EFFECTS OF UV EXPOSURE ON AN OXIDIZED CARBON NANOTUBE POLYMER COMPOSITE

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Abstract.

Multi-walled carbon nanotubes (MWNTs) were oxidized by single step acid functionalization. Various weight percentages (0wt% - 2wt%) of functionalized MWNTs (fMWNTs) were blended with polypropylene (PP) to fabricate fMWNT/PP composites. The pre UV and post UV irradiation composite samples were used to study the effects of UV exposure on the composite samples. The samples were then examined by using mechanical and thermal property tests. The morphology of fracture surfaces of composite samples were investigated by Scanning Electron Microscope (SEM). It was found that 1.5wt% of fMWNTs would have optimum reinforcement performance both for pre-UV and post-UV irradiation at low fMWNTs content. It was also found that even low content of fMWNTs would have significant positive reinforcement effect to PP after UV irradiation.

1 Introduction

Conventional fillers such as glass, Kevlar, graphite, ceramics, metal particles and clays are commonly used in polymer-based composites. However, these fillers offer only a limited contribution to the mechanical properties of the composites. With the advance of nano-technology, more researchers have focus on the application of nano-materials such as nano-clays and carbon nanotubes (CNTs) [1] to reinforce the polymer-based composites. It is believed that nano-scaled fillers can provide unique properties into polymer matrices [2]. CNTs are one of the most promising nano-fillers. CNTs have been well recognized as a nano-structural material with a great potential for improving the properties of polymer-based advanced composites. The Young's modulus of the CNTs was estimated to be in the order of 1 TPa [3, 4]. Studies have showed that the addition of a small amount (~1 wt%) of the CNTs can improve the mechanical properties and electrical conductivity of composites substantially [5]. The CNTs possess superior mechanical strength with low density and large surface contact area, which bring these materials as reinforcements for many engineering applications.

UV degradation has been a critical problem for polymers. CNTs reinforced polymer composites also face to the same problem when they are used in outdoor applications. However, there are only a very limited number of scientific studies focusing on this issue for CNT/polymer composites. Najafi et al. [6] reported that the radiation of UV-ozone (UV wavelength: 254 nm) on multi-walled carbon nanotubes (MWNTs) under an ambient condition would oxidize the surface of the nanotubes, producing quinines, esters, and hydroxyl functional groups. They also reported that the addition of CNT fillers had a reinforcement effect against the degradation by UV irradiations for a thin film nanocomposite [7]. This paper intends to investigate the effects of UV irradiation on a MWNT reinforced polymer composite in order to understand the degradation mechanisms in MWNT/polymer composites.

Polypropylene (PP) was used as a matrix. MWNTs functionalized with carboxylic acid groups at their tubes' ends by acid treatment were used as nano-fillers. The functionalized MWNTs (fMWNTs) were blended with PP by a co-rotating twin-screw extruder, in order to enhance the dispersion of the fMWNTs. The mechanical and thermal properties of pre UV irradiation fMWNT/PP and post UV irradiation fMWNT/PP composite at different weight percentages were compared. Scanning electron microscope (SEM) examination was conducted to investigate the dispersion quality of the fMWNTs and the failure patterns of the composites.

2 Experimental

2.1 Functionalization of MWNT

The chemical vapour deposition (CVD) grown MWNTs (diameter < 10nm, length: 5-15μm) were provided by Shenzhen Nanotech Port Co. Ltd.. The purified MWNTs were suspended in a 3:1 mixture of concentrated H_2SO_4/HNO_3 solution (98%, and 70% respectively) and placed in a sonicated water bath for 3 hours. Thus the end caps of the MWNTs were opened and functionalized with carboxylic acid groups (COOH) [8], which allows forming covalent linkages of polymers with the fMWNTs. After sonication, de-ionized water was used to wash away the acid and the mixture was then filtered with double layers of 0.22μm millipore membrane. These functional groups of the fMWNTs are necessary to provide sites for covalent integration of the MWNTs into polymer structures to produce nanotube reinforced composites.

2.2 Preparation of fMWNT/PP composites

Hakke MiniLab twin-screw micro extruder (Germany) was used to disperse the nanotubes into the PP. PP pellets were dried by oven at 80°C for 24 hours. 0wt%, 0.5wt%, 1wt%, 1.5wt% and 2wt% of fMWNTs were mixing with PP pellets before blending. The dry mixture of PP and nanotubes were compounded inside the extrusion chamber for 15 minutes in co-rotating mode at 100 rpm and 177°C. The blended materials were then transferred into the barrel of Thermo Hakke small scale injection molding machine (Germany). The blended materials were injected into a dumbbell shaped mold (mold temperature: 50°C, sample dimension: ~5x1.5x90 mm^3) to form testing composite samples. All samples were kept at 25°C and 40% humidity environment before performing the tests.

2.3 UV exposure of fMWNT/PP composites

In order to study the effect on the composite sample after UV exposure, UV irradiation was conducted under ambient condition in a UV lamp chamber (40 cm × 40 cm × 13.5 cm) which had a layer of reflective aluminium foil inside to ensure all the sample would have an even exposure to UV. The temperature during UV irradiation was maintained at around 25 °C. The neat PP and fMWNT/PP composite samples were irradiated under a 25 W ultraviolet lamp (Sylvania, Japan) for 72 hours. The primary wavelength of the lamp is 254 nm. Fig. 1 shows the spectral energy distribution of the lamp:
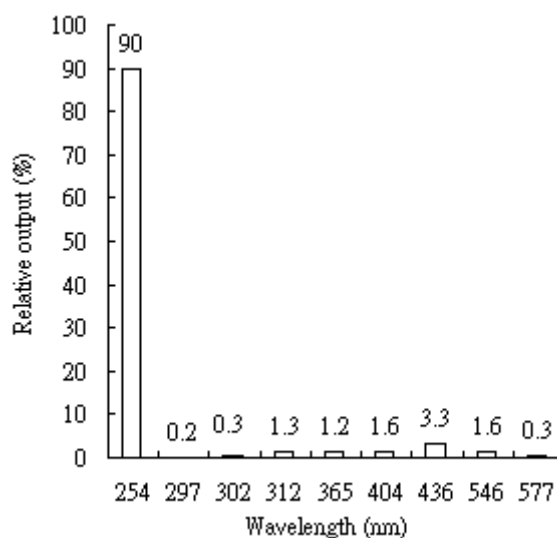

Fig. 1. The spectral energy distribution of the UV lamp.

2.4 Characterization of fMWNT/PP composites

The tensile properties of the composites were determined by a 50kN MTS Alliance RT/50 tensile machine. The loading speed of the cross head was 4mm/minute. Five specimens were tested for each set of variation. The Vickers hardness (H_v) of the composites was measured by a micro-hardness testing machine (Future-tech FM series). Each specimen was measured five times at random locations respectively. The average value obtained from the test was recorded as the hardness value. 100 gram force and 15 seconds of dwell time were used in indentation. The hardness value of the sample was determined by equation (1):

$$H_v = \frac{8F\sin(\theta/2)}{(d_1 + d_2)^2} \qquad (1)$$

where H_v is Vickers hardness. d_1 and d_2 are the two diagonal lengths of the indentation mark. F is the load force and θ is the face angle of a pyramidal diamond indenter (136°).

The thermal stability of the composites could be illustrated by thermogravimetric analysis (TGA). The temperature at the maximum weight loss in differential thermogravimetric (DTG) curve would indicate the thermal stability. Setaram Labsys TG-DTA/DSC (the accuracy was ±1 μg) system was used for TGA. The samples (around 5 mg) were heated from 30 ^{o}C to 600 ^{o}C at a rate of 10°C/minute with the flow of nitrogen. For the differential scanning calorimetry (DSC) test, around 5 mg of composite samples were chopped into small pieces and placed into the heating pans. The pans were

heated from 25°C to 200°C at a rate of 10°C/minute in Perkin-Elmer DSC7 to evaluate the melting temperature of the composite samples.

The morphology of the fracture surfaces of the composite samples after tensile tests were observed by using SEM images (Leica Stereoscan 440, at 20kV accelerating voltage).

3. Results and discussion

3.1 Tensile tests

Fig 3. shows the change of Young's modulus at various fMWNTs content before and after the UV irradiation. It shows that the Young's modules are gradually increased from around 1110 MPa to 1380 MPa for 0 to 1.5 wt% of both pre and post UV irradiation composite samples. For the case of pre UV irradiation, the maximum improvement of Young's modulus for the composite samples is around 24%. But for the case of post UV irradiation, the maximum improvement is around 11%. It is expected that the mechanical properties of the composites would be increased due to the interlocking between the fMWNTs and polymer chains. Thus, fMWNTs are able to play the role of reinforcement. The reduction of stiffness after 1.5wt% of fMWNTs may be due to the aggregation of fMWNTs. The aggregation of CNTs will cause slippage inside the clusters such that it will reduce the stress transfer efficiency and the reinforcement performance [9]. It is obvious that the effect of UV exposure on the Young's modulus of the composite sample is narrow down and reached similar values at 1.5wt% of fMWNTs. In cooperate with Fig.3, UV irradiation strengthens the Young's modulus of PP composite but also weaken the failure strain of the composite. From Fig. 3, although it can be seen that by adding fMWNTs, the failure strain of the neat PP can be reduced, it is a trade off between utilizing the strength and the failure strain of the material. But after UV irradiation, the situation can be different. The UV irradiation causes the reduction of nearly a half of the failure strain value of neat PP. This reduced value is near to the value after adding of fMWNTs. For the fMWNT/PP, UV irradiation causes only a limited effect to its tensile property. Both the pre and post UV irradiation composite samples get very similar failure strain value. According to the literature [7], fMWNTs are able to provide an irradiation protection to the composite material. The further explanation on the UV irradiation protection of fMWNTs can be seen in section 3.2.
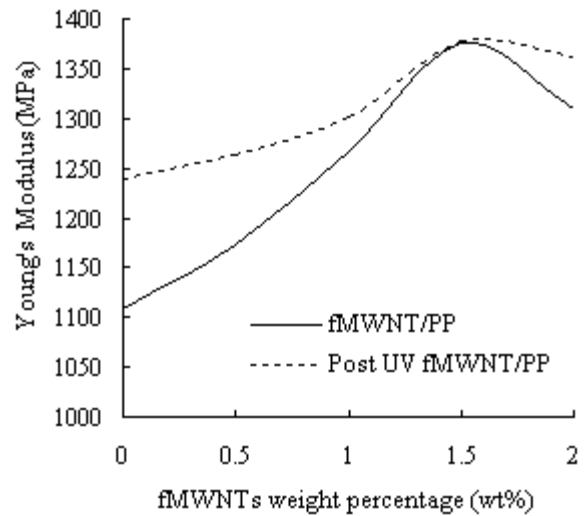

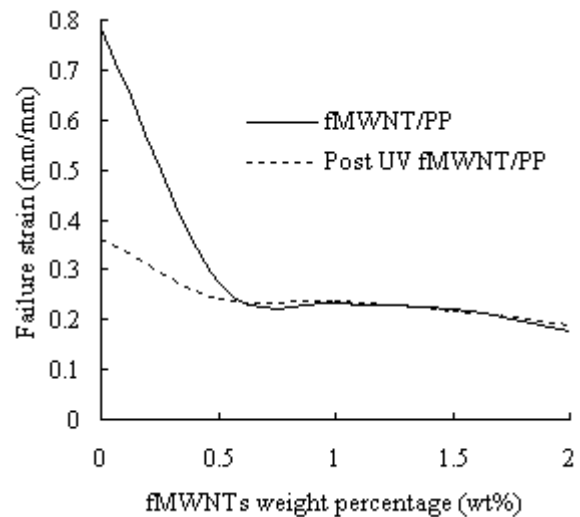Fig. 2. The Young's Modulus of the composite samples before and after UV irradiation.

Fig. 3. Failure strain of the composite samples before and after UV irradiation.

3.2 Vicker's hardness tests

The values of Vicker's hardness of the samples are listed in Table 1. The result shows that, the behaviour of the hardness test result is quite consistent with the tensile test result. The hardness value is generally increased with the increase of the fMWNTs content and 1.5wt% of fMWNTs achieves the best reinforcement result among others. Fig. 4 shows the percentage of improvement of hardness value when comparing with neat PP before and after UV irradiation. It is obvious that, fMWNT/PP results a uniform positive improvement in hardness value after UV irradiation. The Vicker's hardness value of 0.5wt% fMWNT/PP cross-section in Fig. 5 helps to explain the effect of UV irradiation.

Table 1. The value of Vickers hardness of the composite samples.

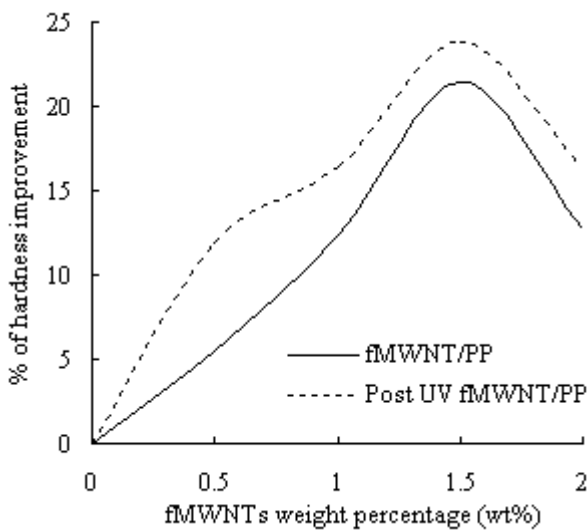|	fMWNT (wt%)	Vickers hardness (Hv)	Improvement (%)
Pre UV irradiation	0	9.05±0.16	0
	0.5	9.54±0.15	5.45
	1	10.17±0.15	12.42
	1.5	10.99±0.17	21.44
	2	10.20±0.11	12.75
Post UV irradiation	0	8.89±0.40	0
	0.5	9.95±0.89	11.93
	1	10.35±0.48	16.43
	1.5	11.00±0.65	23.78
	2	10.33±0.61	16.28

Fig. 4. The percentage of Vickers hardness improvement of the composite samples.

Fig. 5 shows that the Vicker's hardness value of 0.5 wt% fMWNT/PP cross-section is a "U" shape against the distance from sample surface. It implies that UV irradiation only changes the microstructure of the composite surface, and hardens the outermost surface of the sample. This hardened layer likes a layer of protection to the composites. At low fMWNTs concentration (e.g. 0.5wt%), UV is able to penetrate into inner part of the composite. Thus, the hardness between the inner and outer part are quite different. The hardened layer will be the dominated part to strengthen the composite across the cross-section. But for the higher fMWNTs concentration, UV is not easy to penetrate to the inner part of the composite. The hardened layer reaches the threshold

with very thin region and results a very limited reinforcement effect after UV irradiation. The result of the Vicker's hardness value of fMWNT/PP cross-section also provides a possible reason to explain why the difference between Young's moduli of the composite samples is narrowed down and reaches a similar value 1.5wt% of fMWNTs before and after UV irradiation.
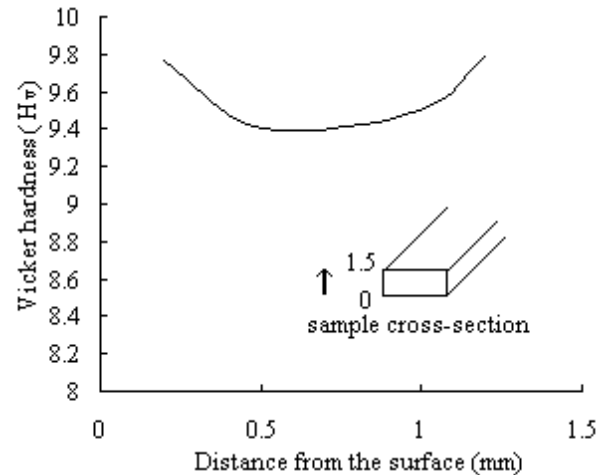

Fig. 5. The Vickers hardness value against the cross section distance of 0.5wt% fMWNT/PP.

3.3 TG analysis

The thermal stability of the composites can be illustrated by TGA. Fig. 6 shows the DTG curves of the composite samples. CNTs have extremely high thermal conductivity [10, 11]. The uniformity of the dispersion of fMWNTs will cause higher thermal conductivity of the composite, therefore higher thermal stability [12].
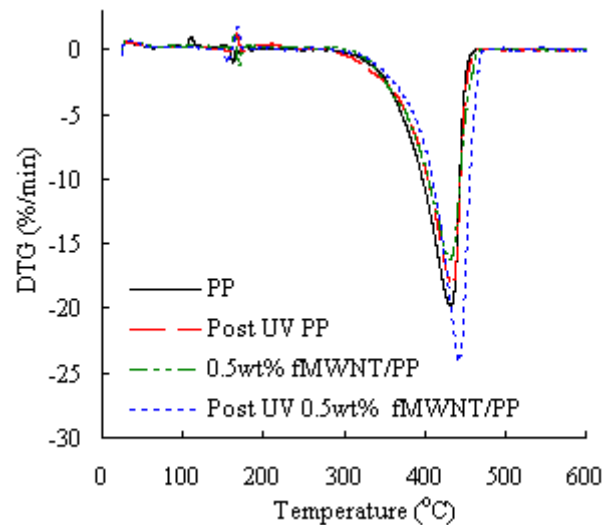

Fig. 6. The differential thermogravimetric (DTG) curves of the composite samples.

The thermal decomposition temperature of neat PP, post UV irradiation PP, 0.5wt% fMWNT/PP and post UV irradiation 0.5wt% fMWNT/PP are 432.4^{o}C, 433.79^{o}C 431.54^{o}C and 442.22 ^{o}C respectively. It can be seen that, the thermal stability values of the samples only have little changes for post UV irradiation PP and pre UV irradiation fMWNT/PP. But after UV irradiation, the thermal stability of 0.5wt% fMWNT/PP is increased by around 10°C. The change of this thermal stability makes an indication that the microstructure fMWNT/PP has been changed after UV irradiation. As Najafi et al. [6] reported that the radiation of UV-ozone on MWNTs under an ambient condition will oxidize the surfaces of the nanotubes, it is believed that the UV irradiation induces some chemical bondings between fMWNTs and PP polymer chains. The hardening effect of the outermost layer of the fMWNT/PP can also be explained by the reason of UV oxidization of fMWNTs.

3.4 DSC tests

Fig. 7 shows DSC curves of the composite samples with different conditions. Since the raw PP material is not isotactic, there are no crystallization peaks in DSC curves. The peaks around 160°C are the melting peaks of the samples. The shape of the peaks is quite consistent, and the width of melting range is qiute similar. There are no significant changes in the melting temperatures (T_m) (Table 2) for all composite samples. This result agrees with Valentini and Seo's [12, 13] findings. UV irradiation does not affect the melting temperature of the composite samples.
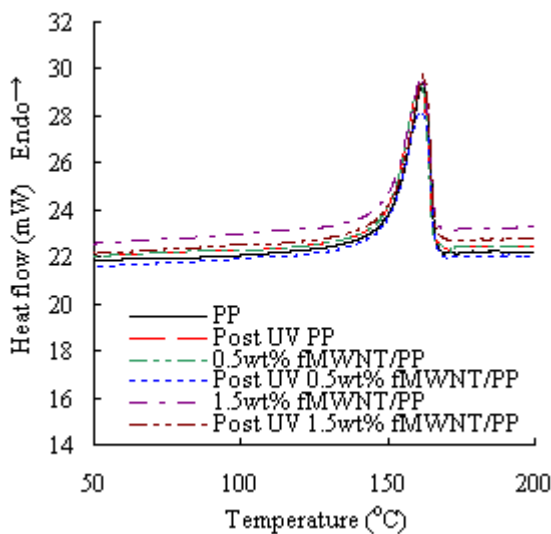

Fig. 7. The DSC curves of the composite samples.

Table 2. Melting temperature (T_m) of the composite samples by DSC tests.

	fMWNTs (wt%)	T_m (^{o}C)
Pre UV irradiation	0	161.83
	0.5	161.00
	1.5	161.50
Post UV irradiation	0	161.67
	0.5	161.33
	1.5	162.17

3.5 Morphology of fracture surfaces

Fig. 8 (A) – (F) shows the SEM images of the fracture surfaces of the composite samples after tensile tests. The white lines in the SEM images (Fig. 8 (E) & (F)) are the fMWNTs that mainly due to their high electrical conductivity properties. It is obvious that the failure pattern of pre UV irradiation PP is very different from the others. The fracture surface of pre UV irradiation PP is relatively smooth, but the fracture surfaces of fMWNT/PP and post UV irradiation fMWNT/PP are very rough. The roughness of the fracture surface is related to the ductility of composite. More brittle sample will have rougher fracture surface. The similar failure patterns of Fig. 8 (B), (C) and (D) imply they should have similar failure mechanism and strength. But the results of tensile test and hardness test were different. This can be understood by higher magnification of SEM images (Fig. 8 (E) & (F)). Although the failure patterns of the pre and the post UV irradiation fMWNT/PP look similar in a macroscopic view, they are different in the view of microscopic.

Fig. 8 (F) shows that more fMWNTs are tore off than in Fig 8 (E). This can be explained by the bondings formed between the fMWNTs and PP polymer chains. After UV irradiation, the oxidized defect site and function groups on fMWNTs are able to form bonding with the polymer chains. During the tensile force is applied to the test sample, the tensile stress is transferred form the polymer chains to the fMWNTs. As a result, the fMWNTs are tore with the polymer chains and play the role of reinforcement. For the case of pre UV irradiation fMWNT/PP, it can also be seen that there are also some fMWNTs were tore off, but the quantity is much smaller than the post UV irradiation sample. Thus the reinforcing effect is smaller than the post UV irradiation's sample.
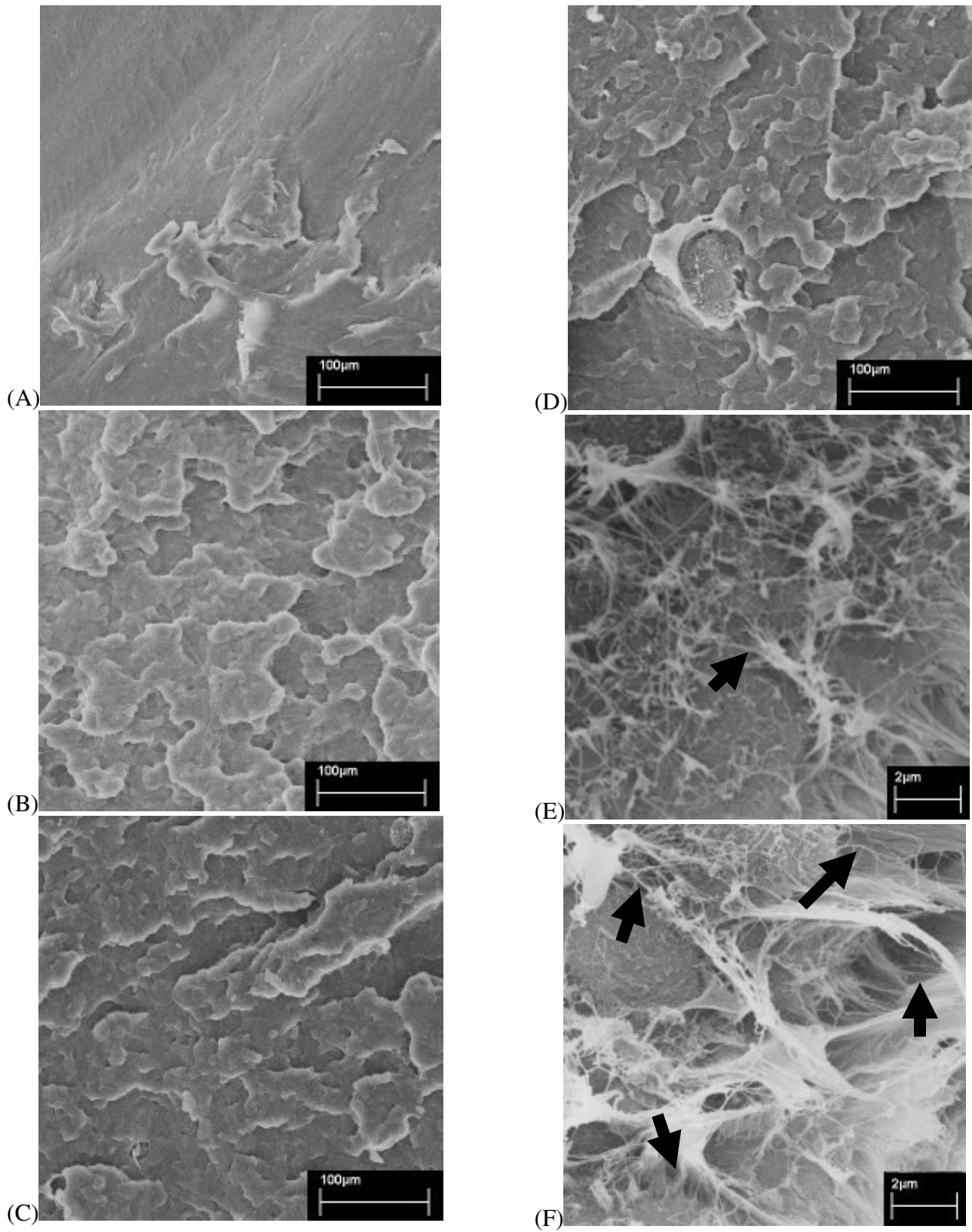
Fig. 8. SEM images of the composite samples fracture surface. (A) Neat PP, (B) Post UV PP, (C) 0.5wt% fMWNT/PP, (D) Post UV 0.5wt% fMWNT/PP, (E) higher magnification of 0.5wt% fMWNT/PP, and (F) higher magnification of post UV 0.5wt% fMWNT/PP.

4. Conclusion

In this study, the effects of UV irradiation on fMWNTs reinforced polymer composites were investigated. Through the mechanical and thermal property analyses, it was found that fMWNTs can diminish the negative effects of UV irradiation on PP. In addition, UV irradiation can form a protective layer on the composites. SEM images also illustrate the reinforcement mechanism of pre and post UV irradiation composites. The result of hardness value across the cross section of the samples in the form of a "U" shape provided evidence that UV cannot penetrate to the core of the samples. It also found that, the concentration of fMWNTs can affect the penetration of UV in the composites.

Acknowledgement

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