MWCNTS Incorporated Natural Rubber Composites: Thermal Insulation, Phase Transition and Mechanical Properties

Sadia Sagar, Nadeem Iqbal, Asghari Maqsood, and M. Bassyouni

***Abstract*—The effect of variant concentrations of multiwalled carbon nanotubes (MWCNTs) on the thermal transport, phase transition temperatures, and mechanical properties of polyisoprene rubber have been studied in the present novel research. MWCNTs were incorporated into the natural rubber (NR) using shear mixing techniques. Microscopy results reveal the uniform dispersion of the nanotubes within the polymer matrix. Thermal conductivity and thermal insulation of the fabricated composites were evaluated according to ASTM standards. Thermal transport through the nanocomposite specimens is restricted by the nanotubes network developed within the polymer matrix. Differential scanning calorimetric study elucidates the reduction of crystallization (T_c) and glass transition (T_g) temperatures, while melting temperature (T_m) enhances with increasing the nanotubes concentration in the rubber matrix. A remarkable enhancement in mechanical properties of MWCNT/NR composites was observed with increasing nanotube to matrix ratio.**

***Index Terms*—Multiwalled carbon nanotubes, thermal transport properties, nanocomposite, thermal stability, phase transition temperatures.**

I. INTRODUCTION

Nanoreinforcements give better mechanical, thermal and electrical results when incorporated into the polymer matrixes compared to macro/micro size incorporations attributed owing to their large low density, specific surface area, and nanoscale interaction with the polymeric chains[1]. Nanofillers, even in little quantity (0.1-5 wt %), have the capability to efficiently enhance the physical and chemical characteristics of the host matrix. Carbon nanotubes (CNTs) have a prominent image among the nanofillers family due to their outstanding features. The tensile strength and elastic modulus equal that of diamond, i.e., 200 Giga Pascal and 1Tera Pascal, respectively. CNTs have high specific surface area up to 1315m^2/g, aspect ratio up to 10^4 and low density (1.3g/cm^3)[2].

Due to the exceptional character of nanotubes, researchers around the world have introduced them into the polymer, metal and ceramic matrixes using different dispersion techniques to fabricate nanocomposites for engineering applications, i.e., automobile industry, sports industry, membrane technology, aerospace industry, energy storage and many more. In order to fabricate an affective composite, aspect ratio of the nanotube should not be diminished. The CNTs/polymer nanocomposites have also shown outstanding thermal stability in nitrogen as well as in oxygen atmospheres. Uniformly dispersed nanotubes develop a network in a polymer matrix that restricts the thermal mobility of polymeric chains in the heat atmosphere [3]. Polyisoprene rubber (NR) with superb thermal/mechanical properties, oil/hot air ageing and swelling resistance has extensively used in automobile and oil industries. Selection and designing of a composite for a specific application necessitate its thermal transport/endurance data. Evaluation of thermal properties for a polymer nanocomposite has great importance to allocate relevance area of application.

This paper reports the novel investigation of thermal impedance, thermal conductivity, thermal composition, heat flow response, glass transition/crystallization/melting temperatures, and specific enthalpies of NR nanocomposites with five diverse loadings of pristine multiwalled carbon nanotubes (MWCNTs).

II. EXPERIMENTAL

A. Materials

Nanocarbon, stearic acid, sulphur and zinc oxide were received from Merck, Germany. Mercaptobenzothiazole (MBTS) and cyclohexyl Benzthiazyl Sulphenamide (HBS) were supplied by Dalian Richon Chemical Co. Ltd, China. Aromatic oil and wax were bought from International petrochemicals (Pvt) Ltd, Pakistan. MWCNTs (fabricated through CVD method with Fe catalyst, Purity > 95%, diameter 20-30nm, and length 50-70μm, average aspect ratio 2400:1) were supplied by Nanoport Co. Ltd and China. Polyisoprene rubber (RSS3) was purchased from Phu An Import Export CO.,Ltd. Viet Nam.

B. Preparation of Rubber Nanocomposites

Nanocarbon and five diverse concentrations (0–1wt %) of MWCNTs were incorporated into the rubber matrix using internal dispersion kneader at 110°C for thirty minutes. Then the post mixing of carbonaceous fillers along with the addition of crosslinker (sulphur), accelerators (MBTS & HBS), activators (ZnO & stearic acid) and plasticizers (aromatic oil & wax) in the NR matrix was carried out using two roller mixing mill at temperature 70°C and 40 rpm roller's speed for 25 minutes. Rubber nanocomposites with

$6.0 \times 6.0 \times 0.12$ inch³ dimensions were fabricated on hot isostatic press at 1400psi and 140°C for thirty minutes. Table I elucidates the basic composition of NR composite (NR1). Five diverse concentrations of MWCNTs were impregnated as 0.1 wt% (NR2), 0.3 wt% (NR3), 0.5 wt% (NR4) and 1 wt% (NR5) in the basic composite formulation without nanotubes (NR1).

TABLE I: FORMULATION OF MWCNT/NR COMPOSITE

Sample ID/ Filler (wt%)	NR1	NR2	NR3	NR4	NR5
MWCNTs	0	0.1	0.3	0.5	1.0
NR: Natural rubber (100 wt%), Aromatic Oil (10 wt%), Wax (2.5 wt%), Zinc oxide (5 wt%), Sulphur (2.5 wt%), Streaic Acid (2 wt%), Carbon black (40 wt%) MBTS: Mercaptobenzothiazole disulphide (2.5 wt%) HBS: Cyclohexyl Benzthiazyl Sulphenamide (2 wt%)					

C. Characterization

Scanning electron microscopy (SEM, JSM 6940A, Jeol, Japan) along with the energy dispersive spectroscopy was used to analyze the dispersion of MWCNTs in the polymer matrix, surface morphology of the post thermal conductivity/impedance tested specimens, elemental analysis of the nanotubes and nanocomposite.

D. Thermal Conductivity and Thermal Impedance Measurements

Thermal conductivity (λ_N) of the nanocomposite specimens were carried out using ASTM E1225-99[4]. The tested specimen has 1inch² area and 3mm thickness. Copper was used as a relativistic material for the measurement of λ_N and R. Schematic illustration of comparative guarded longitudinal heat flow system in Fig. 1 shows the possible locations of temperature sensors, heating source, water heat sink, temperature data logger and a laptop. Time–temperature contours of all thermocouples located at specific positions were monitored on the laptop screen through Grant OQ610 6 Channel Thermocouple Input Data Logger. λ_{NR} of the NR nanocomposite specimens was measured using Equation 1[5]-[6].

$$\text{Thermal conductivity} = \lambda_{NR} = \frac{(Q'_T + Q'_B)(X_4 - X_3)}{2(T_4 - T_3)} \qquad (1)$$

where

Heat flow at top bar $= Q'_T = \frac{\lambda_C(T_2 - T_1)}{(X_2 - X_1)}$

Heat flow at bottom bar $= Q'_B = \frac{\lambda_C(T_6 - T_5)}{(X_6 - X_5)}$

λ_C = Thermal conductivity of the copper meter bar

T_1, T_2, T_3, T_4, T_5 and T_6 are the temperatures of six thermocouples and X_1, X_2, X_3, X_4, X_5 and X_6 are the corresponding positions of these six thermocouples.

Thermal impedance (R) of a material is its ability to resist thermal/temperature fluctuations in a variable heating environment. To evaluate R of the rubber nanocomposites, four thermocouples have been used instead of six in afore mentioned thermal conductivity experimental setup. Thermal impedance (R) of a material is its ability to resist thermal/temperature fluctuations in a variable heating environment. To evaluate R of the rubber nanocomposites, four thermocouples have been used instead of six in afore

mentioned thermal conductivity experimental setup. R was measured according to ASTM D5470-03 and Equation 2.

$$\text{Thermal impedance} = R = \lambda_C(T_A - T_D)\left(\frac{Area}{Q}\right) \qquad (2)$$

where

Heat Flow $(Q) = Voltage\ (V) \times Current(I)$

Temperature of upper meter bar surface in contact with the specimen$(K) = T_A = T_2 - (T_1 - T_2)\frac{x_b}{x_a}$

Temperature of lower meter bar surface in contact with the specimen$(K) = T_D = T_3 - (T_3 - T_4)\frac{x_d}{x_c}$

where

$T_1(K)$ = Upper temperature of upper meter bar
$T_2(K)$ = lower temperature of upper meter bar
$T_3(K)$ = Upper temperature of lower meter bar
$T_4(K)$ = Lower temperature of lower meter bar
$x_a(m)$ = Distance between T_1 to T_2
$x_b(m)$ = Distance between T_2 to S Sample
$x_c(m)$ = Distance between T_3 to T_4
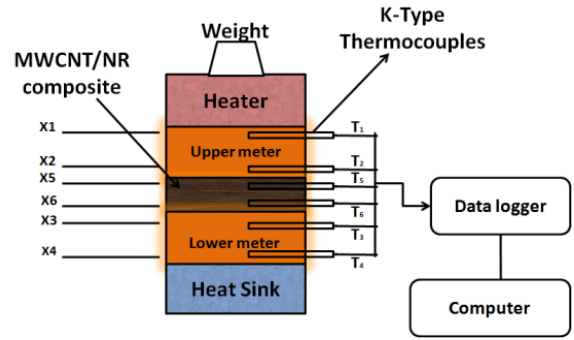$x_d(m)$ = Distance between Sample to T_3

Fig. 1. Experimental setup for the measurement of thermal conductivity and thermal impedance of the fabricated rubber nanocomposites

E. GA/DTA and DSC Study

Thermal decomposition and heat flow response of the polymer composites were carried out using Perkin Elmer Diamond TG/DTA, Japan. Heating rate and temperature range during the Thermogravimetric and differential thermal analyses of the specimens was 10°C/min and 25-800°C, respectively. Perkin Elmer Diamond DSC, Japan was used to examine the physical phase transitions (glass, crystallization, and melting) and their specific enthalpies of the fabricated samples with heating rate (10°C/minute) in the temperature range -75 to 450°C.

F. Mechanical Properties

Tensile strength, elongation at break, and modulus of elasticity of the polymer nanocomposites were executed using universal tensile testing machine (AG-20KNXD Plus, Shimadzu) according to the ASTM D412-98A. Shore A rubber hardness of the composite specimens were carried out using Torsee, Tokyo testing machine.

III. RESULTS AND DISCUSSION

A. Dispersion of MWCNTs

The even dispersion of MWCNTs in the NR matrix can be examined in the SEM micrographs, displayed in Fig. 2 (a, b) along EDS in Fig. 2 (c, d). Appropriate heating environment in the internal dispersion kneader has promoted the

carbonaceous filler diffusion in the rubber mixing. The post mixing of nanofiller on two roller mixing mill, imparts longitudinal and transverse flow during the passage of material through the twin roll nip which enhances the dispersibility of nanotubes in the polymer matrix. The even dispersion of MWCNTs in the host matrix makes a nanocomposite more efficient. Compositional analysis of the nanocomposite (Fig. 2d) confirms the presence of the incorporations listed in Table I. Embedded MWCNTs in the rubber matrix are clearly visible in Fig. 2c. The EDS analysis of the nanotube resulted in 100% carbon [7]-[9].
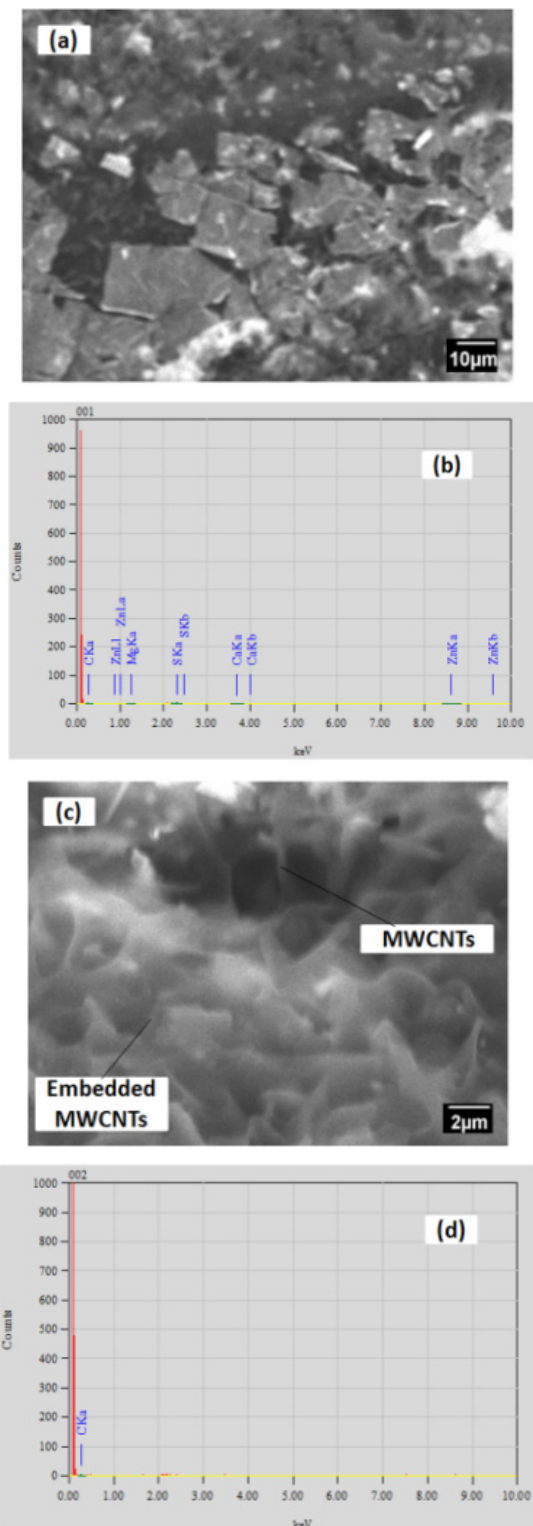

Fig. 2(a, b, c, d). SEM micrographs of MWCNTs dispersion at variant magnifications (a, c) and compositional analysis of carbon nanotubes (d) and the 1wt% loaded MWCNTs in polymer nanocomposites (b)

B. Thermal Conductivity and Thermal Impedance Analyses

Thermal conductivity measurements of the rubber nanocomposites in the temperature range 50 to 250°C are portrayed in Fig. 3. The enhancement of thermal conduction at the start of experiment for NR1 is lower than other nanocomposites[10].
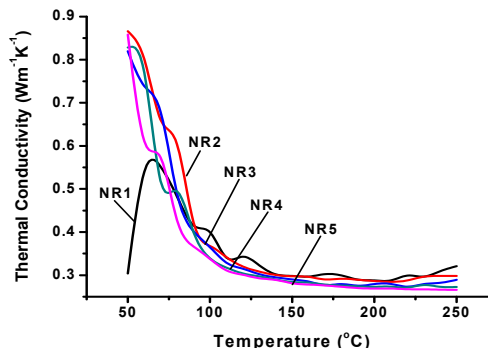

Fig. 3. The effect of MWCNTs concentrations on thermal conductivity of polymer nanocomposites in the temperature range 50 to 250°C

λ_{NR} falls down with increasing upper copper bar temperature up to 100°C, then approximately a constant level of λ_{NR} for all composites is established in the proceeding temperature range. NR5 settles itself at the lowest possible level of λ_{NR} among the other nanocomposites due to the utmost incorporation of MWCNTs in the polymer matrix. Thermal conductivity decreased with increasing MWCNTs concentration into the base composite formulation attributed due to lower thermal conductivity of the incorporated nanotubes compared to the carbon black[11]. During the heat transport through the nanotube, heat dissipation along the CNT and in chiral direction takes place that reduces the heat flow through the carbon filled composite specimen[4].

Fig. 4 illustrates the effect of nanotubes concentration on the λ_{NR} values at three diverse temperatures. λ_{NR} decreases with increasing CNTs concentration in the host matrix. NR5 has 40, 36, and 51% less λ_{NR} compared to NR1 at 100, 150, and 200°C, respectively.
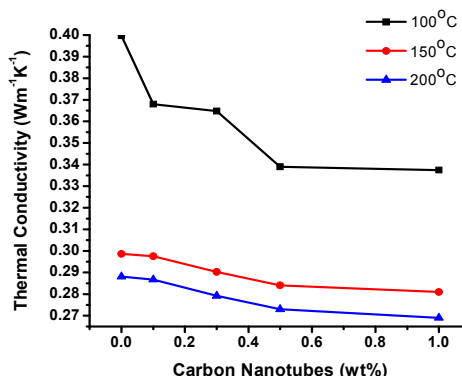

Fig. 4. The effect of MWCNTs concentrations on thermal conductivity of polymer nanocomposites at three diverse temperature i.e.100, 150, and 200°C

Thermal impedance (R) contours of the composite specimens in the same temperature range are depicted in Fig. 5. R elevates up to 230°C for all nanocomposites but the rate of R elevation is augmented with the progressive incorporation of MWCNTs in the rubber matrix. A reduction

in R is observed after this specific temperature. NR5 does maximum fight to resist the input heat in the complete temperature range due to the MWCNTs network in the rubber matrix that captures phonons and resists the thermal mobility of polymeric chains of the NR matrix
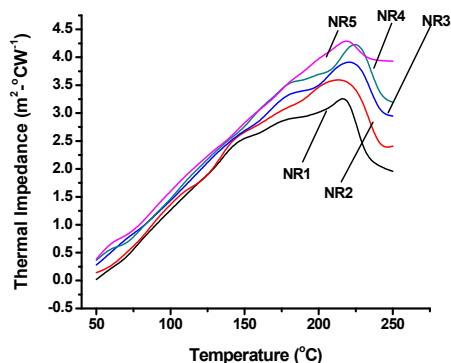

Fig. 5.The effect of MWCNTs concentrations on thermal impedance of polymer nanocomposites in the temperature range 50°C to 250°C

C. *Thermogravimetric and Differential Thermal Analyses*

Thermal decomposition of the fabricated nanocomposites in the temperature range 25 to 800°C is portrayed in Fig. 6. The 40% mass loss was observed in the temperature range 200 to 400°C due to the aromatic oil, stearic acid and wax evaporation and the maximum thermal degradation was noticed after 325°C due to the polymer matrix pyrolysis.

The percentage mass loss data at 200, 400, and 600°C for the polymer nanocomposites are portrayed in Table II, which clears that thermal stability of the nanocomposites increases with incorporating MWCNTs into the rubber matrix. This occurs due to high thermal stability and the ability of MWCNTs to resist polymeric chain mobility[12].

TABLE II: MASS LOSS DATA OF THE RUBBER NANOCOMPOSITES WITH DIVERSE MWCNTs CONCENTRATION AT VARIOUS TEMPERATURES

Sample ID	Mass loss (%) at 200 °C	Mass loss (%) at 400 °C	Mass loss (%) at 600 °C
NR1	2.606	51.683	75.705
NR2	1.707	51.165	73.712
NR3	1.689	49.366	71.675
NR4	1.663	46.342	70.588
NR5	1.424	43.004	70.175

Fig. 7 illustrates differential thermal analysis of the nanocomposites in the same temperature range as for thermal degradation analysis. An exothermic response was observed around 400°C due to aromatic oil exhaust and then all nanocomposites absorbed enormous heat. Heat quenching capability of the composite specimens enhanced with the nanotubes impregnation in the NR matrix as CNTs have the capability to entrap phonons and augmented thermal stability of the rubber nanocomposite.

D. *DSC Study*

Differential scanning calorimetric study in Fig. 8 elucidates the effect of MWCNTs on the glass transition (T_g), crystallization (T_c), and onset/peak melting (T_{m1} & T_{m2}) temperatures of the rubber nanocomposites. The calculated data of these phase changing temperatures are tabulated in Table III from the DSC contours. T_g of the nanocomposite specimens has been reduced with the incorporation of

nanotubes in the polymer matrix and the same response is observed for T_c.
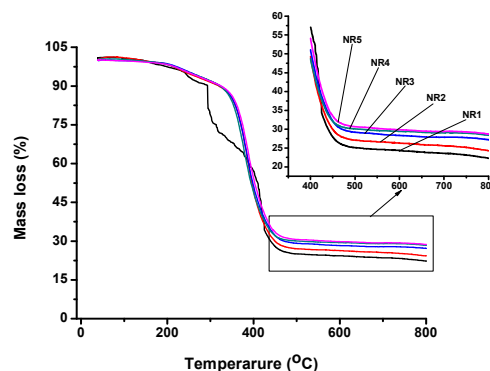

Fig. 6. Thermal degradation behavior of the MWCNTs incorporated rubber nanocomposites in the temperature range 25 to 800°C
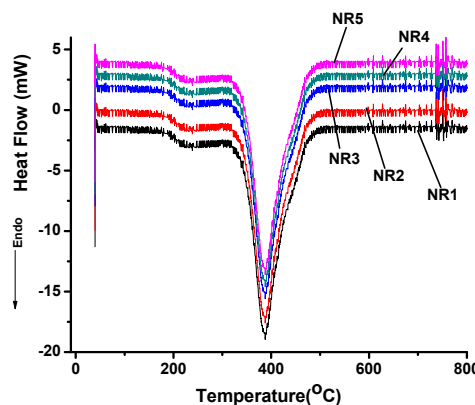

Fig. 7. Heat absorbing capability of the MWCNTs incorporated rubber nanocomposites in the temperature range 25 to 800°C
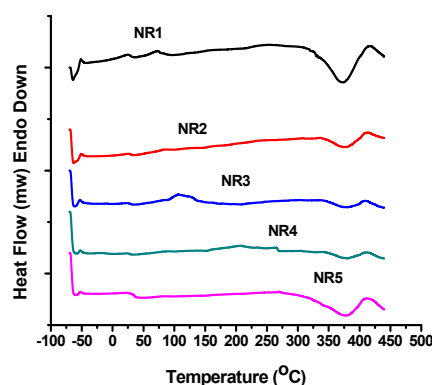

Fig. 8. Differential scanning calorimetric contours of the polymer nanocomposites in the temperature range -74 to 450°C

TABLE III: GLASS TRANSITION, CRYSTALLIZATION, FIRST MELTING PHASE AND SECOND MELTING PHASE TEMPERATURES DATA OF ALL FABRICATED COMPOSITIONS OF THE NANOCOMPOSITES

Sample ID	Glass transition temperature T_g(°C)	Crystallization Temperature T_c(°C)	Onset Melting Temperature T_{m1} (°C)	Peak Melting Temperature T_{m2} (°C)
NR1	-68.48	-51.12	216.95	373.83
NR2	-69.83	-49.75	275.99	375.15
NR3	-70.12	-47.75	286.62	376.38
NR4	-71.18	-46.19	289.32	379.08
NR5	-72.12	-45.75	293.37	381.38

CNT's network in the rubber matrix resists the phase changes by interacting with the polymeric chain at the nanoscale and broadens the rubbery range of the polymer

nanocomposites. It means that NR5 nanocomposite can be operated in more negative temperature compared to other ones up to 3.64°C. T_{m1} and T_{m2} proceed in the forward direction up to 76.42 and 7.55°C, respectively because nanotubes resist the matrix molecular chain mobility by entrapping phonons within the filler's network. Specific enthalpies of the nanocomposite specimens are depicted in Table IV. Glass transition and crystallization are exothermic phenomena but melting of the polymer composite is an endothermic phenomenon [13], [14]. It is observed that specific enthalpies of glass transition and crystallization are diminished while first and second melting phases elevated due to the enhancement of endothermic nature with the progressive addition of CNTs in the rubber matrix as clear for the DTA contours.

Fig. 10. The effect of MWCNTs on the hardness of polymer nanocomposite

TABLE IV: SPECIFIC ENTHALPIES OF THE PHASE TRANSITION TEMPERATURES DURING THE HEAT FLOW THROUGH THE RUBBER NANOCOMPOSITES

Sample ID	NR1	NR2	NR3	NR4	NR5
Specific Enthalpy of Glass transition (J/g)	0.553	0.475	0.461	0.439	0.147
Specific Enthalpy of Crystallization (J/g)	0.515	0.444	0.346	0.321	0.251
Specific Enthalpy of Onset Melting Phase (J/g)	2.699	3.722	4.333	5.322	6.851
Specific Enthalpy of Peak Melting Phase (J/g)	7.596	8.692	10.825	16.843	23.639

E. Mechanical Characteristics

Fig. 9 elaborates the effect of the impregnated carbon nanotubes on the tensile strength and elongation properties of the base polymer matrix. Tensile strength of the rubber nanocomposites was augmented up to 70% and elongation at break was improved up to 130% with the maximum incorporation of the nanotubes into the base composite formulation (NR1) due to the uniform dispersion, high surface area, nano level interaction with the polymeric molecular chains, and the filler–matrix compatibility of the MWCNTs [15].
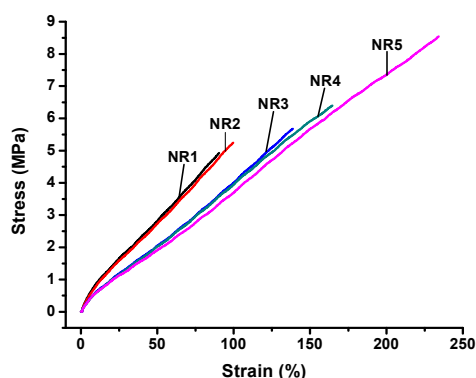

Fig. 9. The effect of MWCNTs on the tensile strength of polymer nanocomposite

Fig. 10 illustrates the effect of the filler concentration on the shore A rubber hardness of the polymer nanocomposites and it is observed that the MWCNTs incorporation remarkably enhanced the rubber hardness of the composite specimens due to the reduction of flow-ability of the host matrix with the carbon nanotubes-polymeric molecular chain linkage development[16].
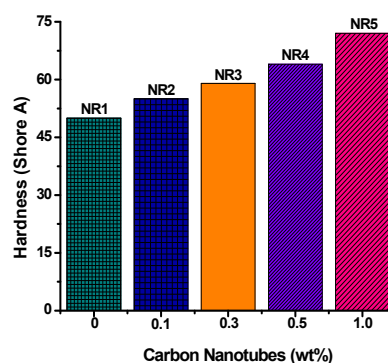
IV. CONCLUSION

MWCNTs are evenly dispersed in the NR matrix using internal dispersion kneader and two roller mixing mill to fabricate rubber nanocomposites for thermal analyses. SEM images and the compositional analyses of the tensile fractured composite samples elucidate the even dispersion of the incorporated nanotubes into the host polymer matrix.

Thermal conductivity of the polymer nanocomposites is reduced down to 50% while thermal impedance enhanced up to 97% with increasing the nanotubes concentration in the polymer matrix which means that the insulation characteristics of the rubber composites is promoted. Thermal stability and endothermic capability of the tested specimens have been remarkably improved with the progressive addition of CNTs in the host matrix. DSC study simulates that glass transition and crystallization temperatures are diminished up to 7 and 6°C, respectively whereas first and second melting phase temperatures are elevated up to 22 and 2°C, correspondingly with increasing MWCNTs impregnation in the rubber matrix and a similar behavior was observed for specific enthalpies of phase changes occurred within the composite specimens. MWCNTs incorporation into the rubber matrix has efficiently enhanced the mechanical characteristics of the fabricated composites.

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