ÓBUDAI EGYETEM
ÓBUDA UNIVERSITY

John von Neumann University

Semester Report

Preparation and investigation of nanocomposites with polymer matrix

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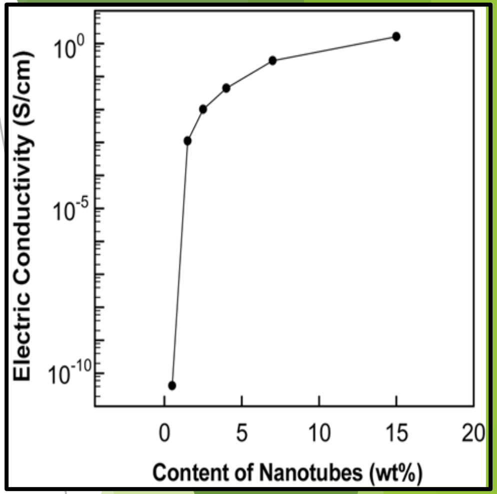
TABLE OF CONTENTS

Literature Review

(1) Effects of Morphology on the Electrical and Mechanical Properties of the Polycarbonate/Multi-Walled Carbon Nanotube Composites. *Chong Ku Kum, Woo Nyon Kim*

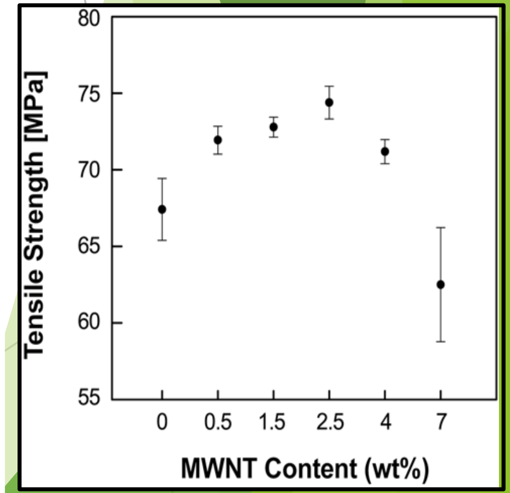
Preparations. PC/MWNT nanocomposites were prepared by melt mixing using twin screw extruder with MWCNT contents of 0.5%, 1.5%, 2.5%, 4% and 7% by weight.



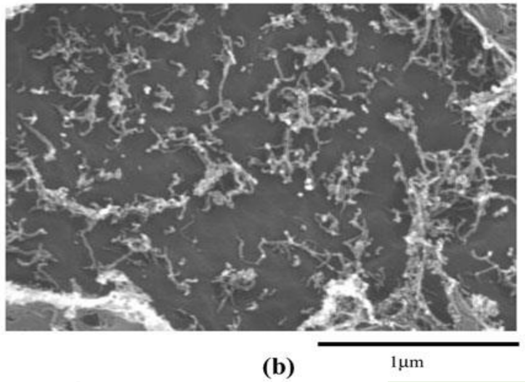
Results and Discussion

Electrical Properties. For the PC/MWNT composites at 0.5 wt% MWNT content, the electrical conductivity shows about 10^{-10}S/cm. For the PC/MWCNT composites at 1.5 and 2.5 wt% MWNT content, the electrical conductivity increases dramatically and shows about 10^{-3} and 10^{-2} S/cm, respectively.

Morphology. Scanning Electron Micrographs of the cryogenically fractured cross-sectional surfaces of the PC/ MWNT composites with 2.5 wt% MWNT. In the high magnification image, it is shown that the MWNT is dispersed homogenously in the PC matrix. The MWNT is appeared to connect closely and forms a pathway between the MWCNT. From the results of the electrical conductivity and morphological results, it is suggested that the percolation threshold of the PC/MWNT composites is closely related with the morphological results.



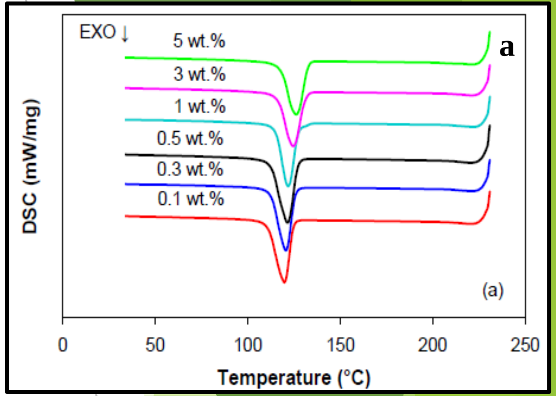
Mechanical Properties. The tensile strength of the PC/MWNT composites with the MWNT content. In the Figure when the MWNT content is up to 2.5 wt%, the tensile strength of the PC/MWNT composites is increased from 67 to 74 MPa with the increase of the MWNT content. When the MWNT content is higher than 2.5 wt%, it is observed that the tensile strength of the PC/MWNT composites is decreased from 74 to 62 MPa.

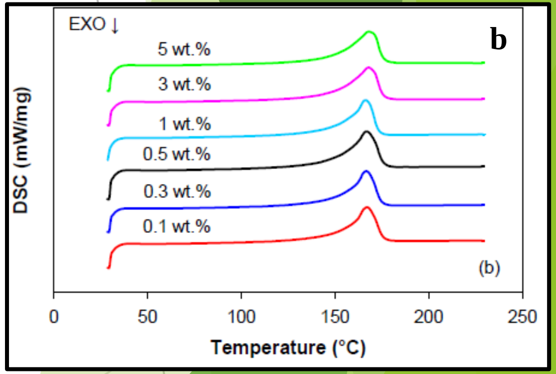


(b)

(2) Thermal, Rheological, and Mechanical Properties of Polypropylene/Multi-Walled Carbon Nanotube Nanocomposites. *Nicoleta-Violeta Stanciu, Felicia Stan, Adriana-Madalina Turcanu , et al.*

Preparations. PP/MCWNT nanocomposites were prepared by Injection Molding with MWCNT contents of 0.1%, 0.3%, 0.5%, 1%, 3% and 5% by weight.



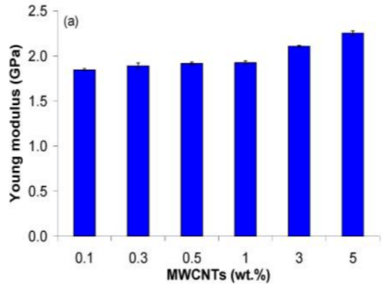


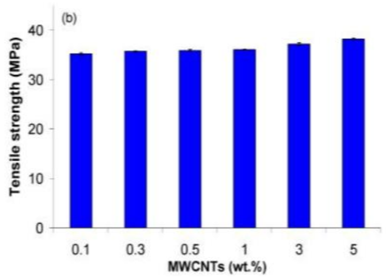
Results and Discussion

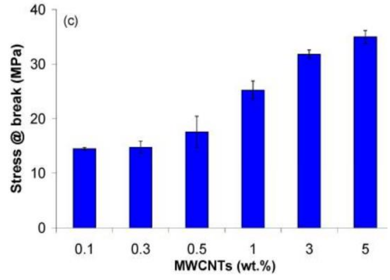
Thermal Properties. The DSC cooling scan displays a single crystallization peak, which shifts gradually to higher temperatures as the MWCNT loading increases, indicating that the crystallization process is facilitated in the presence of MWCNTs(a). The melting, crystallization temperatures and degree of crystallinity of the PP/MWCNT nanocomposites are not significantly affected by the presence of the MWCNTs (b).

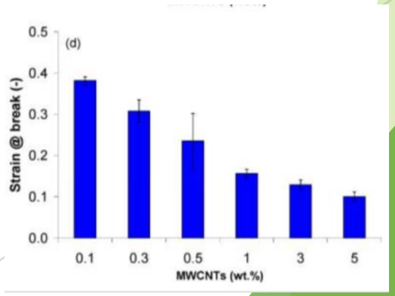
Melt Flow Index. When the MWCNT loading increased to a certain extent (>1 wt.%), the MFI significantly decreased with the increase of MWCNT wt.%. Since MFI is a measure of the flow property, the sharp decrease of MFI reflects the increase of melt shear viscosity as a result of CNT-CNT and CNT-polymer interactions.

Mechanical Properties. The tensile modulus, tensile strength and stress at break progressively increase with increasing MWCNT loading and the effect of reinforcement is more significant above 1 wt.% of MWCNTs. Furthermore, the elongation at break significantly decreases with increasing MWCNT loading.



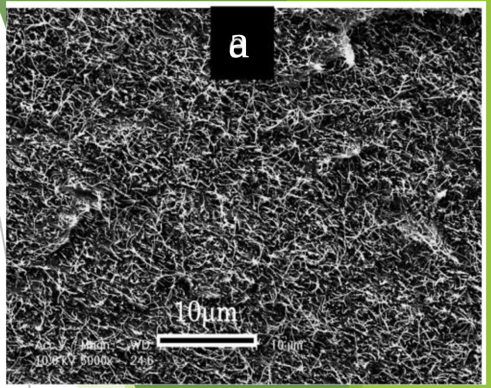


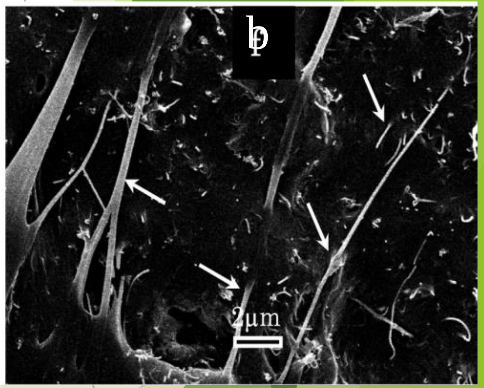




(3) Morphology and Properties of Poly[styrene-b-(ethylene-co-butylene)-b-styrene]/ Multi-Walled Carbon Nanotube Composites Fabricated by High-Shear Processing. *Yongjin Li and Hiroshi Shimizu, et al.*

Preparations. SEBS/MCWNT nanocomposites were prepared by melt blending using a high-shear extruder with a screw rotation speed of 1000 rpm with MWCNT contents of 1.25%, 2.5%, 5%, 10% and 15% by weight.





Results and Discussion

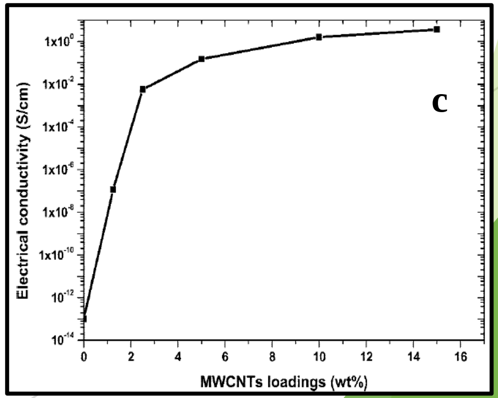
Morphology. It can be seen that the MWCNTs are uniformly dispersed in the SEBS matrix at the MWCNT loadings investigated here. No MWCNT agglomerates are apparent even at the very high MWCNT content of 15 wt % (a). Some discrete nanotubes, apparently pulled out together with the matrix polymer during fracturing, can be distinguished (b).

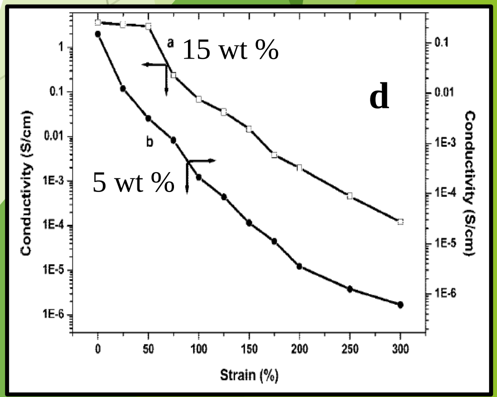
Electrical Conductivity. A sudden increase in the conductivity was observed as the MWCNT loading content increased from 1.25 to 2.5 wt %, indicating the formation of a percolating network (c). The conductivity as a function of mechanical deformation for the prepared nanocomposites with 5 and 15 wt % MWCNTs (d).

Mechanical Properties.

Table 1. Mechanical and Thermal Properties of SEBS and Its Nanocomposites with MWCNTs

MWCNT loading (wt %)	modulus (MPa)	300% tensile stress (MPa)	elongation at break (%)	strain residual (%)	T_g of EB phase (°C)
0	16.3	4.22	949	14.7	−50.7
1.25	35.6	6.27	927	18.2	−50.7
2.5	39.9	6.80	916	22.7	−48.2
5	75.8	7.79	765	30.7	−47.2
10	118.2	11.66	651	51.2	−47.6
15	185.8	13.83	611	76.2	−47.6





(4) Microstructure Evaluation and Thermal–Mechanical Properties of ABS Matrix Composite Filament Reinforced with Multi-Walled Carbon Nanotubes by a Single Screw Extruder. *Thai-Hung Le, Ngoc-Tam Bui, et al.*

Preparations. The ABS pellets and MWCNTs were mixed and extruded using a single screw extruder equipment with MWCNT contents of 0.5%, 1%, 1.5%, 2%, 3% and 4% by weight.

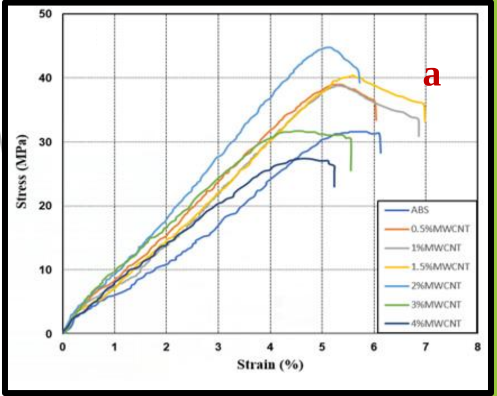
Results and Discussion

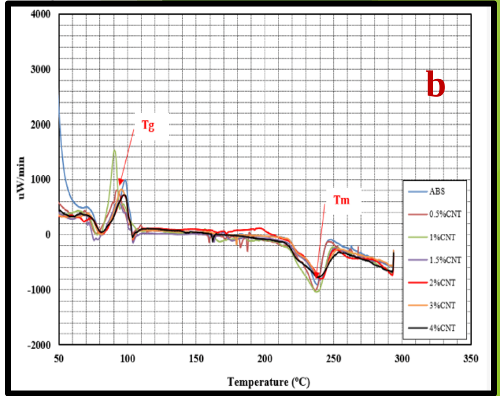
Mechanical Properties. The tensile strength of the samples improved along with the addition of MWCNTs as filler (0.5 wt% to 2.0 wt%), compared to the pure ABS sample. However, there was no change in tensile strength as the MWCNT concentration reached 3.0 wt%, but was slightly reduced in the 4.0 wt% MWCNT sample, compared to the pure ABS condition. (Fig. a)

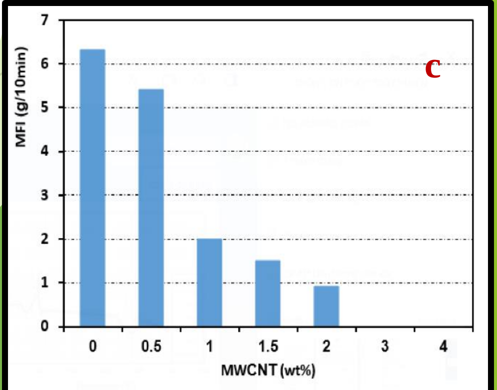
Thermal Properties. The glass transition temperature (Tg) and melting point (Tm) for the different ABS–MWCNT composites were determined at around 90 °C and 240 °C, respectively. This observation indicated a minor effect of MWCNTs, as a filler, on the thermal properties of the ABS matrix. (Fig. b)

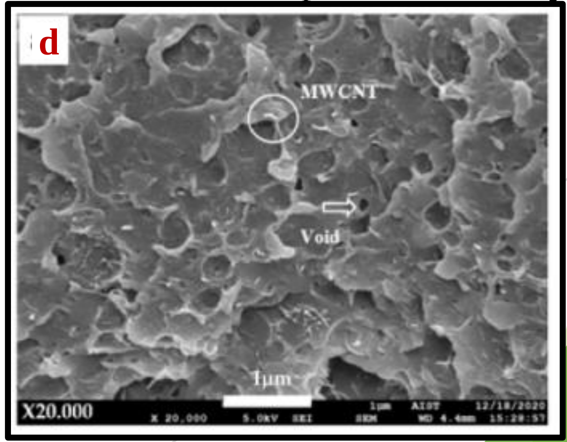
Melt Flow Index. MFI value reached 6.3 g/10 min and 5.6 g/10 min in the blank ABS and 0.5 wt% MWCNT samples, respectively. The decrease of MFI values could be attributed to an increase of composite viscosity, induced by the formation of a nanofiller network. (Fig. c)

Morphology. The 1.0 wt% MWCNT sample exhibited a typical fracture surface with shear lips and few dimples, which means the sample retained high ductility during the tensile test, compared to the ABS polymer. (Fig. d)



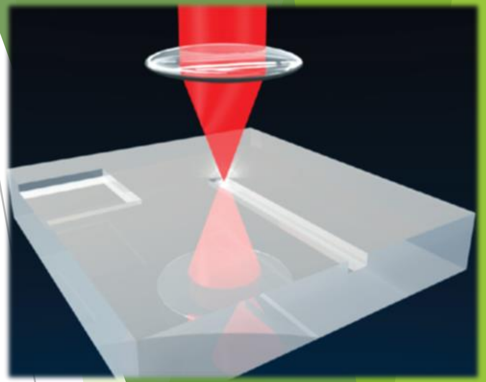






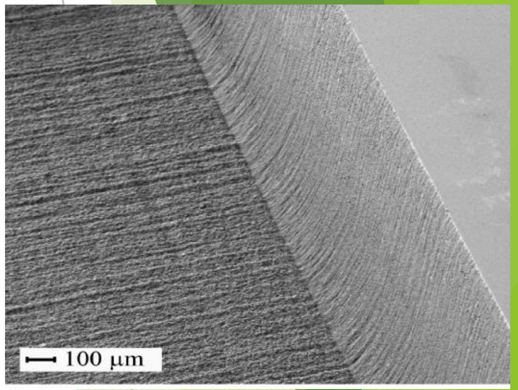
(5) Surface Properties of Femtosecond Laser Ablated PMMA. *Carmela De Marco, and Roberto Osellame*

Introduction. To ablate surface features in the polymer substrates, we applied a regeneratively amplified Ti:Sapphire laser (Integra-C FS-F, Quantronix) with 800 nm center wavelength, 1 mJ maximum pulse energy, *R*) 1 kHz repetition rate, and 150 fs pulse duration with a 100-mm focal length lens (spot size, $2w_0 = 20.4\ \mu m$).



Results and Discussion

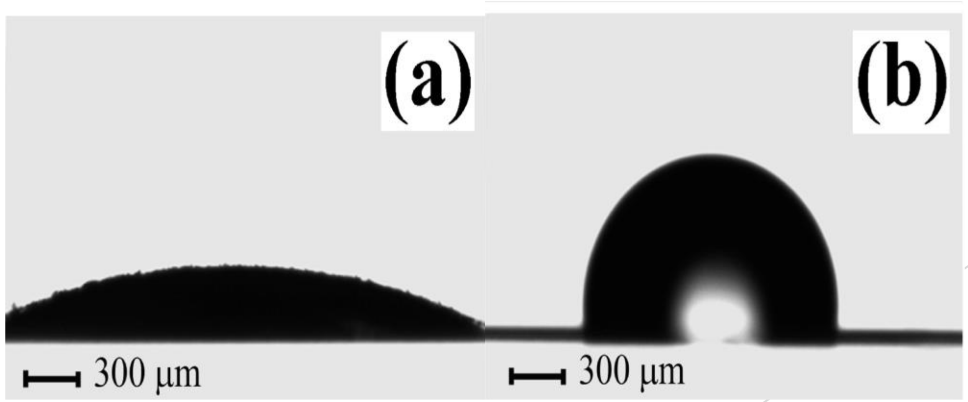
Morphology of the surface structures. The fabricated rectangular cross-section microchannels by performing multiple parallel scans at a single depth and separated laterally by 4 μm. The produced microchannels were of very good quality with sharp edges and low roughness as shown in the SEM image.

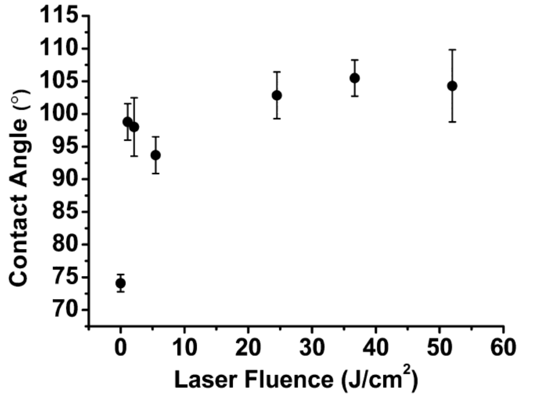


Surface Chemistry. The chemistry of the polymeric substrates was not altered after the laser irradiation, as confirmed by spectroscopic analysis.

Wettability. Femtosecond laser ablation was found to alter the wettability of PMMA. In particular, the PMMA wetting behavior switches from moderately hydrophilic to hydrophobic after laser ablation, independent of the above-threshold laser fluence. Observed that the changed wettability is mainly a consequence of the porous morphology induced at the submicroscale after the laser processing.

- **Fig. of a water droplet on a PMMA sample on a laser ablated area irradiated with 3.1 J/cm^2 for the case of: (a) no rinsing where the debris caused a decreased contact angle and (b) rinsing in water, which showed an increased contact angle and hydrophobic behavior.**

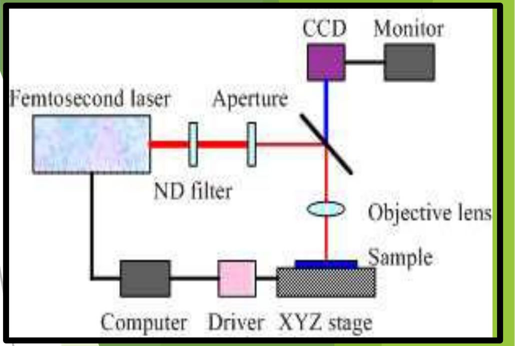




Static water contact angle on pristine PMMA (at 0 J/cm^2) and irradiated PMMA versus laser fluence.

(6) Experimental investigation on femtosecond laser ablation of polycarbonate. *Litao Qi, and Jinping Hu*

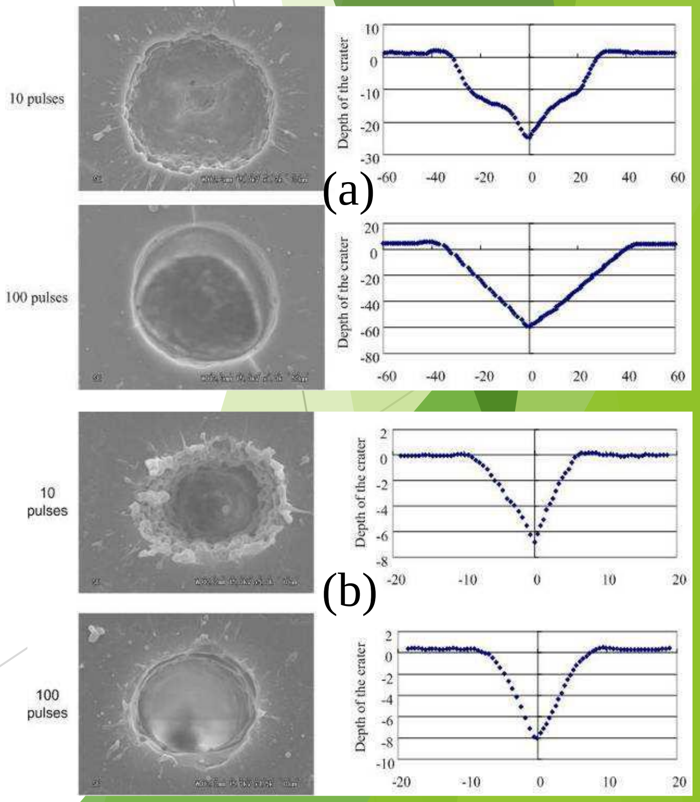
Introduction. In the experiments, a commercially available amplified Ti:sapphire laser system that generated 160 fs laser pulses with a maximum pulse energy (Ep) of 1 mJ at a 1 kHz repetition rate and with a central wavelength of λ = 780 nm was used. The laser beam had a Gaussian profile with a diameter of 6 mm.
The incident laser beam was irradiated onto a polycarbonate sample through a 4 mm aperture positioned normal to the sample and a 10× microscope objective lens with a numerical number of 0.30. The laser spot size on the sample was estimated to 8~10 μm.



Results and Discussion

Ablation threshold. The ablation threshold fluences of the Gaussian laser beam can be calculated by measuring the diameter of the ablated areas versus the pulse energy and extrapolating to zero. Ablation thresholds of femtosecond laser ablation of polycarbonate were obtained and F_{th} = 1.52 J/cm^2 which was close to the value obtained.

Effects of pulse energy and number of laser pulse. The craters are formed under different pulse energies and numbers of laser pulses, and then are measured. The depth of the ablated crater was measured by contact-mode profilometer and the section profiles of the abated crater. SEM photos and profile of the laser ablated crater at Ep=241 μJ (a) and Ep=6.57 μJ (b).

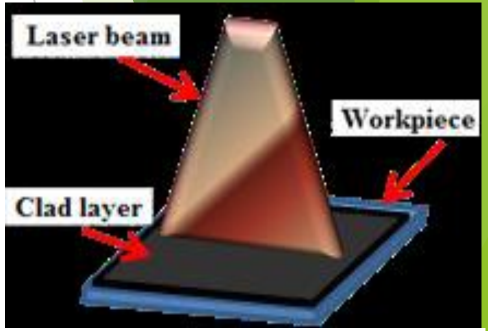


Summary. The ablation threshold decreased as the number of laser pulse increasing because of incubation effect. The ablating rate depends on the pulse energy. The ablating rate is higher when the pulse energy is lower, whereas the ablating rate is lower when the pulse energy is higher.

(7) Creating a Conductive Surface of the PMMA by Laser Cladding with DWCNT and MWCNTS.

Wala I. Rasool and Thaier A. Tawfiq

Introduction. The setup consisted of pulsed Nd:YAG laser of 1064nm, single pulse capability up to 70J/10 ms, pulse duration of 1-50 ms and frequency of 1-100 Hz. This apparatus was adapted to a manipulator through an optical fiber of 400 μm diameter.
Three groups, each one consisted of five work pieces were prepared to have the dimensions of 20 mm×20 mm×2 mm.



Cladding process scheme.

Results and Discussion

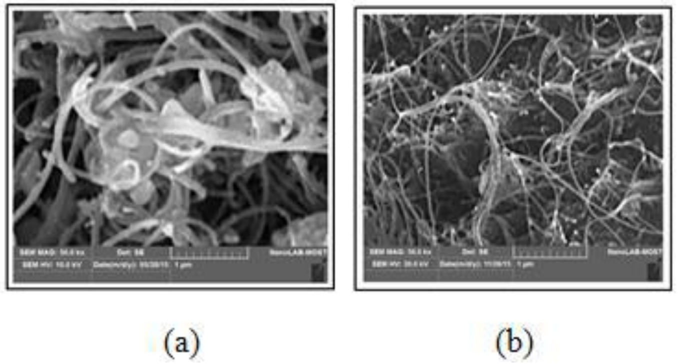
Morphology. SEM images of the work pieces cladded by MWCNTs and DWCNTs respectively in order to distinguish which type of CNTs achieved better cohesion with the base material and to support the results which were obtained from the EDS test. These images demonstrated better distribution of the DWCNTs on the surface of the work piece.

Electrical conductivity. Both types of CNTs changed the PMMA's surface status from being an insulator of 10^{-15} S/m electrical conductivity to a conductor of 0.813×10^{3} S/m, by using the DWCNTs, and of 0.14×10^{3} S/m when using the MWCNTs. Hence, the DWCNTs achieved an increase of almost 6 times than that for the MWCNTs.

Thermal conductivity. The DWCNTs increased the thermal conductivity of the PMMA's surface by 8 times and the MWCNTs by 5 times than its original value.

Thermal conductivities at 34.28 ºC.

Thermal conductivity of PMMA W/mK	*Thermal conductivity of workpiece Cladded by MWCNTs W/mK*	*Thermal conductivity of workpiece Cladded by DWCNTs W/mK*
0.19-0.24	1.203	1.713



(a) Work piece cladded by MWCNTs. (b) work piece cladded by DWCNTs.

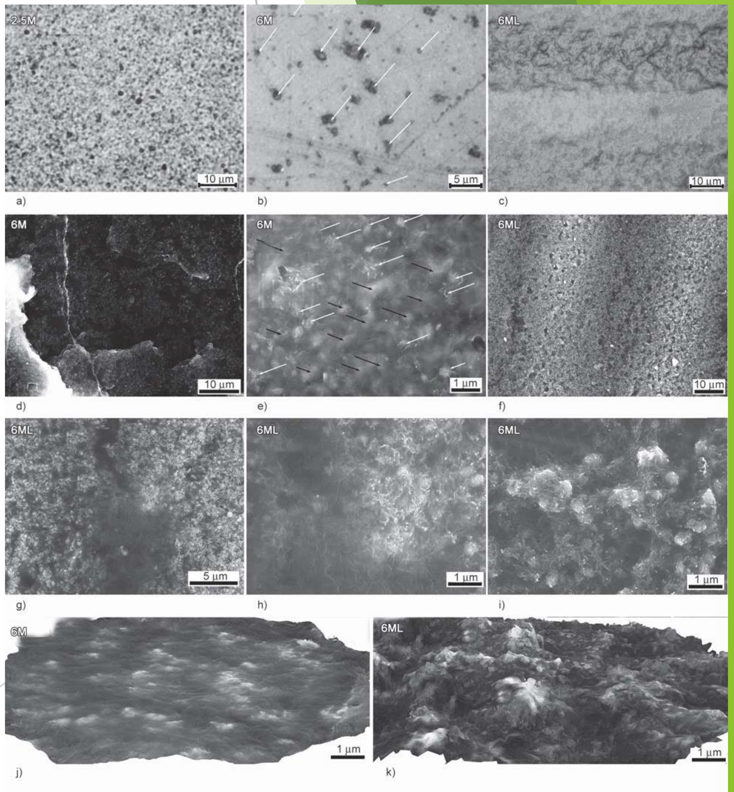
(8) Design of effective surface contacts on polymer composites modified with multi-Walled carbon nanotubes. *S. I. Moseenkov and N. A. Zolotarev, et al.*

Introduction. Investigate the use of laser processing to create effective surface contacts on multi-wall carbon nanotube (MWCNT)/polyethylene composites. The method of mechanical mixing in a melt was used to obtain a series of MWCNT/PE samples with a variable MWCNT content (0.5, 0.75, 1.5, 2.5, 4, 6, 8, 10 wt%).

The samples were designated as 0.5M–10M, where the number indicates the mass content of MWCNTs in the composite.

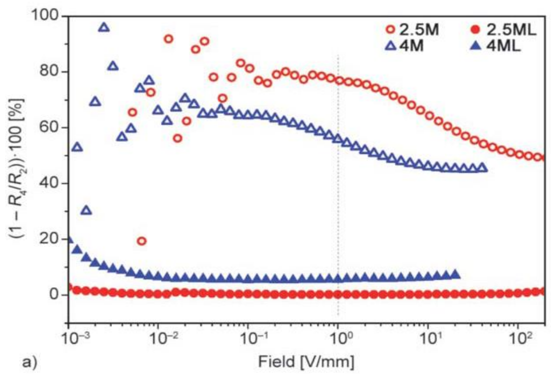
Semiconductor laser source (GH04C05A9G Sharp) with a wavelength of 455 nm and a continuous power of 5 W. Pulse-width modulation (PWM) control with a frequency of 25 kHz was used to control the laser power.

Results and Discussion



Morphology. SEM data, during laser processing of composites, nanotubes provide the effect of photothermal transformation in the near-surface layer of the composite, thereby ensuring the removal of the polymer layer with the formation of a small amount of amorphous carbon. At the same time, the structure of MWCNTs concentrating on the surface of the contacts virtually does not change**.**

Current-voltage. The removal of the near-surface polymer layer reduces the contribution of the contact resistance to the total resistance of the composite measured by the 2-probe method by more than an order of magnitude and makes it possible to get rid of the nonlinear dependence of the current density on the applied field in the range up to 10 V/mm.



Experimental Work

Experiment. 1

Introduction. PC/ABS MWCNTs nanocomposite pieces are welded by using femtosecond laser with varying parameters.

Materials. PC/ABS in the ratio of 80/20 and MWCNTs is 0.15 wt % are used for sample preparation. Femtosecond laser are used, average power 60 W, energy of pulse 80 µJ-1.2 µJ.

Results and Discussion

Surface Morphology with high pulse energy (Ep).

- The cross-section of laser welded crater at high pulse energy as shown in figure with the increase of power, the depth of craters are increases.
- Table 1, shows that there is systematic change in craters depth with power changes, maximum at 30 % is 2 mm.
- This results also supports the uniform mixing of the materials.
- A black carbon are aggregates at the surface.

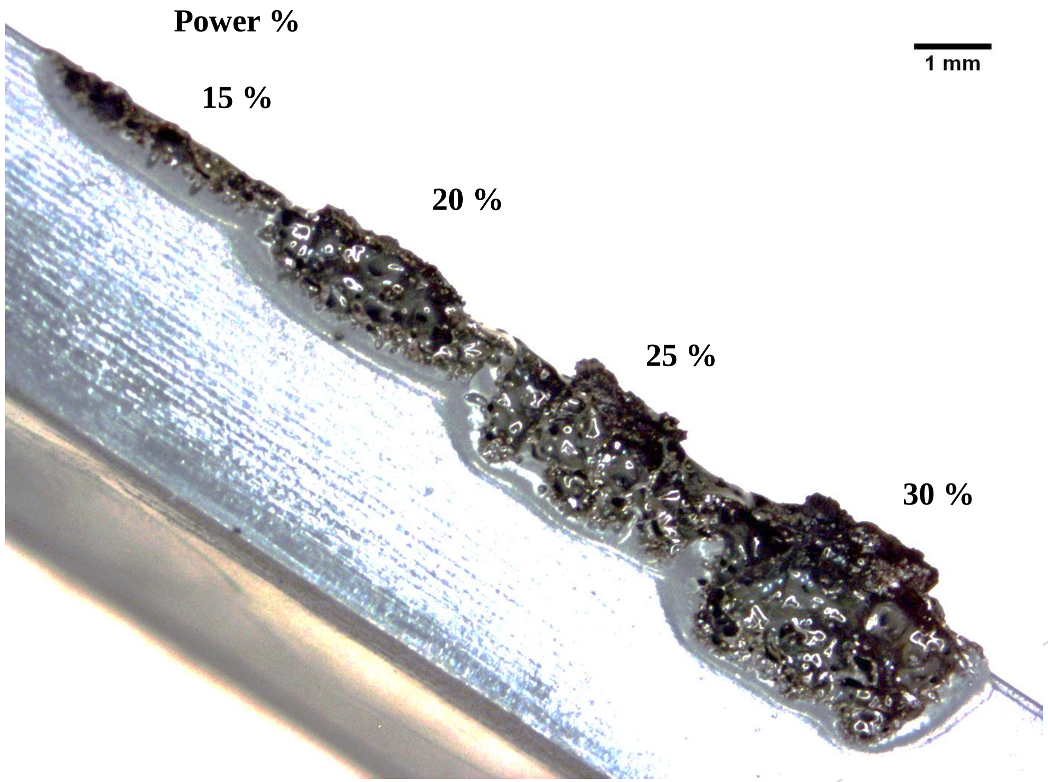
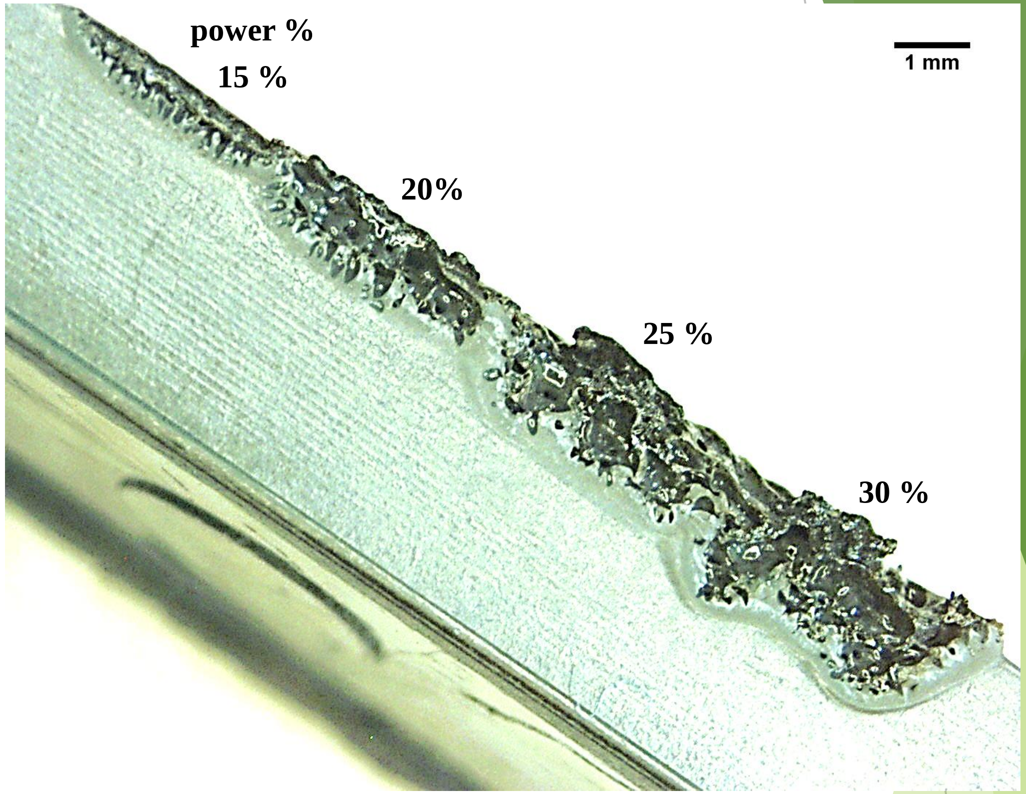


Table. 1. Using software imagej

Sr.No.	Power %	Craters Depth (mm)
1	15	0.84
2	20	1.297
3	25	1.774
4	30	2.006

Surface Morphology with low pulse energy (Ep).

- At low pulse energy the cross-section of laser welded crater as shown in figure with the increase of power the depth of craters are increases.
- Table 2, shows that there is not linear change in craters depth with power changes, maximum at 30 % is 1.6 mm.
- In the figure it is clear that the depth of the craters are less than the high pulse energy.



Sr.No.	Power %	Craters Depth (mm)
1	15	0.664
2	20	1.123
3	25	1.553
4	30	1.651

Table. 2. Using software imagej

Conclusions.

- It is clear that the high pulse energy creates high depth in the materials. But the sample are burning during the laser inflation.
- The surface are more smooth in low pulse energy samples.
- High pulse energy used for creating more depth crater according to the applications.
- 20 % Power is suitable for this material.

Future Work.

- **Research**

- **Preparation of polymer composite with different wt % MWCNTs and study the laser effects on the surface morphology and properties.**

- **Polymers are SEBS, PP, PC, ABS, PC/ABS, with MWCNTs contents of 0.5%, 1.0%, 1.5%, 2% and 2.5% by weight.**

- **Changes the parameters of laser.**
  - **a. power**
  - **b. Line distance**
  - **c. Mark speed**
  - **d. Scanning speed**
  - **e. Pulse energy**

- **Different lasers will be used like femtosecond, Nd:YAG, and CO_2 laser.**

- **Writing a scientific article.**

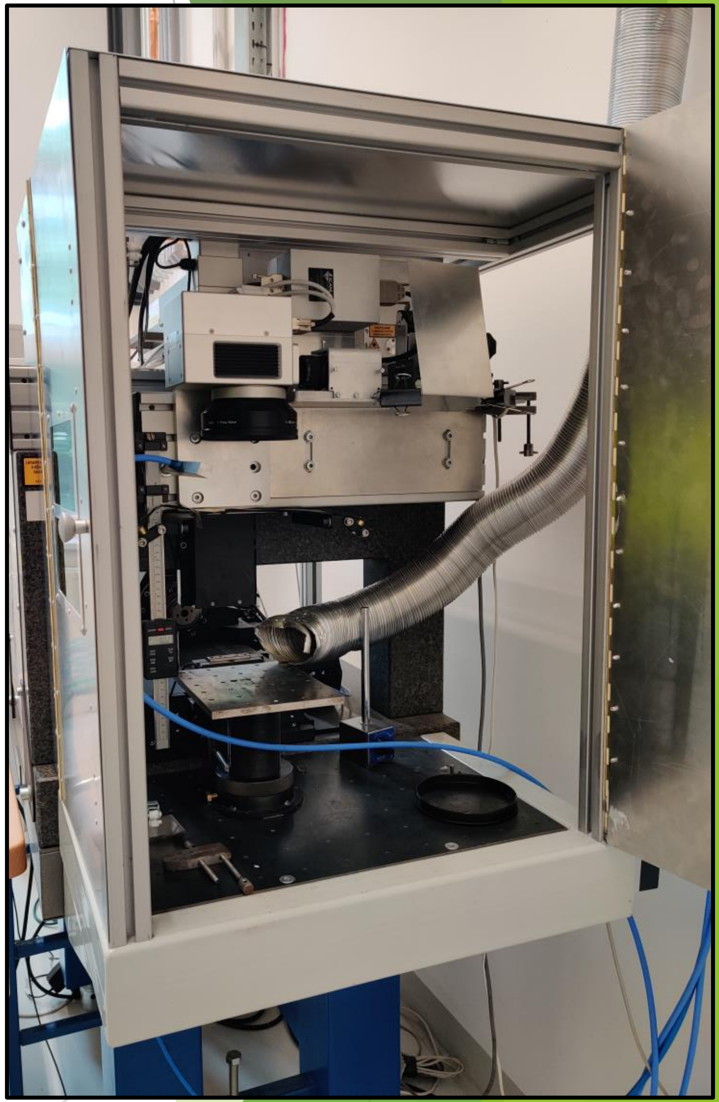


Fig.: Femtosecond laser setup

Semester Activities.

- **I have taken the two courses:**

  *** "Experimental Design" with Horváthné Dr. Drégelyi-Kiss Ágota**

  *** "Polymer chemistry and physics" with Dr. Pekker Sándor**

- **I have been doing the literature review related to polymer-MWCNTs nanocomposites and laser effects on the surface morphology and properties of polymer nanocomposites.**
- **I have performed the experiment, femtosecond laser effects on PC/ABS-MWCNTs nanocomposite for the study of surface morphology.**

Thanks for your Attention