled M 97 sample. For details on processing, see text.

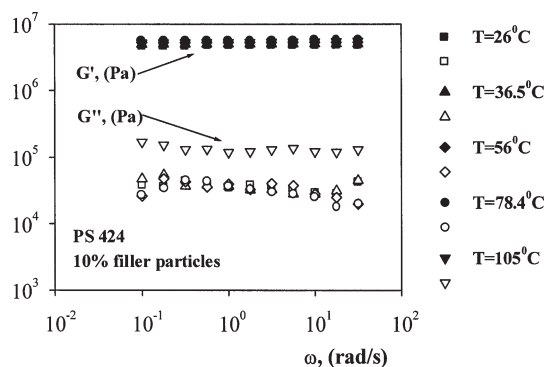


Fig. 3b: Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the 10% filled PS 424 sample.

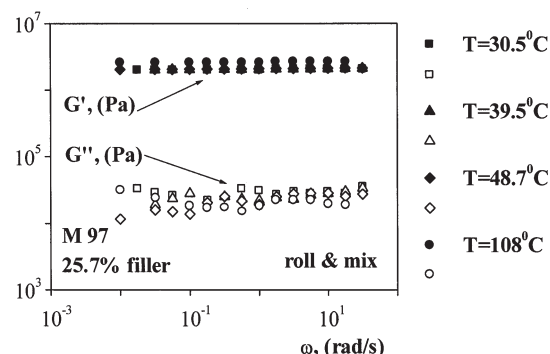


Fig. 4b: Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the 25.7% filled M 97 sample. For details on processing, see text.

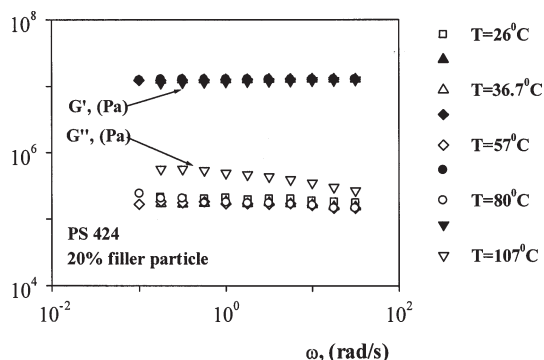


Fig. 3c: Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the 20% filled PS 424 sample.

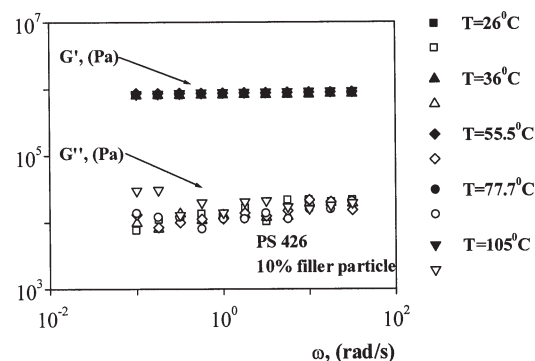


Fig. 3d: Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the 10% filled PS 426 sample.

the data in order to obtain a master curve for either  $G'$  or  $G''$ . Hence, TTS principle can not be used for the systems studied here to predict long-time linear viscoelastic behaviour because of our inability to obtain from the present data a complete viscoelastic spectrum. A phenomenological interpretation for this behavior may be given within the

conceptual framework of spectral decomposition: TTS may be understood as being valid when all the mode relaxation times of different temperature spectra have the same temperature dependence. However, in the present case, a different temperature variation of the individual relaxation modes characterizing the relaxing species (polymer segments between crosslinks) seems to occur.

Figures 4a and 4b present the data for the M 97 samples. In this case, despite some scatter in  $G''$  (due to transducer sensitivity), both  $G'$  and  $G''$  moduli remain horizontal for all the temperatures investigated in this study. This is typical of viscoelastic behaviour of rubbers at low frequencies (relative to  $\omega_g$ , the dynamic glass transition frequency) and high temperatures (relative to  $T_g$ ). As result of the featureless frequency and temperature spectra no conclusion may be drawn concerning TTS.

The microstructure strongly influences the macroscopic viscoelastic response. First we can observe as expected, that for PS 424 (7.5% vinyl content) the equilibrium shear modulus values inferred from the plateau values of  $G'$  increase with filler concentration. Second, PS 426 (1% vinyl content) exhibits, for 10% filler, a plateau modulus of about  $9 \cdot 10^5$  Pa which is 6.6 times lower than the value obtained for PS424 (7.5% vinyl content) with the same filler concentration (table 3). On the other hand, the M 97 samples (25.7% filler concentration) show little influence of the processing on their viscoelastic behaviour (compare figs. 4a, 4b and table 3). Specifically, the plateau values are  $2.3 \cdot 10^6$  (Pa) for the "roll only" and  $2.1 \cdot 10^6$  (Pa) for the "roll and mix", as measured at 40°C. However, in the latter case, the highest temperature (108°C) modulus is 30% greater than the moduli measured at lower temperatures. This is quite close to the 25% increase expected from rubber elasticity theory according to  $G \sim (\rho/M_c)RT$ . The difference in plateau moduli measured for the three different polymer

**Table 3**  
THE G' PLATEAU VALUES, MEASURED AT 25°C FOR PS424, PS426 AND M97 "ROLL ONLY" AND AT 30°C FOR M97 "ROLL AND MIX" (FOR DETAILS SEE THE TEXT)

Sample	Filler concentration, % (wt.)	G', (Pa)
PS424	0	$3.5 \cdot 10^6$
PS424	10	$6.0 \cdot 10^6$
PS424	20	$1.3 \cdot 10^7$
PS426	10	$9.0 \cdot 10^5$
M97 "roll only"	25.7	$2.3 \cdot 10^6$
M97 "roll and mix"	25.7	$2.1 \cdot 10^6$

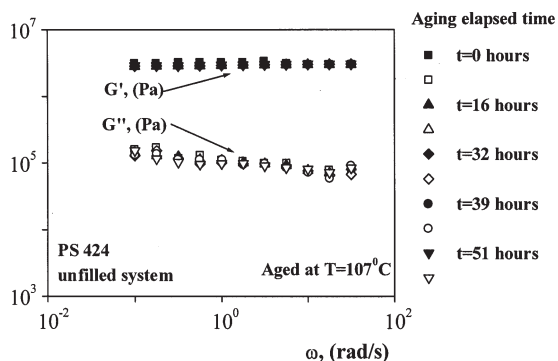


Fig. 5a. Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the unfilled PS 424 sample during thermal aging.

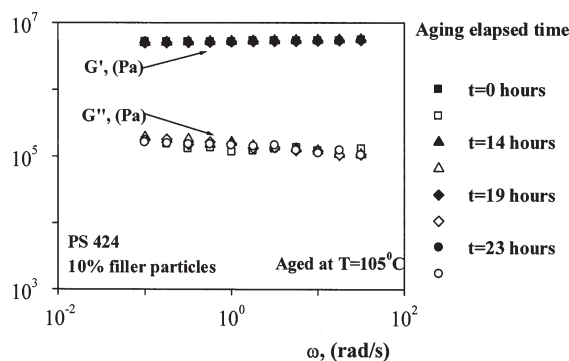


Fig. 5b Isothermal complex moduli  $G'(\omega)$  and  $G''(\omega)$  for the 10% filled PS 424 sample during thermal aging.

matrices (PS 426, PS 424 and M 97) reflect their different chemical and polymer network structure.

Figures 5a and 5b show isothermal complex moduli measurements for different aging times, in the case of the sample PS 424, chosen as an example. It is observed that for the aging times considered here, no significant influence is observed, the unfilled and 10% filled elastomer being unaffected. We may conclude that if any thermal aging effects occur for our composites, they will be observed after much longer aging times. Another aspect that remains to be studied is the possible influence of the strain history on the aging phenomenon.

## Conclusions

In the present study the linear viscoelastic behaviour of two series of filled crosslinked PDMS samples has been analyzed. Above the glass transition temperature  $T_g$ , our experimental results have shown that time temperature superposition (TTS) principle can not be used to construct master curves mostly due to the featureless viscoelastic spectra which allows horizontal shifts to the curves. In the case of the samples M 97, the "roll" and "roll and mix" processed materials were found to have very little influence on the thermorheological behaviour. Also, the short time aging studies reported here have shown to have no significant influence on the viscoelastic behaviour. Our results do not show any particle migration contrary to the observations made on uncrosslinked silica-filled PDMS systems [48-50]. Presently, we are unable to determine whether the high crosslinking density and low chain mobility in our systems prevents filler migration entirely or just slows down migration kinetics below our detection level over the finite experimental observation time. This point requires further study, may be within the framework of a recently proposed model for filled polymers [51]. Moreover, it is hoped this study will help understanding the rheological behaviour of more complex composite materials such that glass fiber reinforced polymer composites, e.g. [52].

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