

Effect of Conductive Fillers on the Cyclic Stress-Strain and Nano-Scale Free Volume Properties of Silicone Rubber

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Abstract The effect of carbon black (CB) and graphite (G) powders on the macroscopic and nano-scale free volume properties of silicone rubber based on poly(di-methylsiloxane) (PDMS) was studied through thermal and cyclic mechanical measurements, as well as with positron annihilation lifetime spectroscopy (PALS). The melting temperature of the composites (T_m) and the endothermic enthalpy of melting (ΔH_m) were estimated by differential scanning calorimetry (DSC). T_m and the degree of crystallinity (χ_c) of PDMS composites were found to decrease with increasing the CB content. This can be explained due to the increase in physical cross-linking which results in a decrease in the crystallite thickness. Besides, χ_c was found to be dependent on the filler type. Cyclic stress-strain behavior of PDMS loaded with different contents of filler has been studied. Mullins ratio (R_M) was found to be dependent on the filler type and content. It was found that, R_M increases with increasing the filler content due to the increase in physical cross-linking which results in a decrease in the size of free volume, as observed through a decrease of the *o*-Ps lifetime τ_3 measured by PALS. Moreover, the hysteresis in PDMS-CB composites was more pronounced than in PDMS-G composites. Furthermore, a correlation was established between the free volume V_f and the mechanical properties of PDMS composites containing different fillers. A negative correlation was observed between V_f and R_M .

Keywords: Positron annihilation; Positronium; Free volume; Si-rubber; Composite; Cyclic mechanical properties.

INTRODUCTION

Rubber composites are of great importance and have many applications because they exhibit some different physical and mechanical properties compared with those of their individual components. They are often compounded with reinforcing fillers to improve their mechanical properties^[1, 2]. The effectiveness of filler depends on filler characteristics such as size and shape of the particles and, more significantly, on the strength of polymer-filler interactions. These interactions increase the effective degree of cross-linking and such an effect is particularly strong if the particles have some reactive surface groups^[3, 4].

Carbon black (CB) is the predominant reinforcing filler used in rubber compounds. Addition of CB to the rubber compounds significantly improves their durability and strength. CB produces large cohesive strength between the individual fine particles which leads to aggregates of these particles; the diameter of aggregates in this case is not less than several microns^[5]. Recent studies^[6–10] show that carbons have active sites (surface sites) which are capable of dissociative chemisorbing oxygen. These sites are primarily associated with edge sites or defects on the carbon surface. So, the chemical properties of carbonaceous materials should be influenced by the

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relative fraction of the active sites which varies widely with the structure and size of the particles. Coltharp and Hackerman^[8] reported that the percentage of active sites on a high-surface-area CB is 68% of the total surface area (*ca.* 110 m²/g). Such high percentage is not likely to exist with large graphite particles of dimensions greater than 1 µm. For example, Chung *et al.*^[11] considered a circular disk as a representation of a graphite flake and calculated a percentage of 1% for particle diameter of 10 µm and thickness of 0.1 µm. Indeed, the surface of the commercial carbon blacks is covered with carbonaceous deposits which consist of small aromatic compounds, thereby masking active sites for interaction with the elastomer. The secondary ion mass spectrometry results showed that on the high-surface-area carbon blacks, the amount of carbonaceous deposits was slightly less than on the lower-surface-area ones^[12]. It is reasonable to assume that the carbonaceous deposits are formed preferentially at surface irregularities, thus reducing the surface roughness, thereby decrease the tendency to form aggregates.

Silicone rubber exhibits a list of excellent characteristics including oxidation resistance, thermal stability, climate resistance, low surface tension and unique high permeability because of the unique structure of polysiloxane^[13–15]. Therefore, it is used for high performance gasketing, thermal shielding, vibration mounts, press pads, weather resistance coatings^[16, 17]. However, silicone rubber which is based on the Si—O chain structure has weak intermolecular forces among polymer chains, because the Si—O bond has larger bond length and less alkyl groups than C—C bond. As a result, silicone rubber has low mechanical strength, which limits its practical application. Therefore, how to strengthen the mechanical properties has attracted more and more attentions.

Positron annihilation lifetime (PAL) spectroscopy can provide direct information about the polymer free volume. PAL is an ideal non-destructive method for the detailed study of polymers and polymer composites^[18–21]. When a positron enters a polymer, it may be annihilated directly with an electron or may capture an electron from the surrounding molecules to form a bound state, a so-called positronium (Ps) atom. Ps is known to exist in two ground states. *para*-Positronium (*p*-Ps), consisting of an electron-positron state with anti-parallel spins and *ortho*-Positronium (*o*-Ps), in which the spins of the two particles are parallel, more details about this technique will be given soon.

Jobando and Quarles^[22] studied the change of free volume in CB filler rubber composites during the curing process and in other work^[23] during the deformation of the composite. Other investigators studied the change of free volume in rubber blends under certain conditions^[24, 25]. As was noticed, little attention has been given to the topic of studying the cyclic mechanical and thermal properties of silicone rubber loaded with carbon black and graphite, as conductive fillers, and to correlate these physical properties with the positron annihilation parameters and this represents a gap which should be filled.

EXPERIMENTAL

Materials and Sample Preparation

Silicone rubber, (Grade ELASTOSIL® R 401/30 S), polymer type polydimethylsiloxane (PDMS), vulcanized with dicumyl peroxide (DCP), was supplied by Dow Corning, USA. Carbon black (CB) was supplied by Transport and Engineering Company (TRENCO), Alexandria, Egypt, and graphite fine powder (G) was provided by Central Drug House (P) LTD, New Delhi with the physical characteristics presented in Table 1.

Table 1. Some physical characteristics of the fillers

Filler	ASTM designation	Average particle size	Surface area (m ² /g)
Carbon black	N220	23 (nm)	115
Graphite	Graphite	10 (µm)	11

PDMS was mixed with different contents and/or types of fillers on a two roll mill of 300 mm length, 170 mm diameter with speed of slow roll (18 rev/min) and gear ratio (1.4). After mixing, the rubber composites were left for about 24 h and then molded in an electrically heated hydraulic press at 180 ± 2 °C under a pressure of 4 MPa. The test materials have the composition shown in Table 2.

Table 2. Formula of the PDMS composites loaded with different contents and types of fillers ^a

	C_x	G_x
Silicone rubber (PDMS)	100	100
Carbon black (C-samples) ^b	0–25	0
Graphite (G-samples) ^c	0	0–20

^a All values are expressed as part per hundred parts of rubber by weight (phr);

^b C_x samples refer to PDMS loaded with different amounts of carbon black, where $x = 5, 10, 20$ and 25 phr;

^c G_x samples refer to PDMS loaded with different amounts of graphite, where $x = 5, 10, 15$ and 20 phr

Testing

The PAL apparatus is a typical fast–fast coincidence system. A ^{22}Na radioactive source, $20\ \mu\text{Ci}$, is sandwiched between two identical pieces of the sample and placed between two scintillation counters. The timing resolution of the system is about $240\ \text{ps}$ for ^{60}Co with a time calibration $52\ \text{ps/ch}$. We analyze the PAL spectra by using PATFIT^[26] and LT 9.0^[27] programs, using three Gaussian resolution functions and resolved into three lifetime components without source correction, the variance of fit was less than 1.3.

The long-lived lifetime component τ_3 identified as due to the *ortho*-positronium (*o*-Ps) pick-off process in free volume holes in amorphous regions of polymers. It directly correlates with the size of the free volume holes by using the Tao-Eldrup semi-empirical equation^[28, 29], the cavity hosting of Ps is assumed to be a spherical void with effective radius R . The relationship between τ_3 and radius R is as the following:

$$\tau_3 = 0.5 \left[\frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(2\pi \frac{R}{R + \Delta R} \right) \right]^{-1} \quad (1)$$

where the units of R and τ_3 are nm and ns, respectively and $\Delta R = 0.1656\ \text{nm}$ ^[30] for polymers and is derived from fitting the observed *o*-Ps lifetimes in molecular solids with known hole sizes and the size of free volume hole which can be calculated from the equation $V = \frac{4}{3} \pi R^3$.

Cyclic stress-strain measurements were performed on dumbbell shaped samples of constant width (3 mm) and thickness of about (1 mm). The stress–strain measurements were conducted according to ASTM D 412 with a tensile testing machine (AMETEK, USA). A digital force gauge (Hunter Spring ACCU Force II, 0.01 mol/L resolution, USA) connected to a microprocessor was used to measure extension force. A home-made motor attachment was used to control the displacement rate through a gearbox. Calibration of this part was previously carried out by comparing the obtained results with those of similar samples tested on other standard equipments. The displacement rate was preset using a variable DC power supply, and was measured using a micro-switch attached to the apparatus wheel. The accuracy of displacement measurement was about 0.1 mm. The displacement rate throughout the experiment was fixed at 1 mm/sec.

Differential scanning calorimetry (DSC) measurements were carried out at the temperature range from $-140\ ^\circ\text{C}$ up to $300\ ^\circ\text{C}$ by using a Shimadzu 50, differential scanning analyzer with a scanning speed of 5 K/min.

RESULTS AND DISCUSSION

Positron Annihilation Lifetime Spectroscopy (PALS)

The variation of the free volume V_f with the filler content for PDMS composites is shown in Fig. 1. It was found that V_f decreases as the filler content increases in both C-samples and G-samples. This behavior can be explained as follows, adding fillers to the rubber matrix inhibits the formation of *o*-Ps due to filling up some of the free volume holes in this matrix and as a result the size of these holes decreases^[31]. Indeed, the values of V_f for G-samples are larger than those for C-samples. This can be attributed to the filler particle size and its surface area, since CB has smaller particle size and larger surface area than G, then it will occupy greater holes than that of G and also for CB it has the tendency to form aggregates which decreases the free volume holes.

The dependence of the free volume V_f on the filler type for PDMS composites is shown in Table 3. It's clear that V_f of the composites varies with the filler type and the value of V_f is larger in the case of Graphite. This may

be ascribed to the different particle size of the fillers. The smaller the particle size of the filler, the smaller are the free volume holes.

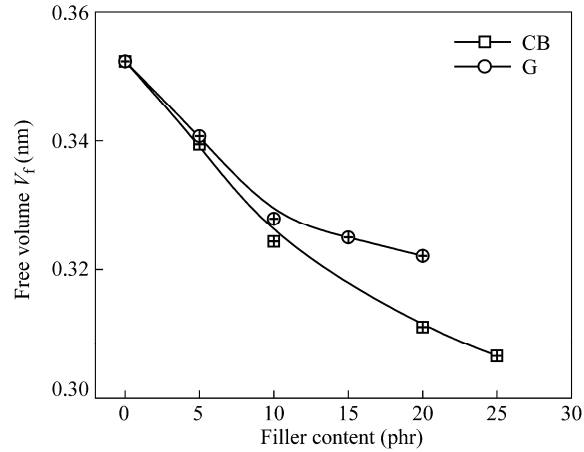


Fig. 1 The variation of free volume (V_f) with the filler content

Table 3. The dependence of V_f , χ_c and R_M on the filler type for PDMS composites containing 20 phr of filler

Filler	Average particle size	Free volume, V_f (nm³)	Degree of crystallinity, χ_c	R_M (1 st cycle)
Carbon black	23 (nm)	0.311 ± 0.002	52.56	0.48
Graphite	10 (μ m)	0.322 ± 0.002	54.39	0.31

Differential Scanning Calorimetry (DSC)

DSC is appropriate to analyze the behavior of silicone rubber at low temperatures and this is due to the flexibility of the polysiloxane backbone and the remarkably low glass transition below -120 °C if compared to other polymers. This is why PDMS remains fluid and silicone elastomers remain flexible at low temperatures. The PDMS samples, at least for a fraction of the polymer, crystallize on slow cooling below -50 °C^[32].

The melting behaviors of the composites (T_m); and heat of fusion (ΔH); were estimated by DSC. The melting temperature was measured at the position of the peak maximum. The endothermic enthalpies (ΔH_m) of melting were determined by measuring the area under the corresponding peaks, and they are proportional to the polymer crystallinity. By considering the melting enthalpy of 100% crystalline PDMS (ΔH_o) as 26 J/g^[33], we have estimated the degree of crystallinity χ_c of neat PDMS and PDMS-fillers composites by the equation;

$$\chi_c \% = \frac{\Delta H_m}{\Delta H_o} \times 100 \quad (2)$$

The DSC thermo-grams of the PDMS composites loaded with different contents of CB is shown in Fig. 2. It's clear that the melting temperature (T_m) shifts towards lower values due to the addition of CB, since CB introduces physical cross-linking in the matrix, which weakens the inter-molecular interactions. Furthermore, the increase in the CB content induces more shifts to the lower temperature side due to the diminishing in the crystallite thickness as a result of the physical cross-linking effect of CB^[33].

The degree of crystallinity χ_c of PDMS composites as a function of CB content is shown in Fig. 3. It's clear that χ_c decreases with increasing the CB content. This decrease in χ_c , implies a decrease in the crystal size and/or perfection of crystals^[34] and this is due to the increase in the physical cross-linking with increasing CB content.

The dependence of the degree of crystallinity χ_c on the filler type is presented in Table 3. It is obvious that χ_c has lower value for C₂₀ composite (particle size of 23 nm, 20 phr), exhibiting 52.56%, than for G₂₀ composite (particle size of 10 μ m, 20 phr), χ_c in this case is 54.39%. This behavior can be ascribed to the difference in the particle size, surface area and surface activity of the filler particles as mentioned before.

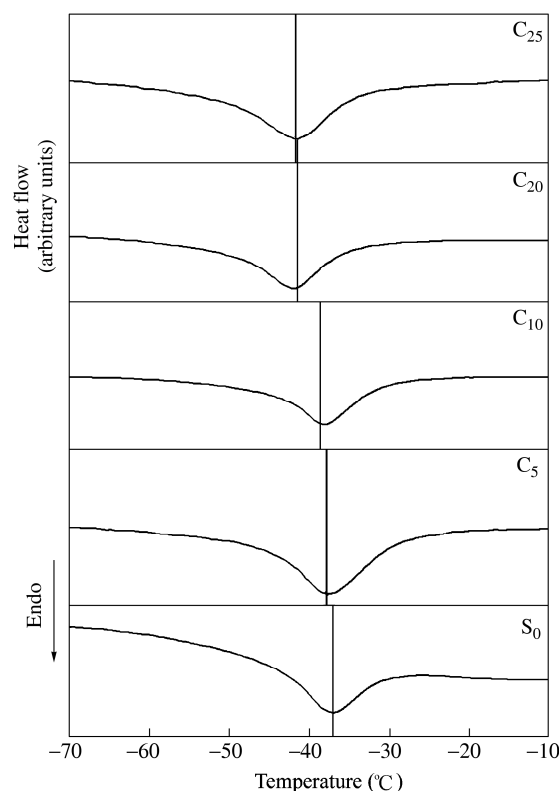


Fig. 2 The DSC thermograms of the PDMS composites loaded with different contents of carbon black

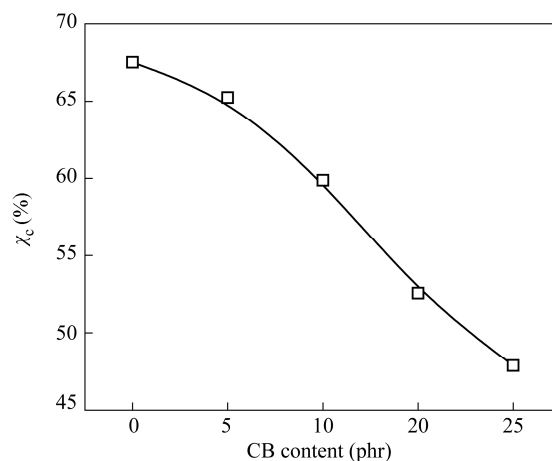


Fig. 3 The degree of crystallinity (χ_c) as a function of the CB content

Cyclic Stress-Strain-Hysteresis

Figures 4 and 5 show the first, second and the third cycles of the cyclic stress-strain of PDMS composites. Generally the addition of any type of fillers to PDMS rubber increases the hysteresis and it increases with increasing the content of filler. Comparing the mechanical hysteresis in the different samples, it is to be noted that the hysteresis in the PDMS rubber samples loaded with carbon black is greater than that of samples with graphite. So, one can conclude that the energy required to break the reticulated structure of carbon aggregates and rubber molecules is higher than that needed to overcome the interaction between graphite and rubber chain segments. The presence of particulate fillers such as carbon black which has smaller particle size and larger

surface area than G leads to an increase in the cross-links and a decrease in the segmental mobility and hence increase the viscosity and internal friction between rubber chains leading to an increase in the hysteresis.

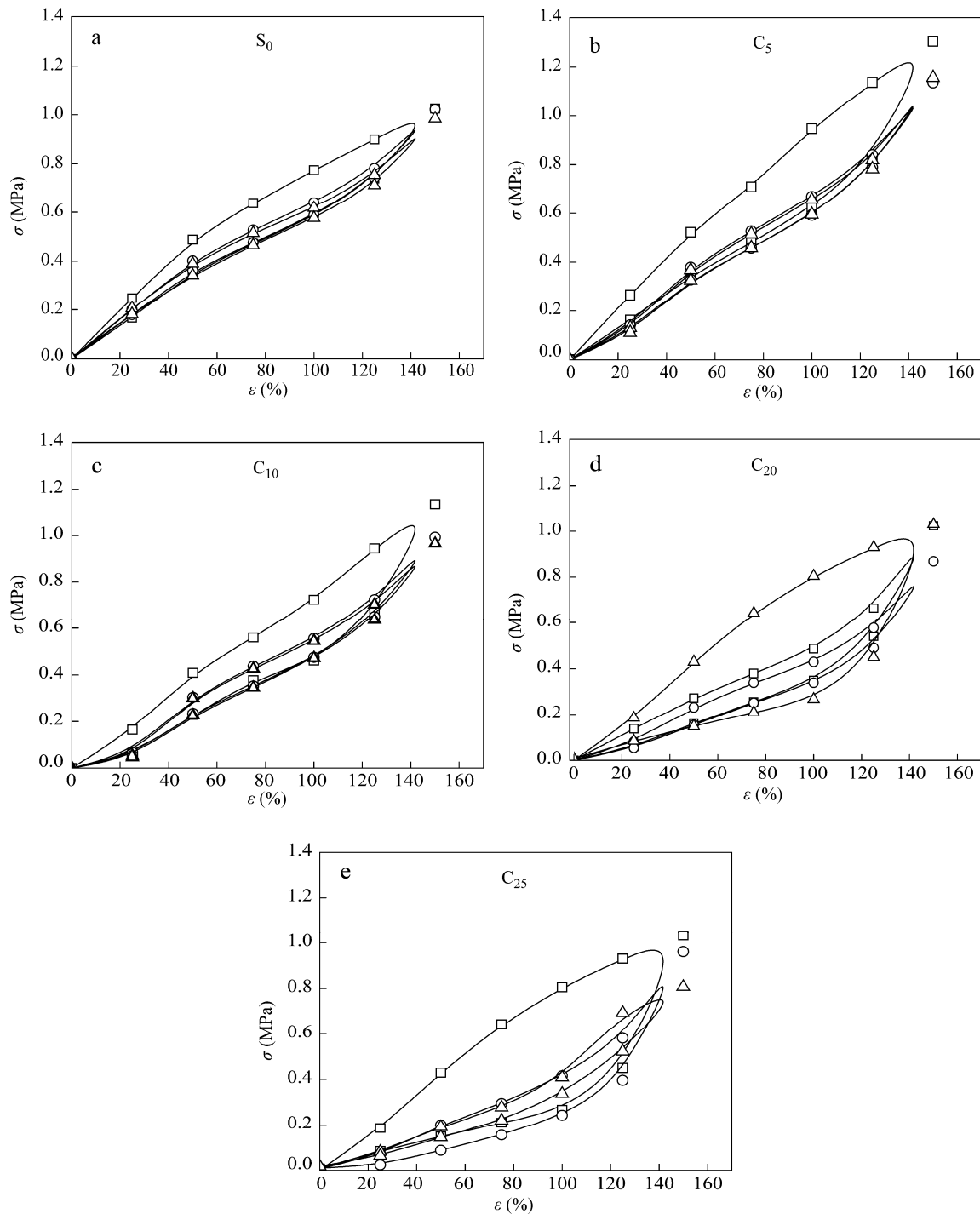


Fig. 4 Cyclic stress-strain curves for PDMS rubber loaded with different contents of carbon black ($\square$ 1st cycle, $\circ$ 2nd cycle, Δ 3rd cycle)

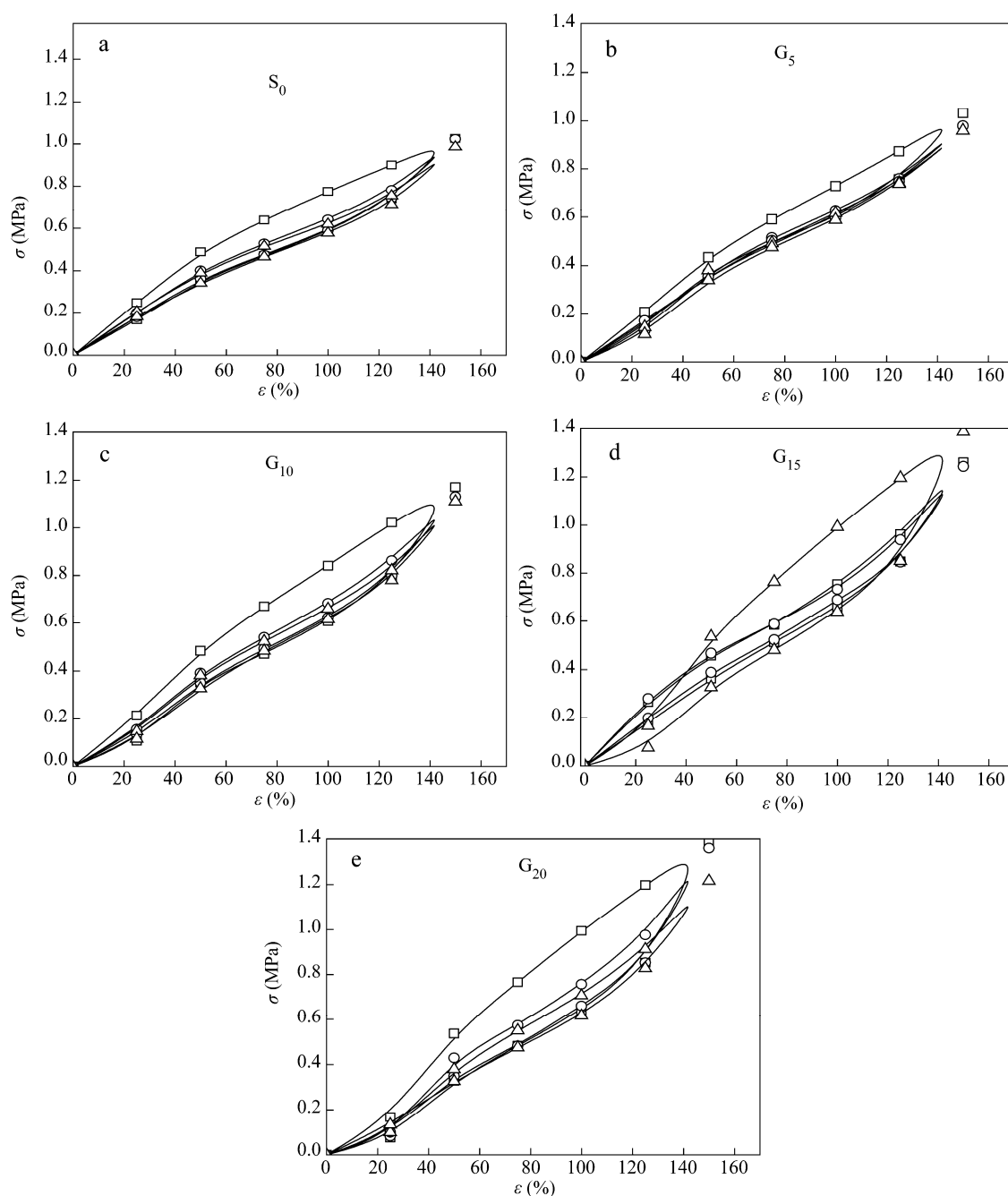


Fig. 5 Cyclic stress-strain curves for PDMS rubber loaded with different contents of graphite ($\square$ 1st cycle, $\circ$ 2nd cycle, Δ 3rd cycle)

This is the result of rearrangement of the molecular structure under applied load and subsequent sliding of chains past each other. On the other hand, the CB particles tend to form a loose reticulated structure because of their surface activity or mutual interactions. The breakdown of these aggregates and the matrix/CB interfacial bonds due to loading gives rise also to increase hysteresis. The second cycle hysteresis is smaller than the first cycle one. However, in the third cycle the amount of hysteresis is almost the same as or less than that in the second cycle.

Rubber-like materials exhibit a particular damage behavior called the Mullins effect. This is visible when cyclic tension tests are performed with increasing values of deformation. Material is deformed up to a fixed strain value and then unloaded. When a second load is applied it is possible to see a stress softening effect. Mullins effect consists of a change in material properties between its original state (un-stretched) and after the material has been subjected to a load. It was first observed and studied by Mullins and Tobin^[35]. They idealized that rubber could exist in two phases: a hard phase and a soft phase. When the material is virgin it shows only the hard phase, but, when greater and greater deformation is applied, more and more rubber degrades in the soft phase^[36]. In this work, the hysteresis associated with the Mullins effect was characterized as the ratio of the dissipated mechanical energy (area of the hysteresis) over the energy of first loading (area below the first loading curve) as explained in Fig. 6 as the ratio $R_M = \frac{A}{A+B}$ where A is the area between the loading and the unloading curves and B is the area under the unloading curve.

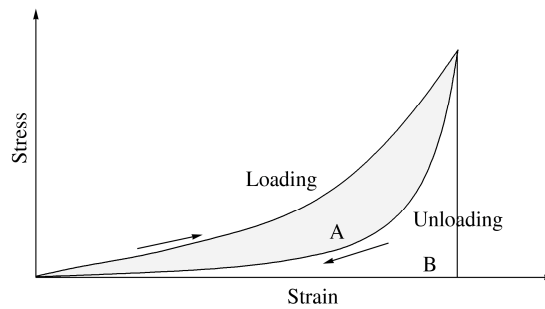


Fig. 6 Definition of the Mullins ratio $R_M = \frac{A}{A+B}$

As far as literature is concerned and to the best of our knowledge, the relation between R_M and V_f has not been studied before. Figure 7 shows the evolution of R_M and V_f as a function of the filler content during the first cycle for the composites containing CB and G. It's clear from the figure that R_M increases with increasing the filler content. Also, the values of R_M for the C-samples are higher than those of the G-samples. Indeed, there is a negative correlation between the free-volume V_f and the macroscopic mechanical properties, R_M in the present work, of PDMS composites containing conductive fillers.

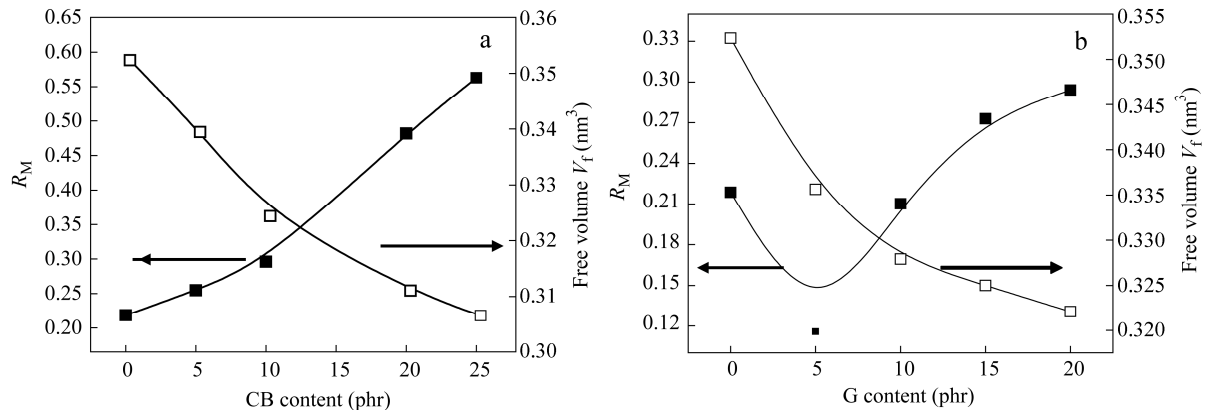


Fig. 7 V_f and R_M versus the filler content: (a) C-samples and (b) G-samples

By comparing the values of R_M for the different types of fillers (see Table 3), it is found that R_M for C₂₀ has higher values than G₂₀. This has been explained before due to the difference in particle size and surface area of the filler. Again CB has smaller particle size and larger surface area than G-particles, which are responsible for increasing the physical cross-linking, so that the values of R_M for C-samples are higher than those of G-ones.

Finally, the dependence of the Mullins ratio R_M as a function of the number of cycles is shown in Figs. 8 and 9. It's clear that R_M decreases with increasing the cycling. This behavior is called the stress softening which is due to the modification and reformation of rubber network structures that contribute to weak hysteresis variations. The main features contributing to the stress-softening behavior involve chemical effects, micro-structural damage, multi-chain damage and micro-void formation.

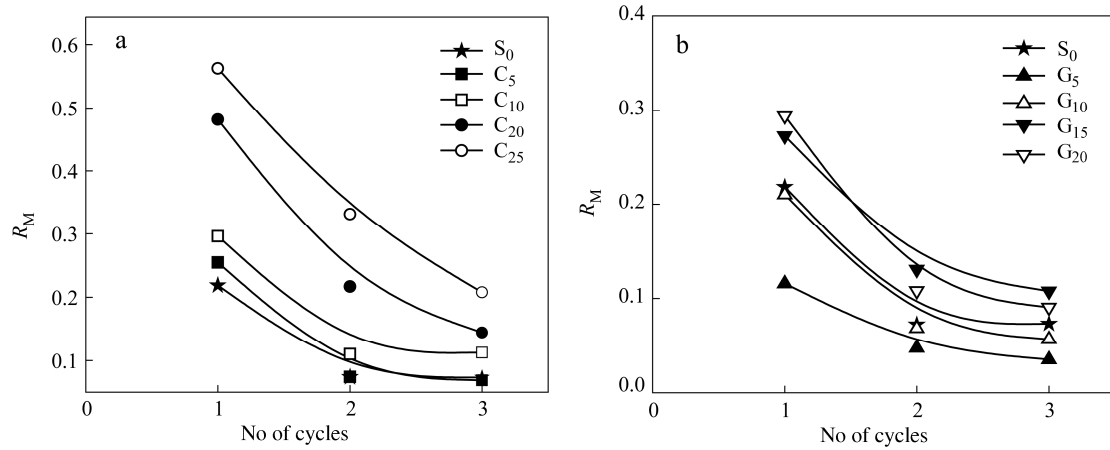


Fig. 8 R_M as a function of the cycles' number for PDMS composites loaded with different contents of (a) CB and (b) G

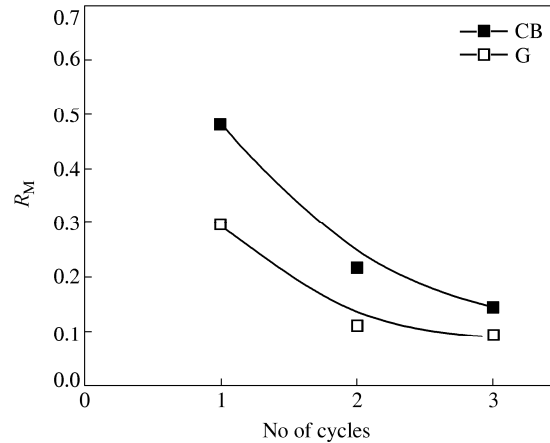


Fig. 9 R_M as a function of the cycles' number for PDMS composites loaded with 20 phr of different fillers

CONCLUSIONS

The effect of CB and G powders on the macroscopic and nano-scale free volume properties of silicone rubber was studied and it was found that:

1. The free volume V_f decreases as the filler content increases in the PDMS composites containing CB and G.
2. The melting temperature T_m and the degree of crystallinity χ_c decrease as CB content increases.
3. The hysteresis in the CB loaded PDMS composites is greater than that of graphite loaded ones.
4. Mullins ratio R_M increases with increasing the filler content.
5. A correlation was established between the free volume V_f and the mechanical properties of PDMS composites containing different contents and/or types of fillers.
6. V_f , χ_c and R_M were dependent on the filler type for PDMS composites.

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