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Morphology, Mechanical and Dynamic Mechanical Studies of Silicon Elastomer Nanocomposites

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Abstract: Multiwalled carbon nanotube (MWCNT) reinforced silicone elastomer nanocomposites are prepared. The morphology of the nanocomposite samples have been studied from scanning electron microscope (SEM). The effect of MWCNT loadings on mechanical properties like hardness, tensile strength, elongation at break, modulus have been studied. It shows increase in tensile strength, hardness and modulus and decrease in elongation at break with MWCNT loading, attributed towards better silicone elastomer-MWCNT interaction. At higher MWCNT loading the rate of increase slowly decreases due to percolation threshold. Dynamic mechanical properties of nanocomposites have also been studied. The effect of MWCNT loading on storage modulus, loss modulus and loss tangent has been observed. Cole-cole plots explain the non-linearity in the nanocomposites as well as excellent distribution of MWCNT in the elastomer matrix.

1. INTRODUCTION

Nanocomposites are filled polymers, whose at least one dimension is in the nanometer scale. The addition of such nanoscale fillers such as clay, carbon nanotube, silica particle etc into the polymer matrix was found to enhance the thermal stability and mechanical properties efficiently. This enhancement was attributed to the unique characteristics of the nanofillers [1]. A significant part of investigations in this field concerns carbon based composites using (CNTs) [2], carbon black [3] as filler. Carbon nanotubes (CNTs) have exceptional electrical, mechanical, electrochemical, chemical, thermal and thermo electric properties [4]. CNTs have high aspect ratio (length to radius ratio), high conductivity and an added advantage of achieving percolation at lower concentration than spherical fillers, which make them an excellent choice for electrically conducting composites. CNTs are widely used as filler in polymer matrix in order to improve the mechanical properties (reinforcement) and to transform insulating material into a conducting one. MWCNTs with extra ordinary mechanical and electric properties have the potential application as the reinforced material in polymer composites. [5]. However, it is generally difficult to disperse MWCNTs in polymer matrices because they have large surface area, possess strong Vander Waal forces, which result in significant aggregation [6]. The composites demand uniform dispersion of the MWCNTs in the polymer matrix without their aggregation and good interfacial adhesion between the MWCNTs and polymer matrix.

Silicone rubbers (SiR) have been shown various applications due to their good chemical resistance, thermal stability and elasticity [7]. The systematic study of the properties of silicon rubber, particularly filled with MWCNTs has not received much attention till today. The aim of this study is to identify the influence of additional MWCNTs as nanofiller on the morphology, mechanical and dynamic mechanical studies of the silicone elastomer. To probe the mechanical properties of interest, the dynamic mechanical analysis (DMA) to study the visco-elastic properties of the elastomer and to directly measure the temperature dependency of the modules, study was used.

2. EXPERIMENTAL

2.1. Materials

Silicone Elastomer (Mooney viscosity ML_{1+4} at 100°C =60) was procured from Bayer AG. Multiwall carbon nanotube (MWCNT) of purity $\geq$ 95% were purchased from Nanoshel LLC, USA. Before usage, the nanotubes were treated with acid mixture under ultrasonication to remove amorphous carbon and metallic impurities. Other chemicals like zinc oxide specific gravity of 5.4, stearic Acid and di cumyl peroxide used as curing agent were chemically pure grade procured from standard suppliers.

2.2. Compounding and sample preparation

The rubber was compounded with the ingredients according to the formulation of the mixes (Table 1). Compounding was done in a brabender plastograph at 60rpm followed by laboratory size (325x150 mm) two roll mixing mill at a friction ratio of 1:1.25 according to ASTM D 3182 standards while carefully controlling the temperature, nip gap, time of mixing, and uniform cutting operation. The temperature range for mixing was 65–70°C. After mixing the elastomer compositions were molded in an electrically heated Moore hydraulic press at a pressure of 10MPa and at 160°C using

moulding conditions determined by Monsanto Rheometer (R-100) according to ASTM D2084 and ASTM D5289 procedures.

Table 1 Compounding formulation for silicon elastomer nanocomposites

Ingredient	Phr
Silicone Rubber	100
Stearic Acid	2
ZnO	5
DCP	2
MWCNT	0 (SiR1), 2 (SiR2), 4 (SiR3), 6 (SiR4)

2.3. Testing

2.3.1. Scanning electron microscopy (SEM)

Morphology of the compounds has been studied by using an INCA Penta FETX3-8113 (Oxford instrument, England) Scanning Electron Microscope (SEM). Prior to SEM studies, the sample surface was sputtered / coated with gold. The fractured surfaces from tensile test were also studied.

2.3.2. Mechanical studies

Hardness was measured using a Shore-A Durometer as per ASTM D 676-59T. Mechanical properties of dumbbell specimen like modulus, tensile strength and elongation at break were measured using a Hounsfield H10KS Universal Testing Machine according to ASTM D 412 procedure.

2.3.3. Dynamical mechanical analysis (DMA)

DMA was carried out using TA instrument over a temperature range of -100 to 100 ^{o}C, at a frequency of 1 Hz and at 1% strain. Storage modulus (E'), loss modulus (E") and loss tangent (tanδ) curves were plotted versus temperature from measured data.

3. RESULTS AND DISCUSSION

3.1. Morphology

The SEM photomicrographs of razor cut surfaces of silicone elastomer nanocomposites are shown in figure 1. Three compositions are shown in figure and the concentrations of MWCNT in matrix were 2, 4 and 6 phr respectively. The dark phase represents the polymer matrix and the bright phase represents the MWCNTs. The MWCNTs (bright dots) are found to disperse homogenously in the rubbery matrix. At a low MWCNT concentration, there was no clear observation of a double phase structure because of partial compatibility between silicon elastomer and MWCNT. All the

microphotographs show good distribution of the MWCNTs. SEM studies reveal that the dispersion of MWCNT is homogenous in the polymer matrix but aggregation takes place as filler loading increased, which is clearly observed from the photomicrograph of sample containing 6 phr loading.
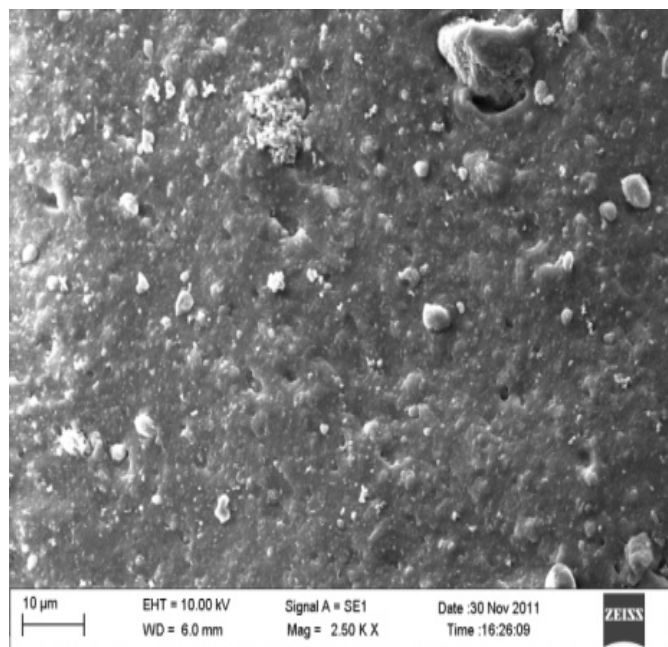
3.2. Mechanical properties

Mechanical properties like hardness, tensile strength, elongation at break and modulus are shown in Table 2. The ultimate tensile strengths and young's moduli increase with higher MWCNT loading. Clearly there is reinforcement as evidenced by considerable improvements in stiffness and tensile strength of the composites with the filler loading.
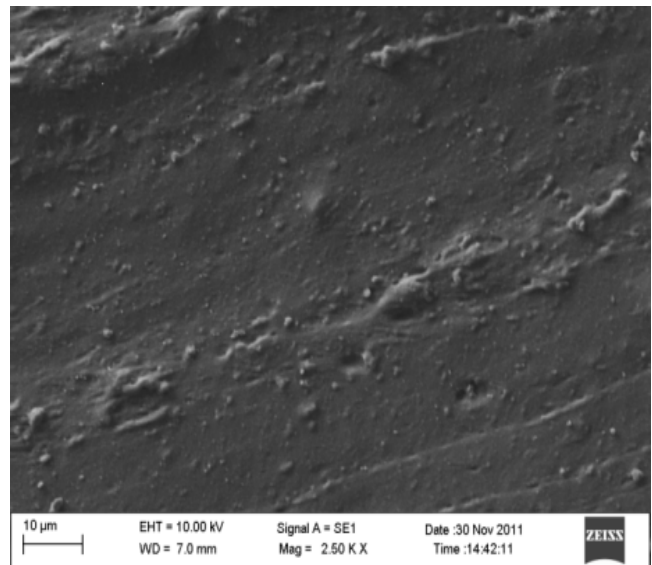
(a)
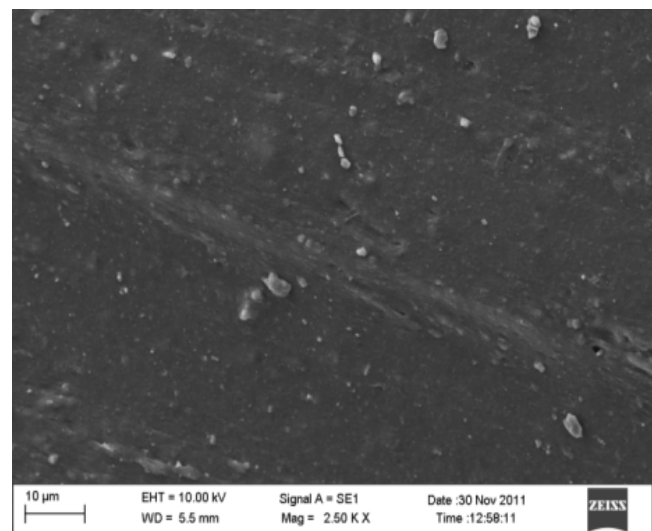
(b)

(c)

Fig. 1 SEM photomicrographs of razor cut surfaces of Silicone elastomer nanocomposites: effect of MWCNT loadings, (a) 2 phr (b) 4phr (c) 6phr.

Table 2 Mechanical properties of unfilled and MWCNT filled silicone elastomer nanocomposites.

Mix No	Hardness (shore A)	Tensile Strength (Mpa)	Elongation at Break (%)	Modulus (100%) Mpa	Modulus (200%) Mpa	Modulus (300%) Mpa
SiR1	41	5.5	530	1.03	1.86	2.72
SiR2	44	5.12	360.29	1.47	2.79	4.37
SiR3	47	5.6	370.29	1.55	3.01	4.77
SiR4	49	6.17	400.21	1.71	3.28	5.06

The tensile strength increases with MWCNT loading. The incorporation of filler into the silicone rubber increased the tensile strength to make tougher and more resistant to deformation. The Shore A hardness of the unfilled and filled nanocomposites, show the expected increase in hardness with increasing surface area of the MWCNT. It has been well established that the hardness of composite is an expression of their elastic modulus, i.e. their resistance to deformation. As the degree of crosslinking increases, the hardness progressively increases. The more compact the networks, the shorter are the molecular segments between the crosslinks and hence the tighter is the network, which causes increase in hardness. High value of hardness is due to high reinforcing nanotube having very high surface area.

The elongation at break decreases with increasing concentration of MWCNT loading. At lower loading

crosslinking density decreases which may cause increase in elongation at break, whereas at higher loading crosslink density and viscosity both increases which causes decrease in elongation at break. It is noted that the tensile stress at 100, 200 and 300% elongation shows that the stress at a given elongation increases with increasing surface area of the MWCNT. The factors controlling the young's modulus also apply to tensile stress, with the exception that at such high elongation, especially 300%, the contribution of MWCNT agglomeration has ceased to be important.

However, at high strain, the orientation of polymer chains in the original agglomerates along the direction of strain may also easily reach the limitation of finite chain extensibility, giving higher stress at given elongation. In other words, even if the agglomerates are broken down at high elongation, the more developed multi-attachment of polymer chains in the agglomerates may also contribute to the higher stress at high deformation, as long as detachment of the polymer chains from filler surface does not occur. In this regard, high surface area MWCNT will also favor high tensile stress and depend upon highly developed filler network and polymer-filler interactions. The extent of reinforcement depends on several filler characteristics such as its modulus, geometry and orientation within the host matrix [8-9].

The properties of composites materials depend on the individual component and their interaction. In order to explain the reinforcing effect of colloidal fillers on elastomer, Guth and Gold used Einstein's equation derived for the flow characteristics of polymer filled with spherical particles and proposed the following equation.

$$E = E_0(1 + 2.5\phi + 14.1\phi^2) \tag{1}$$

Where E and E_0 are the initial modulus of the filled and unfilled elastomer respectively and ϕ is volume fraction of the filler. It appears that Einstein's equation was modified by adding a mutual disturbance term caused by the spherical particles. Later Guth developed the following well-known equation by introducing a shape factor f (length/breadth), modifying equ (1) to extend its application to non spherical fillers [10].

$$E = E_0(1 + 0.67f\phi + 1.62f^2\phi^2) \tag{2}$$

The Halpin–Tsai model [11] also predicts the stiffness of the composites as a function of the aspect ratio. The longitudinal modulus measured parallel to perfectly oriented fibers is expressed in the general form:

$$E = \frac{E_0(1 + 2f\phi\eta)}{1 - \phi\eta} \tag{3}$$

Where η is given by

$$\eta = \left[\frac{\dfrac{E_f}{E_0} - 1}{\dfrac{E_f}{E_0} + 2f} \right]$$

(4)

E_f is the modulus of the filler. In elastomeric composites, $E_f \gg E_0$, so Eq (3) reduces to
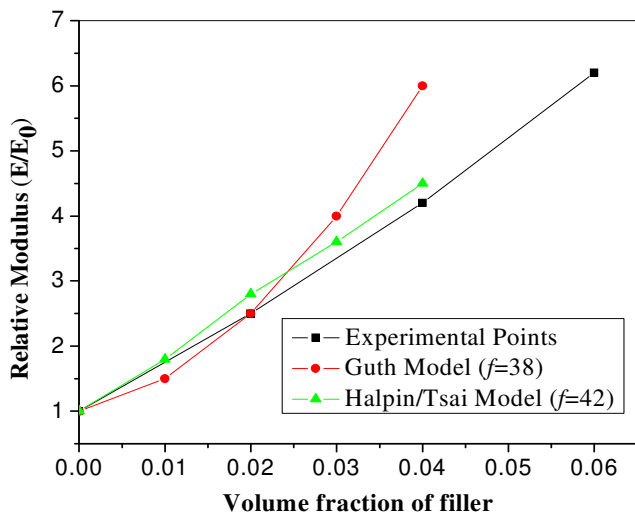
$$E = \frac{E_0(1 + 2f\phi)}{1 - \phi}$$

(5)

Fig. 2 Experimental modulli plotted versus volume fraction of MWCNTs and comparison with theoretical predictions.

In Figure 2 the experimental values of E/E$_0$ are compared with the Guth and Halpin-Tsai predictions using the respective aspect ratios of 38 and 42 to fit the data. While the Guth model departs from the experimental results at the highest filler loadings, the Halpin-Tsai model, for perfectly aligned fibres, shows good agreement within the volume fraction range investigated. Both the models yield almost similar aspect ratios. The values required to fit the experimental data are the lower than that calculated from the average dimensions of the MWCNTs. It is most probably due to aggregation of the nanotubes which reduces the aspect ratio of the reinforcement.

3.3. Dynamic mechanical properties

3.3.1. Effect of temperature on Loss Tangent

Figure 3 shows the loss tangent spectra of silicone elastomer vulcanizates reinforced with increasing amount of MWCNTs as a function of temperature. It can be observed that the location of maximum value of loss tangent ($\tan \delta_{max}$) is not significantly affected by the extent of filler loading. All the samples show the glass transition in the narrow temperature range of -10°C to -5°C. This can be explained on the basis of relaxation dynamics of the polymer matrix. One of the main features of reinforced elastomers is that majority of polymer chains are in contact with the filler surfaces. Addition of filler into the polymer matrix induces a gradient of glass transition temperature in the polymer chains that are in the vicinity of the fillers due to the existence of strong dynamical heterogeneities [12-13]. These heterogeneities originate from thermal fluctuations of density, and the heterogeneous nature polymer composites. When a polymer is cooled through the glass transition region, the physical properties of the polymer in the nonequilibrium state (at temperature lower than T_g), such as volume and enthalpy, gradually recover to new equilibrium values through the configurational rearrangement of polymer segments. The rate of rearrangement of relaxation process depends on the local environment surrounding the relaxation entities and hence reflects the extent of environmental restriction on those entities.
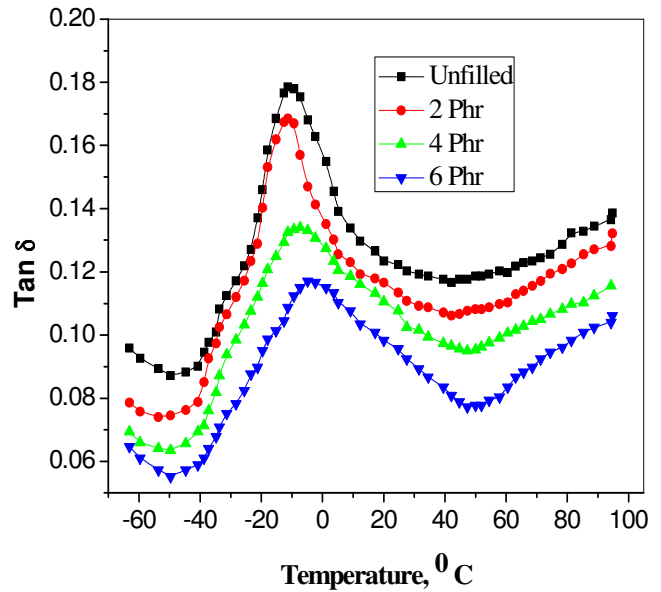

Fig. 3 Variation loss tangent (Tanδ) with temperature as a function of MWCNT loading in silicone elastomer nanocomposites.

But increasing filler loading shows decrease in the magnitude of the loss tangent with simultaneous broadening of the peak.

3.3.2. Effect of temperature on Storage and Loss Modulus

The variation in storage modulus (E') as a function of temperature (-120°C to +90°C) is shown in Figure 4.

Fig. 4 Variation of storage modulus with temperature as a function of MWCNT loading in silicone elastomer nanocomposites.
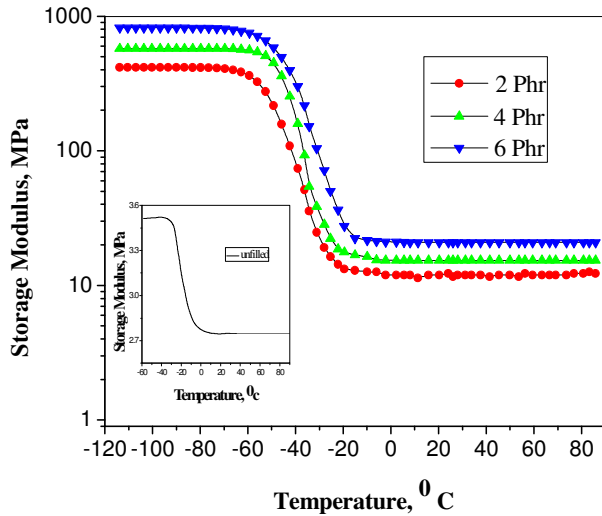

Fig. 5 Variation of loss modulus with temperature as a function of MWCNT loading in silicone elastomer nanocomposites.

Irrespective of the MWCNT loadings all the curves show characteristics sigmoidal variation of E' with temperature. Generally, the augmentation of E' with filler in the glassy region (-120 to -50°C) can be attributed to the hydrodynamics effect of filler particle embedded into the polymer continuum. The effect of incorporation of a filler (be it a reinforcing filler or not) on the mechanical properties of elastomeric materials can be partially explained as follows: if particles of high elastic modulus are dispersed through a low elastic-modulus matrix, it is obvious that the modulus of the mixture will be higher than that of the matrix, solely because of the decrease in volume content of matrix substance.

However, for a filler to be really reinforcing in nature, many other factors come into the picture, the most important being the force of adhesion of the matrix to the particle surface which plays a crucial role. If adhesion between filler and polymer matrix is very low then significant increase in modulus (except due to hydrodynamics effect) is observed. But, if the particle-to-matrix adhesive force is large, then the modulus of the mixture is primarily determined by the magnitude of the polymer filler interactions.

Figure 5 represents the temperature dependence of the loss modulus (E'') for various compositions. For all filled compositions, a distinct peak (a transition) is observed around -50°C that can be attributed to conformational transitions occurring in the silicone elastomer backbone caused by micro-Brownian motion. The amount of MWCNT does not affect the temperature at α peak; however the intensity of α peak increases slightly with MWCNT loading due to increase in reinforcement.
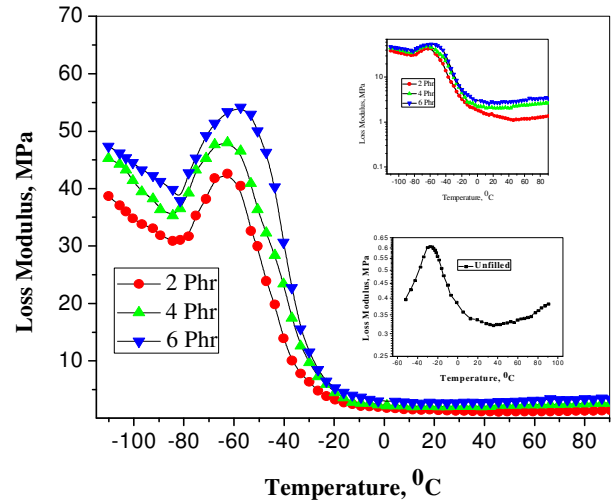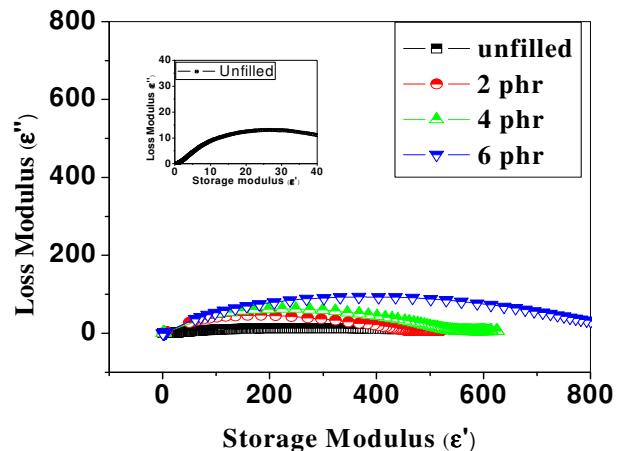

Fig. 6 Cole-cole plots of silicone elastomer nanocomposites with increasing MWCNT loadings

At higher MWCNT loadings, it results a percolated network of filler particles can influence relaxation on a different scale. The percolation effect is usually considered to be effective for relaxation of longer time scales, such as the terminal relaxation observed in some rheological measurements. However, recent dynamic mechanical experiments for composites solids seem to indicate that restriction effects in fact do result from the formation of a percolation network. [14-16]. Nevertheless, reports regarding the restriction effects of percolated networks on the segmental relaxation are not fully conclusive, and the issue awaits more detailed and systematic study.

Cole–Cole plots (the relationship between storage modulus and loss modulus) for multiwalled nanotube reinforced SiR Nanocomposites are shown in Figure 6. Irrespective of

MWCNT loading at all concentrations of the filler, the usual depressed semi-circular arc can be observed which indicates the presence of a reinforcing element. The large change observed on the arc radius in the Cole–Cole plot indicates the relaxation dynamics and a significant alteration of chain conformation due to MWCNT interaction [17]. McLachlan et al. correlated the shape of Cole-Cole plots with the homogeneity of MWCNT dispersion in the polymer matrix. Irrespective of MWCNT concentrations, smooth arcs are observed with no humps indicating good dispersion of MWCNT in the polymer matrix [18].

4. CONCLUSIONS

We have demonstrated the preparation of silicone elastomer nanocomposites consisting of 2-6 wt% of MWCNT. The nanocomposites were prepared through a mechanical mixing technique. SEM micrographs show excellent distribution of MWCNT in the polymer matrix. It reveals that the dispersion of MWCNT is homogenous in the polymer matrix but aggregation takes place as filler loading increased, which is clearly observed from the SEM photomicrograph of sample containing 6 phr filler loading. Tensile strength and modulus increase with MWCNT loading, whereas elongation at break gradually decreases.

With MWCNT loading hardness also gradually increase, due to increase in crosslink density. Guth model departs from the experimental results at the highest filler loading whereas Halpin-Tsai model shows good agreement within the volume fraction range.The dynamic mechanical analysis of the nanocomposites shows that the addition of the MWCNT has no significant effect on the glass transition temperature, T_g. However on increasing MWCNT loading the intensity of tan☐ curve decreases. This has been explained in terms of filler polymer interaction and interaggregate interaction. Broadening of the relaxation region was observed in the plots of storage and loss modulus with temperature.

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