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Study of carbon nanotubes based Polydimethylsiloxane composite films

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Abstract. Thanks to their remarkable characteristics, carbon nanotubes (CNTs) have fields of applications which are growing every day. Among them, the use of CNTs as filler for polymers is one of the most promising. In this work we report on Polydimethylsiloxane (PDMS) composites with different weight percentages (0.0% to 3.0%) of multiwall carbon nanotubes (MWCNTs) having diameter 10-30 nm and length 20-30 μm. To achieve optimum dispersion of CNTs in PDMS matrix, high speed mechanical stirring and ultrasonication were performed. By using the doctor blade technique, 70 μm thick uniform films were produced on glass. They were subsequently thermally cured and detached from the glass to get flexible and self standing films. The surface morphological study done by FESEM, shows that CNTs are well dispersed in the PDMS. Raman spectroscopy and FTIR were used to investigate the possible structural changes in the polymer composite. To examine the optical behavior UV-VIS spectroscopy was employed in both specular and diffused modes. A linear increase in absorption coefficient is found with the increasing percentage of CNTs while the transmittance decreases exponentially. The results confirm the dependence of optical limiting effect on the quantity of MWCNTs. Based on optical study, MWCNTs/PDMS composite films can be a promising material to extend performances of optical limiters against laser pulses, which is often required in lasing systems.

1. Introduction

The breakthrough of carbon nanotubes (CNTs) has got remarkable progress in various fields of research and applications due to their peculiar structural, electrical, mechanical, optical and magnetic properties [1]. CNTs diameters are in the 1-100 nm range and they can be up to millimeters long [2]. These dimensions lead to very high aspect ratios as compared to that of carbon fibers. This combination of properties allows better interaction in composite matrices, resulting in improved properties and performance [3].

The incorporation of CNTs into the polymer can enhance the properties of material by increasing mechanical strength and electrical conductivity. However the formation of aggregates and low dispersions of CNTs in the polymer matrix are the major cause of poor and inhomogeneous composites [4]. The interface between the CNTs and the polymer matrix plays as well a vital role in achieving good dispersion. Successful incorporation of CNTs in polymer matrices could result in different types of lightweight and strong materials for flexible electronic devices and sensors [5].

So, for the exploitation of the potential of CNTs, the issues regarding economical and controlled fabrication of well dispersed reinforced composite materials has to be tackled and solved. We report here an efficient and inexpensive process of incorporating carbon MWCNTs into a PDMS

(polydimethylsiloxane) matrix. Furthermore, we focused on structural and optical properties of CNTs and summarize the current issue and future viewpoint on this subject.

2. Fabrication of MWCNT/PDMS composite films

The commercial MWCNTs used in this work were purchased from CHEAPTUBES®. These nanotubes are produced by catalyzed chemical vapor deposition and have a 99.9% purity. Their diameter is in the 10-30 nm range and their length is in the 20-30 μm range (figure 1). The FESEM micrographs show that MWCNTs are highly entangled due to Van der Waals attractive forces.

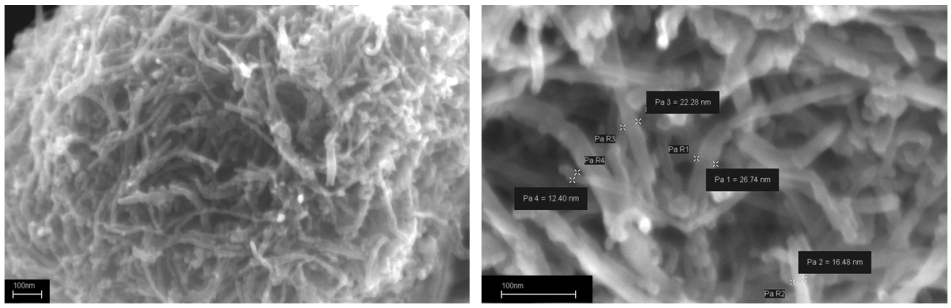

Figure 1. Field emission scanning electron microscopy of MWCNTs used in our work

In order to prepare MWCNTs-PDMS composites with different percentages of carbon nanotubes, the desired quantity of fillers has been added to the PDMS monomer and dispersed by means of high speed mechanical stirring (1000 rpm for 10 min). After the addition of hardener, the matrix is mixed for 10 more minutes. The final step to achieve a uniform dispersion of MWCNTs in the composite solution is sonication (ultrasonic frequency 37 KHz for 15 min) at room temperature. The composite films with an average thickness of 70 micrometers and different weight percentages of MWCNTs (from 0.0 % to 3.0%) were prepared on glass by Doctor Blade Technique as described in the figure 2. The films were then degassed in vacuum to get rid of entrapped bubbles. Subsequently, films were thermally cured at 70°C for 4 hours and finally detached from the glass surface to get flexible and self standing films.

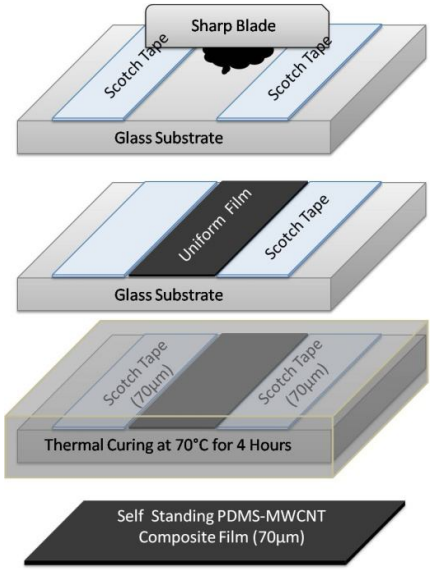

Figure 2. Schematic of steps involved in the fabrication of MWCNT/PDMS film

3. Surface morphology of films

After the preparation, these films were cryofractured and characterized by field emission scanning electron microscopy (ZEISS SUPRA 40, FESEM). This technique allows to investigate the dispersion of MWCNTs inside the polymer composite. The samples were coated with a thin metal layer before measurement to avoid charge accumulation and obtain a better insight on the CNTs distribution in the matrix. Figure 3 shows the cross sectional view of PDMS with different percentages (1wt%, 2wt% and 3wt %) of MWCNTs at 100kx resolution.

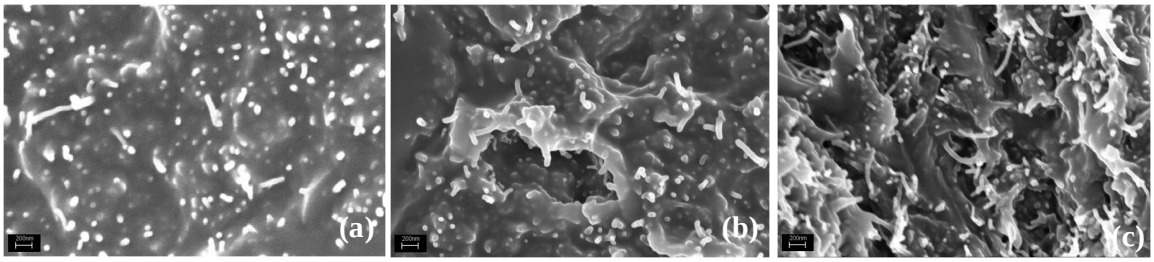

Figure 3. FESEM micrographs of PDMS with different weight percentages of MWCNTs a). 1.0 wt% b). 2.0 wt% c). 3.0 wt% at 100kx magnification

In figure 4, micrographs of the PDMS composite with 3.0 wt% of MWCNTS are shown at different magnifications. These micrographs show that most of the CNTs are well dispersed and randomly oriented into the polymer. The high magnification micrograph (figure 4-c) shows that the diameter of a single nanotubes-like structure is larger than that of CNTs (figure 1), even duly taking into account the increase due to metallization. This is attributed to the strong linkage between nanotubes and polymer matrix that leads to a decoration of CNTs by polymer molecules.

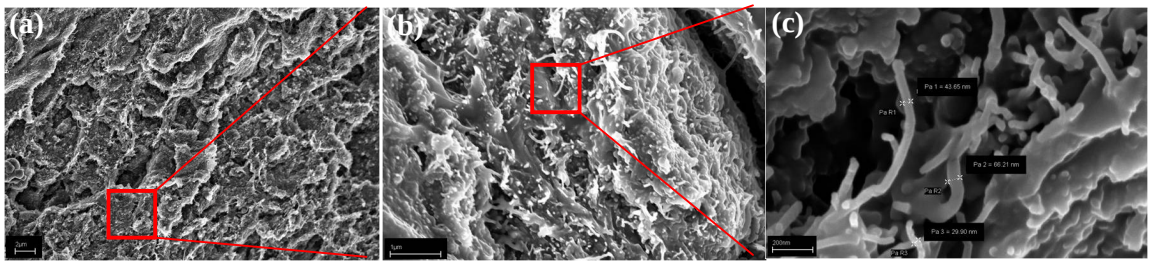

Figure 4. FESEM micrographs of PDMS+MWCNTs (3.0 wt %) at a). 10kx b). 50kx c). 200kx

4. Raman Spectroscopy

Raman spectroscopy is a non destructive technique which gives relevant structural information on carbon based materials.

Raman spectroscopy of PDMS-MWCNTs composite films (figure 5) was performed using a green laser source (wavelength 532 nm). The D-peak (located between 1300-1400 cm^{-1}) and the G-peak (located between1550-1615cm^{-1}) are the characteristic peaks of MWCNTs [6, 7]. The intensity of D and G peaks of carbon structures are increasing proportionally with the increase in CNTs inside the polymer, proving the fact that they are well dispersed and the films are enough uniform.

The other peaks in Raman spectra are attributed to the PDMS structure, in agreement with the characteristic peaks of well polymerized polydimethylsiloxane PDMS [8]. There are significant and gradual changes in the intensity and broadening of PDMS characteristic peaks which appears after the inclusion of CNTs shown in the figure above. Their investigation is however outside the purpose of the present work and will be discussed elsewhere.

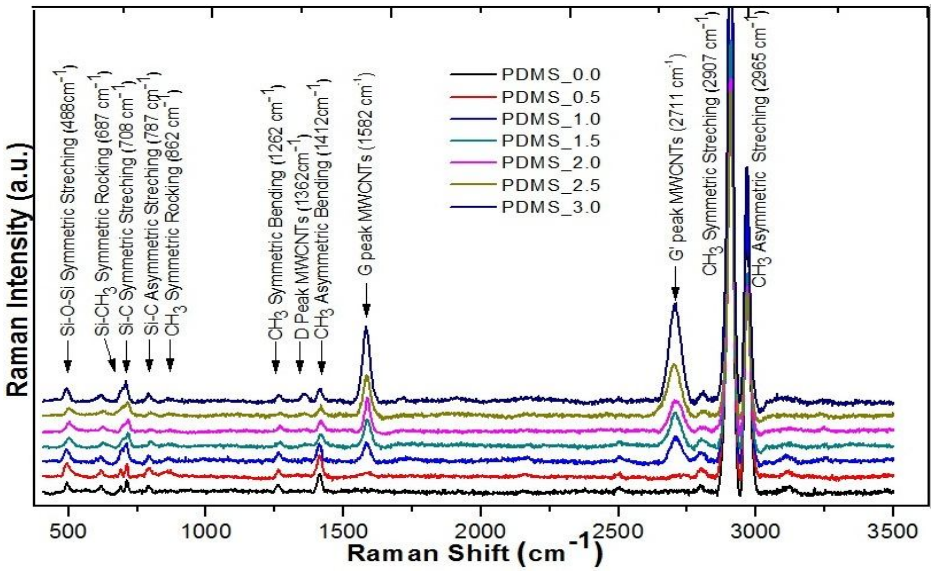

Figure 5. Raman spectra for PDMS composite films for different wt % of MWCNTs

5. FTIR Spectroscopy

Figure 6 summarizes the positions of IR absorption bands of the chemical groups found in the PDMS-CNT composites. -CH_3 wagging related peaks are located at 1410 cm^{-1} and at 1258 cm^{-1}. A wide multi-component peak ranging from 1000 cm^{-1} to 1100 cm^{-1} corresponding to symmetrical Si–O–Si stretching is also present. There is a minor decrease in the peak at 930 cm^{-1} which shifts to lower wave numbers as the concentration of MWCNTs increase in PDMS. In addition the ratio between the two transmissions values at 900 cm^{-1} and 930 cm^{-1} decrease with increasing CNT content as highlighted in the inset of figure 6. This is in good agreement with the literature [9] as this effect is also observed for other carbon materials based composites. Si–C bands and rocking peaks for $Si(CH_3)_2$ are observed in 835–855 cm^{-1} and 785–815 cm^{-1} regions, respectively [10,11].

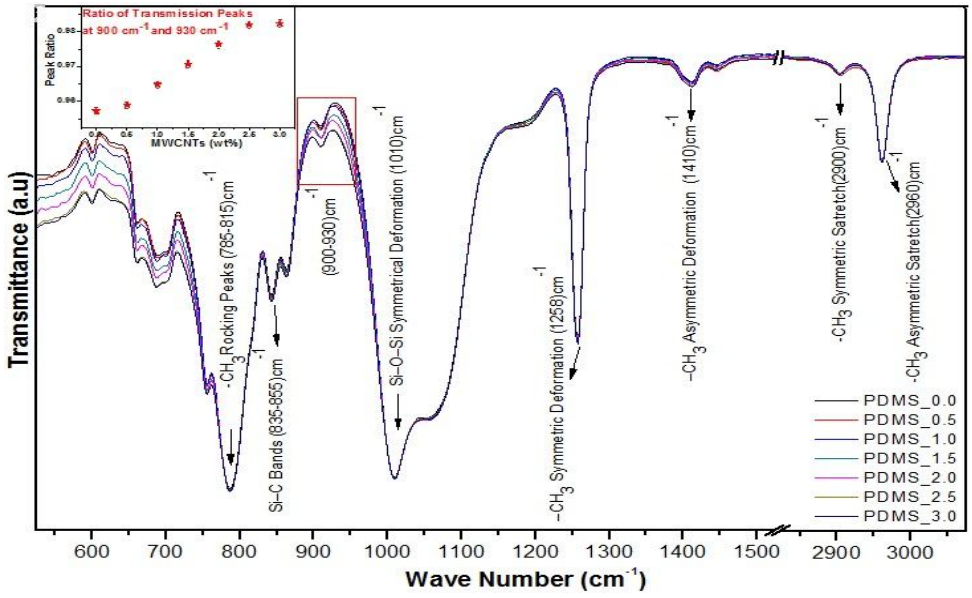

Figure 6. FTIR Spectra for Pure PDMS composite with different weight percentages of MWCNTS

6. UV-VIS Spectroscopy

For the comprehensive study of optical behavior of these polymeric films, optical characteristics were measured both for direct as well as diffused light. In figure 7, total reflectance (a) and transmittance (b) spectra are shown for the various composites. As expected, the addition of nanotubes to PDMS has reduced the transmittance as well as reflectance of the films. For the inclusion of 3wt% carbon nanotubes, the films have an almost negligible transmission.

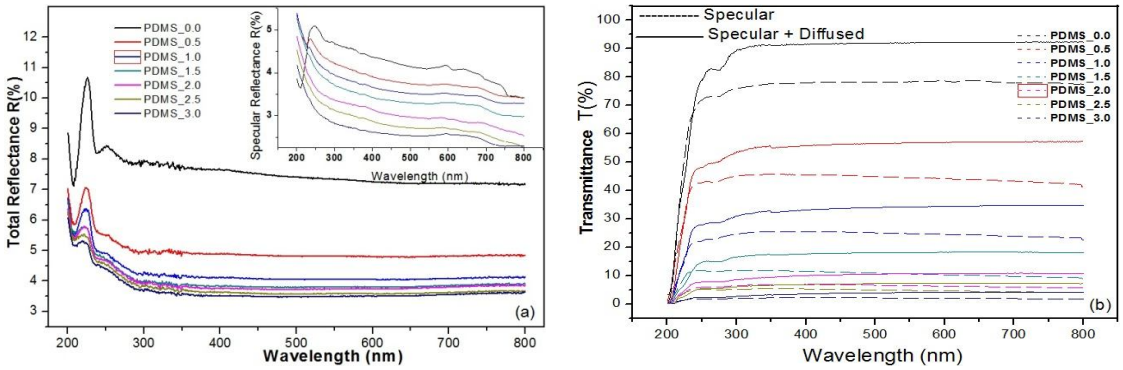

Figure 7. Comparison of specular and diffused measurements: a) Reflectance b) Transmittance

The overall absorptance (absorption) of each film is evaluated as

$$A=100-(R_d+R_s)-(T_d+T_s) \quad (1)$$

where R and T denote reflectance and transmittance, while $_d$ and $_s$ stand for diffused and specular respectively [12]. The results concerning A values are shown in the figure 8-a. The absorption coefficient α has been calculated as

$$\alpha=1/t \ *log(1-R)/T \quad (2)$$

where t is the thickness of the film and R and T are the total reflectance and transmittance respectively [12]. The absorption coefficient increases with increasing content of CNTs as shown in figure 8-b.

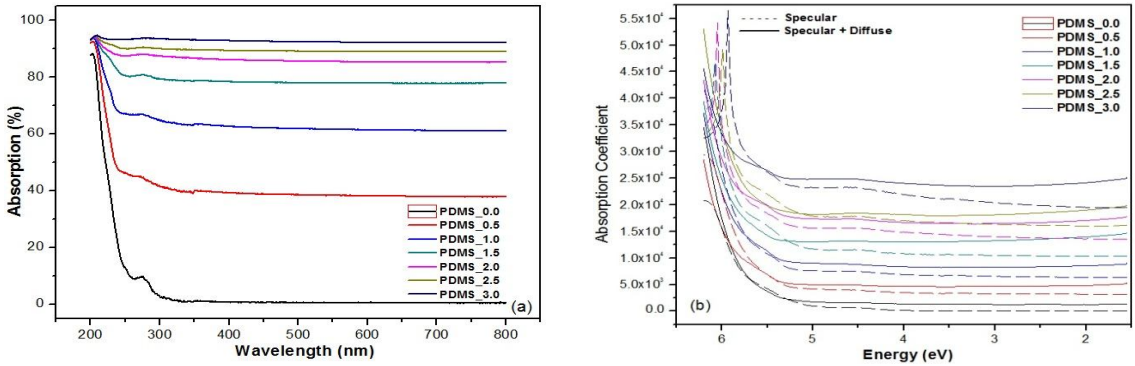

Figure 8. The Absorption (a) and the Absorption Coefficient (b) of the PDMS-MWCNTs Composites

7. MWCNTS/PDMS composite film for optical limitation

The absorption coefficient increases linearly with the increasing content of carbon nanotubes (figure 9-a) while the transmittance decreases exponentially (figure 9-b).

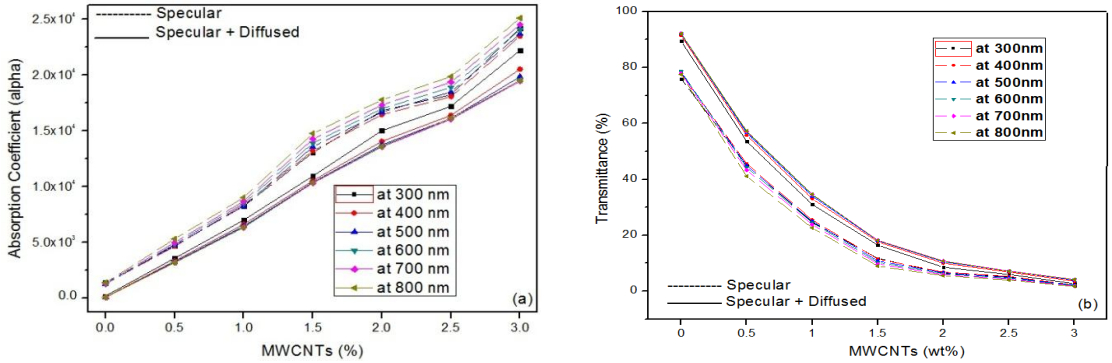

Figure 9. Dependence of absorption coefficient (a) and transmittance (b) on MWCNTs (wt%)

Optical density spectra, calculated [12] as

$$OD = log\ (1/T) \qquad (3)$$

for the different percentages of MWCNTs are compared in figure 10-a. The optical density is increased by increasing the weight percentage of MWCNTs. However, it remains almost constant throughout the visible range for a given CNTs content.

Diffusivity is defined as

$$D = (T_d+R_d)/(1-A) \qquad (4)$$

and describes the rate at which light diffuses in the substance. The diffusivities of the PDMS-MWCNTs films are shown in figure 10-b. While in pure PDMS diffusivity is almost wavelength independent, the presence of CNTs lead to diffusivity increasing with increasing wavelength in composites.

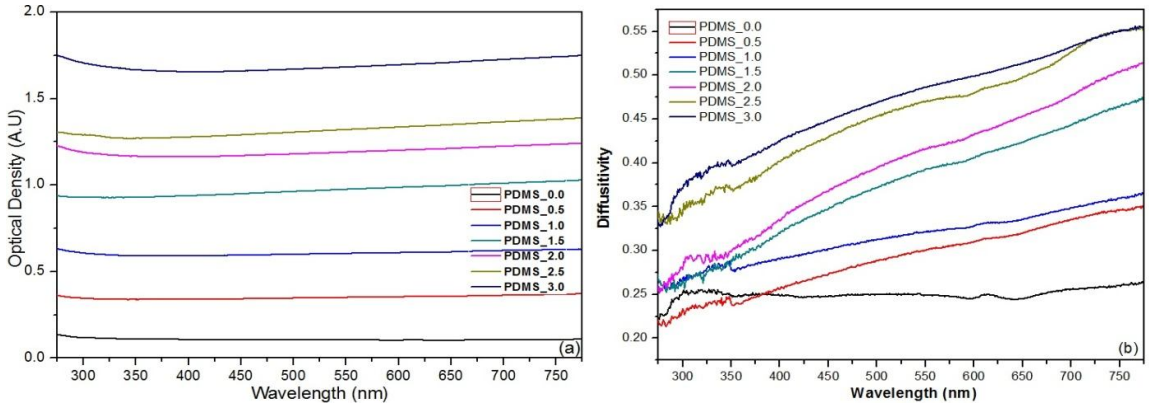

Figure 10. The spectra of (a) Optical Density and (b) Diffusivity

The above results suggest that, through a tuning of the specular transmittance, these films might be of interest in laser technology as optical absorbers to tune the laser beam power density.

8. Conclusion

Embedding CNTs in the PDMS matrix can open new fields of application for this well established polymer. The morphological study proved reasonably well dispersion and random orientation of CNTs into the PDMS composite films. The Raman Spectroscopy as well as FTIR analysis demonstrated the bonding between CNTs and polymer. The optical characteristics established that PDMS-MWCNTs composite film are promising materials to extend performances of optical limited devices. CNTs proved excellent candidate material for optical limiting and the optical limiting effect depends on the quantity of CNTs.

Acknowledgement

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