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## Synthesis and Characterization of Polyurethane Based Composites and Reinforced by Carbon Nanotubes

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### ABSTRACT

Polyurethane nanocomposites were prepared based on hydroxylterminated polybutadiene as well as a mixture of hydroxylterminated polybutadiene and Castor oil and isophorone diisocyanate by a batch process. Two methods had been used to fabricate polyurethane matrix / carbon nanotubes into polymer matrices ( noncovalent attachment) and in situ polymerization at their surface ( covalent attachment) . The effect of the concentration of the previously prepared surface modified multiwall carbon nanotubes (0.5-1.0wt%), on the morphology, electrical and thermal properties of polyurethane based composites had been evaluated by FESEM, TGA, DSC and FTIR. The mechanical properties were tested by Nanovea indentation mechanical tester technique. The results showed that the thermal stability, electrical conductivity, hardness, Youngs modulus values were improved as the concentration of multiwall carbon nanotubes was increased.

**Key words:** Multiwalled carbon nanotubes, mechanical properties. Polyurethane based composites

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### Introduction

Carbon nanotubes (CNTs) were used as reinforcement materials in composites with metals, ceramics or polymer matrices because of their exceptional morphology, electrical, thermal and mechanical characteristics (Michele and Yurii, 2010).

One of the most important applications of nanotubes based on their properties was the reinforcement in composite materials (Jonathan *et al.*, 2016a).

The most common method for preparing CNT- polymer composites was done by mixing both components into a composite film (Jonathan *et al.*, 2016b). A solid state mechano- chemical pulverization process, namely pan milling, was used to prepare a CNT/ polypropylene composite powder (Xia *et al.*, 2004). Multi mixing had been a very valuable technique for the fabrication of CNT-based composites. This method was suitable with polymers that could not be processed with solution technique due to their insolubility in common solvents (Breuer and Sundararaj, 2004).

In situ polymerization of vinyl monomers in the presence of CNT material had been studied for the preparation of functional composites depending on required molecular weight and molecular weight of polymers, chain transfer, radical, anionic, and ring opening. Metathesis polymerization could be used for in situ polymerization processing. The main advantage of this method was that it produced polymer grafted tubes, mixed with free polymer chains (Putz *et al.*, 2004).

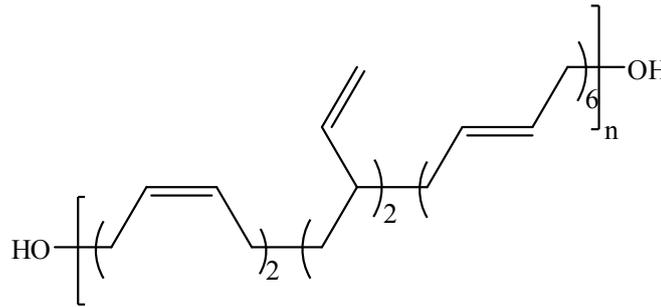
### Material and Experimental:

*Materials:*

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*Hydroxyl Terminated Polybutadiene, HTPB*



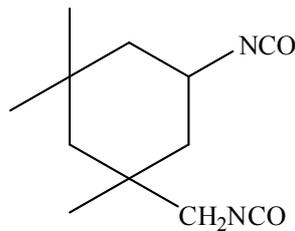
$n \approx 50$

Source	: ARCO, USA
OH value	: 0.805 meq/gm
Viscosity at 30°C	: 5630 cp
Density at 30 °C	: 0.9009 gm/ml
H2O Content	: 0.031%

Microstructure of HTPB:

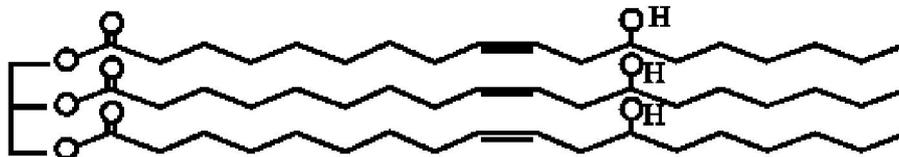
Cis	: 20%
Trans	: 60%
Vinyl	: 20%

Isophorone diisocyanate, IPDI



Name	: 5-isocyanato-1-(isocyanatomethyl)-1,3,3- trimethylcyclohexane
Source	: Sigma-Aldrich, Germany
Assay	: > 98%
NCO value	: 8.1 meq/gm
Density	: 1.0614 gm/ml
Flash point	: 155 °C
Vapor pressure at 35°C	: 0.04 Pa

- Castor oil, CO



**Castor Oil**

Source	: Alpha chemica
NCO value	: 8.68 meq/gm
Denisty	: 0.959 gm/ml
Boiling point	: 313 °C
Melting point	: -12 °C

**Synthesis of Pu and Pu / MWCNTs nanocomposites based on HTPB:**

For the preparation of polyurethane (Pu), Pu / multiwalled carbon nanotubes (MWCNTs) nanocomposites loaded with 0, 0.1, 0.2, 0.5 and 1 wt% of MWCNTs ; the nanotubes were dispersed in acetone to get a suspension system via an ultra sonicator for 2 hours at room temperature, then adding the suspension slowly to hydroxylterminated polybutadiene (HTPB) under mechanical stirring for 2 hours . The suspension of the mixture of MWCNT and HTPB was then degassed by applying vacuum oven at 80 – 90 °C for 12 hours until no bubbles coming out of the system , then cooled to 40 °C . Further, the produced suspension after degassing was mixed with the appropriate amount of isocyanate (IPDI) (table 1) via mechanical stirring at 40 °C for 1/2 hour.

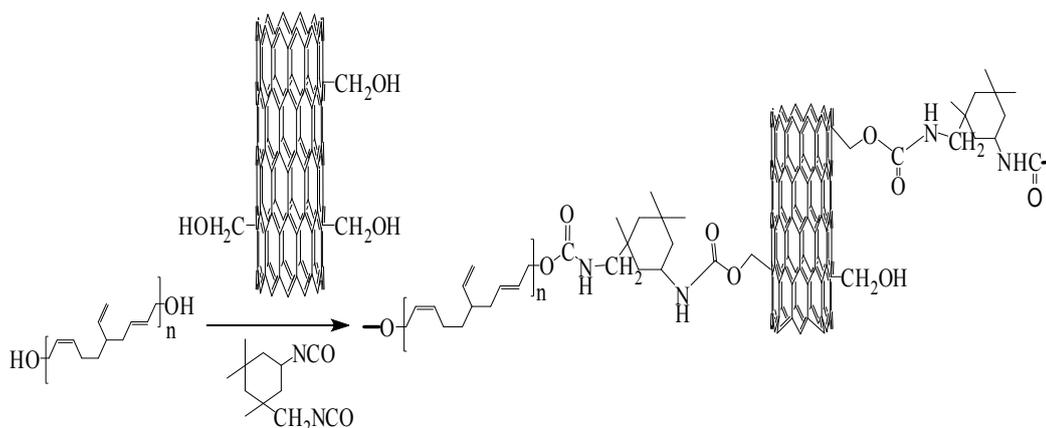
**Table 1:** Preparation of PU and reinforced PU

Sample	HTPB (g)	IPDI (g)	Castor oil (CO) (g)	Modified MWCNT (%)
PU	126	12.52	-	0.0
PU/MWCNT	126	12.52	-	0.1
PU/MWCNT	126	12.52	-	0.2
PU/MWCNT	126	12.52	-	0.5
PU/MWCNT	126	12.52	-	1.0

A metal mold (200 x 200 mm) was lubricated by spraying a thin layer of fluorocarbon and then preheated to the curing temperature (60 °C). The prepared mixture of Pu / MWCNT was then poured into the preheated metal mold until the thickness of the produced sheet was 5mm . Further , the Pu / MWCNT was cured in a dehumidation oven at ( 60 ±0.5) °C until the hardness of Pu was steady for 3 days . Scheme 1 showed the reaction between HTPB , IPDI and CNT.

**Synthesis of Pu nanocomposite based on HTPB and Castor oil (CO) with different mass ratio:**

For the preparation of polyurethane (Pu) with different mass ratio of HTPB and castor oil (table 2), HTPB was added to castor oil under mechanical stirring for 2 hours. The produced suspension was then degassed by applying a vacuum oven at 80 – 90 °C for 12 hours until no bubbles coming out of the system, then cooled to 40 °C . Further, the produced suspension was mixed with isocyanate (IPDI) by mechanical stirring for ½ hour. The lubricant metal mold was preheated to the curing temperature (60 °C). Then the mixture was poured into the preheated mold to 5 mm thickness then cured at 60 + 0.5 °C until the hardness of Pu was steady for 7 days.



**Scheme 1:** Reaction between HTPB , IPDI and CNT

**Table 2:** Preparation of polyurethane nanocomposite by using HTPB and CO with different mass ratios

Sample	HTPB (g)	IPDI (g)	CO (g)	Modified MWCNT (%)
PU-CO	31.5	60.16	53.22	0
PU -CO/MWCNT	31.5	60.16	53.22	0.1
PU -CO/MWCNT	31.5	60.16	53.22	0.2
PU -CO/MWCNT	31.5	60.16	53.22	0.5
PU -CO/MWCNT	31.5	60.16	53.22	1

**Synthesis of polyurethane, polyurethane / MWCNTs nanocomposite based on HTPB and Castor oil with mass ratio 25 : 75%:**

For the preparation of Pu – CO, Pu –CO / MWCNTs nanocomposite, loaded with 0, 0.1, 0.2, 0.5 and 1 wt % of MWCNT was carried out as follows:

The nanotubes were dispersed in acetone to get a suspension via an ultrasonicator for 2 hours at room temperature, then adding the suspension slowly to HTPB under mechanical stirring for 2 hours then adding castor oil (CO) and mixing for 1 hour. The produced suspension was degassed by applying vacuum oven at 80 – 90 °C for 12 hours, cooled to 40° C. Further, the suspension was mixed with isocyanate (IPDI) by mechanical stirring at 40 °C for ½ hour (table 3)

**Table 3:** Preparation of Pu – CO and reinforced Pu – CO.

Sample PU (HTPB:CO) (%)	HTPB (g)	IPDI (g)	CO (g)
25:75	31.5	60.16	53.22
50:50	63	44.26	35.48
75:25	94.5	28.4	17.74

The produced mixture was poured into the preheated mold till the thickness 5mm, then cured in dehumidification oven at 60 °C until the hardness of the nanocomposite was steady for 7 days.

The influence of this process of preparation of Pu nanocomposite on electrical conductivity, thermal analysis and mechanical properties of the prepared composites had been investigated.

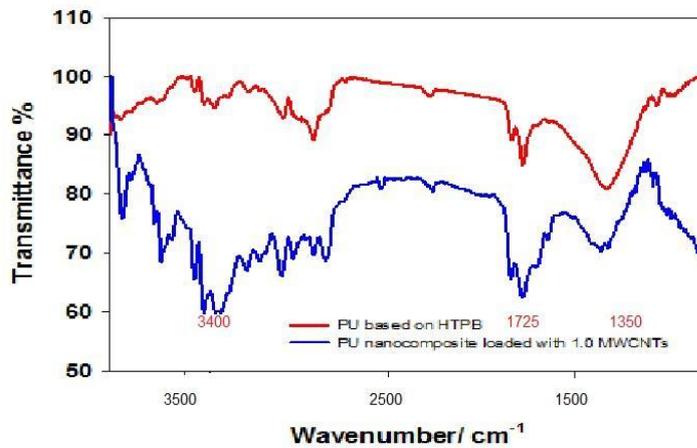
**Results and Discussion**

The previously synthesized and modified MWCNT using 40% Fe - MgO catalyst was used in this work (Shokry *et al.*, 2014). Its inner diameter (I.D) was 7.6nm and the outer diameter (O.D) was 32.3 nm, number of walls was 33 and 0.34nm as internal spacing. Two methods had been used to fabricate polyurethane matrix /MWCNTs nanocomposites; direct incorporation of the modified MWCNT into polymer matrices (noncovalent attachment) and in situ polymerization at their surface (covalent attachment).

**Fourier –Transform Infrared Spectrophotometer (FTIR) Analysis for polyurethane nanocomposites:**

Fig.1 reported the FTIR spectra of Pu / MWCNTs nanocomposite with mass ratio 1 wt% of modified MWCNT and based on HTPB, in the range of 400 - 4000 cm<sup>-1</sup>. Polyurethane nanocomposite exhibited three main bands which were attributed to N-H stretching , C= O stretching and C-N stretching and C-O stretching at wave lengths of 3400 , 1725 , 1350 and

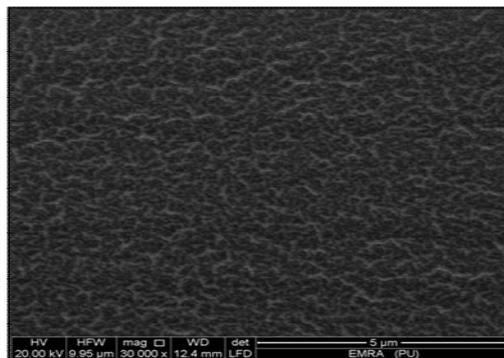
1100  $\text{cm}^{-1}$  respectively. These bands appeared due to the presence of the urethane links produced during the synthesis.



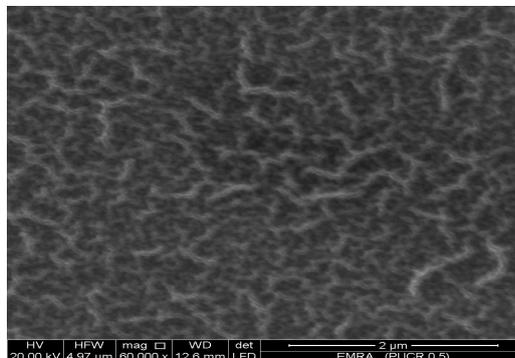
**Fig. 1:** FTIR for Pu nanocomposites

### Field emission scanning electron microscope (FESEM) of polyurethane nanocomposites:

FESEM was used to examine the morphology and dispersion of MWCNT in polyurethane matrix as shown in (Fig. 2) where A, B, C were the FESEM images of the nanocomposites containing 0, 0.5 and 1 wt% modified MWCNT respectively. (Fig. 2A) showed the fracture surfaces of the Pu nanocomposite containing 0 wt% MWCNT, appeared as bright points and lines in the micrographs which showed the morphology of Pu domain. (Fig. 2B) showed that the bright points disappeared in the fracture surfaces of Pu / MWCNT - 0.5 composite



**Fig. 2A:** FESEM images of the Nanocomposite containing 0 wt% modified MWCNT

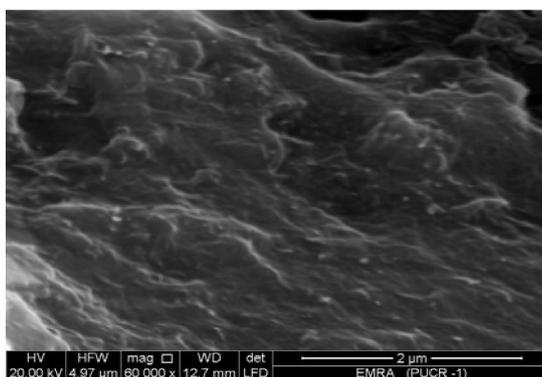


**Fig. 2B:** FESEM images of the nanocomposite containing 0.5 wt% modified MWCNT

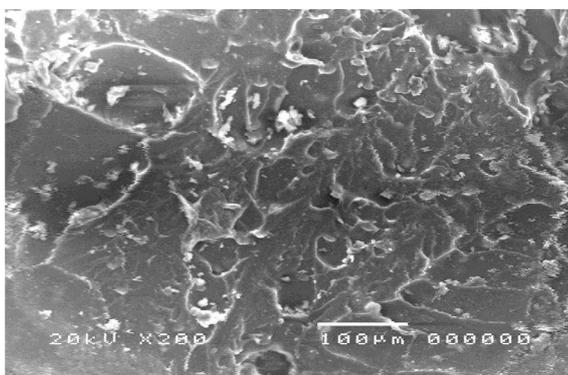
This was due to the thicker layer of Pu that covered the MWCNT surface and highly dispersed CNT (Wei *et al.*, 2006). While (Fig. 2C) had shown that the Pu – embedded 1wt % MWCNT appeared as bright points and lines. In the micrograph, the bright dots increased with the increase in MWCNT content .this meant that the MWCNT was pulled out from the fractured surface. These results were in agreement with literature (Chengshuang *et al.*, 2011) .

Figure 3 showed the fracture of Pu –CO / MWCNT-1 nanocomposite that revealed high dispersion of MWCNT and all the CNT<sup>s</sup> had not been observed in polyurethane matrix. The MWCNT might be totally covered by polymer matrix (Jiawen *et al.*,2008).

The effective surface of MWCNT influenced the native structure of Pu, the large enough MWCNT prevented the formation of soft domains within the frame of Pu structure. The covalent bonding of the MWCNT with Pu i.e ( CNT-OH) should lead to improve the disagglomeration and dispersion of the nanotubes bundles into the polymer . This was attributed to the increase in polarity of MWCNT by the interaction of the – OH group of CNT with isocyanate group (-NCO-) of the Pu matrix (Aruna and Deba, 2011).



**Fig. 2C:** FESEM images of polyurethane/MWCNTs nanocomposite based on HTPB with mass ratio, 1 wt% modified MWCNT



**Fig. 3:** FESEM images of the fracture of Pu- CO/ MWCNT-1 nanocomposite

### ***Thermogravimetric analysis (TGA) of Pu nanocomposites:***

Figure 4 & Figure 5 showed the thermogravimetric analysis simultaneous with Differential Scanning Calorimetry (DSC) curves for neat Pu, Pu / MWCNT and Pu - CO , Pu - CO /MWCNT nanocomposites. For all the samples, degradation was observed in two stages. The first stage was associated with the breakdown of the urethane linkage (-HNCOO-) to the original polyol and isocyanate (Dongyu *et al.*, 2012). After that, the polyol and di-isocyanate further undergo cleavage to form small molecules (primary amine, alkane, aldehyde, ketone, carbon dioxide, and water (Simon *et al.*, 2012).

The thermal stability of Pu / MWCNT nano composite was found to be improved as compared to their neat Pu counterparts. (Fig. 4 & Fig. 5) showed that Pu decomposed at 337 °C, and complete degradation at 472 °C. Also they indicated that the MWCNT uniformly interacted with Pu molecular structure and thus delayed the thermal degradation of Pu matrix. The higher heat

transfer was due to the higher thermal conductivity of Pu / MWCNT and the formation of the CNT bonded macroradicals which were the main factor for the increase in thermal stability of the Pu matrix.

The temperature of the complete degradation of Pu / MWCNT nanocomposites was shifted towards higher temperature (489 °C) as compared to Pu – CO / MWCNT matrix (486 °C). This was attributed to the excellent thermal stability of the attached functional groups on the surface of the MWCNT which also helped in good interaction between them.

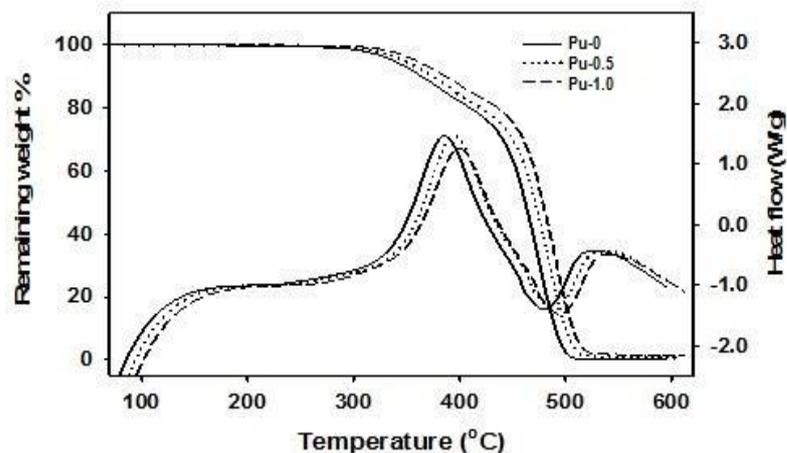


Fig. 4: TGA thermograms of neat Pu and its nanocomposites containing (0, 0.5, 1) wt% of MWCNT

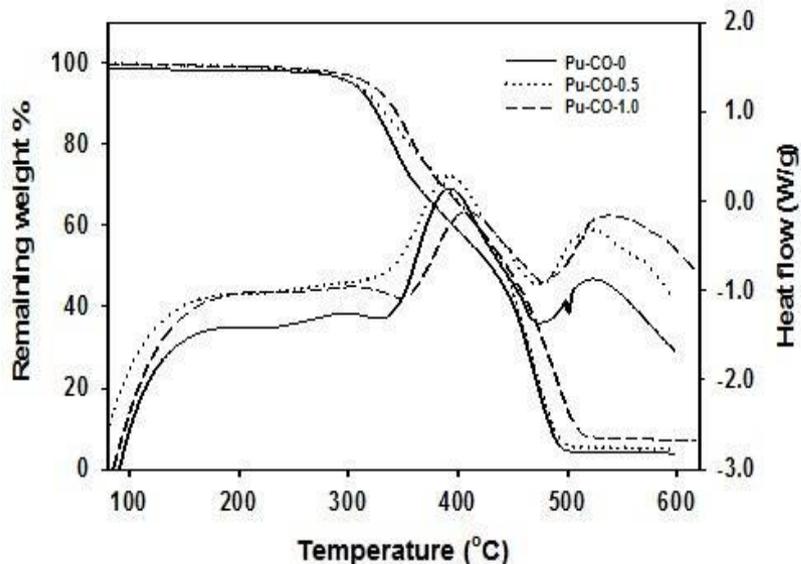
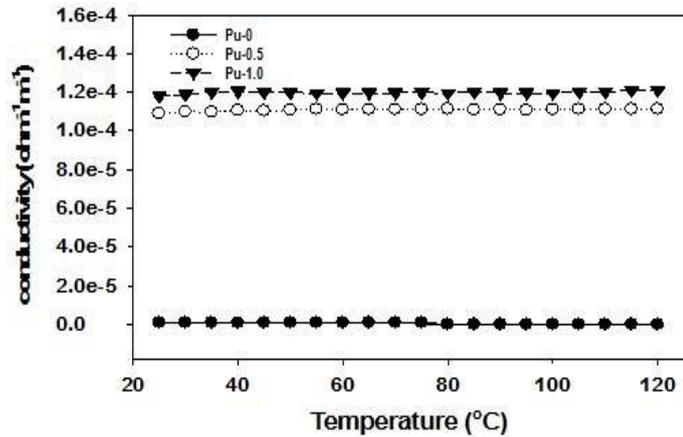


Fig. 5: TGA thermograms of neat Pu-CO and its nanocomposites containing (0, 0.5, 1) wt% of modified MWCNT

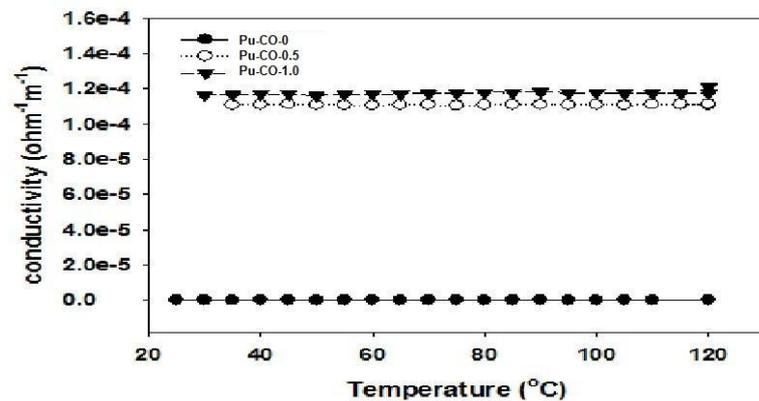
#### ***Electrical conductivity of polyurethane nanocomposite:***

The electrical conductivity of Pu as a function of the nanofiller content was studied. It had been shown that the addition of MWCNT in polymers was expected to affect the electrical conductivity of the final material system (Bauhofer and Kovacs, 2009). Fig. 6 showed that Pu based on HTPB was an insulator and had conductivity equal to  $0 \text{ ohm}^{-1}\text{cm}^{-1}$ . At 0.5 wt% of MWCNT nanofiller, the conductivity increased to  $1.1 \times 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$  and at 1 wt% nanofiller concentration, the conductivity became  $1.2 \times 10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$ .

A similar behavior was exhibited for Pu based on a mixture of HTPB and castor oil (fig. 6) and (table 4). CNT/ polymer composites exhibited percolation behavior, in which the presence of interconnected nanotubes network resulted to increase in their electric conductivity. The percolation threshold and conductivity depended on the polymer type, synthesis method, aspect ratio of CNT and degree of alignment.



**Fig. 6:** Electrical conductivity of neat Pu (based on HTPB) and its nanocomposites containing (0, 0.5, 1) wt% of MWCNT



**Fig. 7:** Electrical conductivity of neat Pu (based on mixture of HTPB, CO) and its nanocomposites containing (0, 0.5, 1) wt% of MWCNT

**Table 4:** Electrical conductivity of polyurethane nanocomposite

Sample	Electrical conductivity (ohm <sup>-1</sup> m <sup>-1</sup> )	MWCNTs %
Pu-0	0	0
Pu-0.5	1.1 × 10 <sup>-4</sup>	0.5
Pu-1	1.2 × 10 <sup>-4</sup>	1
Pu-CO-0	0	0
Pu-CO-0.5	1.1 × 10 <sup>-4</sup>	0.5
Pu-CO-1	1.18 × 10 <sup>-4</sup>	1

***Nanoindenter mechanical tester for the synthesized Pu/MWCNT:***

Mechanical properties by nanoindentation played a crucial role in testing the mechanical properties of samples, the dimension of which were small in at least one direction.

Nanoindenter, permitted precision load and depth control, thus the nanoindentation was not only a method to determine one hardness value (H) and one indentation modulus (E) of a

certain material, but permitted to study H and E as functions of a variety of parameters as load, temperature and time (Wolf and Paufler,1999; Dresden and Wolf , 2000).

Nanoindentation mode gave the stress – strain data using a spherical tip and by increasing cyclic loads that measure the properties of the material under increased stress. The nanoindenter mechanical tester provided these tests from the sub mN range to 200 N. The main parameters that were measured by this method were the hardness and elastic modulus versus depth. Table 5 gave the mechanical properties of the neat Pu (P1-0) , Pu of 0.1 wt% MWCNT (P1-1) , Pu of 0.2 wt% MWCNT (P1-2) , Pu of 0.5 wt% MWCNT (P1-3), Pu of 1 wt% MWCNT (P1-4) and Pu / CO (P2-0) , Pu – CO of 0.1 wt% MWCNT (P2-1) , Pu – CO of 0.2 wt% M WCNT (P2-2) , Pu – CO of 0.5 wt% M WCNT (P2-3) and Pu - CO of 1 wt% MWCNT (P2-4) .

Table 5 showed that , the hardness of the neat Pu was improved from 0.00099 to 0.016 GPa with the incorporation of 0.2 to 1wt% CNTs ( P1-2 to P1-4) due to the reinforcing effect of the dispersed CNTs filler. The hardness of the nanocomposite containing 0.1wt% CNTs decreased slightly than the neat Pu (P1-0) because of the poor comptability of CNTs with Pu. While, Pu – CO (P2-0) which was unfilled and the filled Pu - CO (P2-2 &P2-3) had almost the same values of hardness (0.016), while P2-4 gave a higher value of hardness (0.032 GPa) i.e nearly 20 times the hardness value of (P1-4).

This indicated that Pu - CO (P2-4) filled with 1wt% CNTs had inherent ability to resist the localized deformation caused by applying external stimuli than Pu filled with 1wt %CNTs (P1-4) ( nearly 20 times).

**Table 5** Nanovea Mechanical Properties of Pu (P1) with different mass ratio of MWCNT & Pu - CO (P2) With different mass ratio of MWCNT (0 , 0.1, 0.2 , 0.5 , 0.1 wt%)

Sample	p1 - 0	p1 - 1	p1 - 2	p1 - 3	p1 - 4
Max. depth (nm)	21977.23	25935.86	20223040	20493.27	19171.3
Max. load (nm)	1.457	1.484	2.066	1.571	1.867
Plastic depth	12754.35	19621.6	11904.75	10384.23	9248.21
Hardness (GPa)	0.00099	0.00083	0.00147	0.00122	0.00158
Reduced Modulus (GPa)	0.00275	0.00368	0.00441	0.0029	0.00364
Flow Stress (GPa)	0.000329	0.34391	0.0004883	0.0004073	0.0005256
Flow Strain (GPa)	1727602	0.0002761	0.6670155	0.1609494	0.5536283
Elastic Recovery Parameter	0.73714	0.34391	0.7206	0.9833	1.0873
Indentation Radius (nm)		23788.37	20876.94	20118.66	19203.53
Sample	p2 - 0	p2 - 1	p2 - 2	p2 - 3	p2 - 4
Max. depth (nm)	1814.82	2753.47	1504.52	2000.82	805.58
Max. load (nm)	3.01	3.01	3.01	3.01	3.01
Plastic depth	1121.31	2389.86	1116.71	1289.93	583.5
Hardness (GPa)	0.01791	0.00841	0.01725	0.01559	0.03198
Reduced Modulus (GPa)	0.24849	0.366842	0.42624	0.2364	1.01854
Flow Stress (GPa)	0.0058375	0.144	0.0057516	0.5514	0.3715
Flow Strain (GPa)	0.0572088	0.0028031	0.0573885	0.005198	0.0106609
Elastic Recovery Parameter	0.616	0.0823805	0.345	0.0609679	0.0419842
Indentation Radius (nm)	7154.85	10297.56	7173.56	7620.98	5248.52

Youngs modulus of the unfilled Pu (P1-0) was (0.0028) while for the nanocomposites with different loading of nanotubes showed higher modulus, it increased up to 0.0036 by incorporation of 1 wt % CNTs, indicating the significant increase in the stiffness of Pu.

The modulus increased linearly with CNT concentration up to 1 wt % CNTs .The neat Pu – CO (P2-0) had indenter modulus of 0.248 and increased linearly by adding CNT from 0.1 to 1 wt %. The maximum value was 1.02 at 1 wt %CNT. Comparing the Pu dispersed with CNTs filler and Pu - castor oil loaded with different concentrations of CNTs, Pu - castor oil nanocomposites (P2-4) leading to 250 times the indenter modulus of (P1-4) nanocomposites.

The function of CNTs was to improve the interfacial loading between the CNTs and Pu matrix. This functionalization improved both dispersion and stress transfer (Zdenko *et al.*, 2010).

## Conclusions

FESEM images for the Pu matrix / CNT nanocomposites showed that by increasing the weight of the modified CNT up to 1wt% , good dispersion of nanotubes was achieved.

The results of the thermal analysis showed that for all the samples, degradation was observed in two steps. A much better improvement in thermal stability of the composites could be possible by incorporating higher quantities of MWCNT. The thermal degradation of Pu matrix was successfully delayed by the addition modified CNT which indicated that the modified CNT uniformly interacted with Pu structure.

Pu based on HTPB as a polymer was an insulator, at 0.5 wt% nanofiller concentration, the system was starting to perform as a conductor and further increase in conductivity at 1wt% nanofiller concentration . A similar behavior was exhibited for Pu based on a mixture of HTPB and castor oil. The nanoindentation method indicated that, the hardness of Pu nanocomposites (P1-4) dispersed with 1 wt% CNT had the highest value (0.0016 GPa). The hardness of P2-4) was 0.032 GPa, i.e. the hardness of P2-4 was 20 times the hardness of P1-4. It meant that P2-4 had inherent ability to resist the localized deformation caused by applying external stimuli.

The indenter modulus of P2-4 nanocomposites had 250 times the indenter modulus of P1-4 nanocomposites and thus high increase in the stiffness of the P2-4 nanocomposites.

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