Investigation of the Effects of Magnetic Additive Cobalt/Carboxyl functionalized Multi-walled Carbon Nanotubes for Enhancing the Machinability of Polycarbonate Composites under Magnetic Field

Investigation of the Effects of Magnetic Additive Cobalt/Carboxyl functionalized Multi-walled Carbon Nanotubes for Enhancing the Machinability of Polycarbonate Composites under Magnetic Field

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Abstract. Polycarbonate (PC) has been widely applied in various industrial areas including biomedical, optical, and defence systems. According to the optical requirements of PC devices, a high-quality surface with better surface finish and transparency are necessary. However, due to the mechanical property of PC, poor surface finish due to tool marks generated during machining [1]. In this paper, a novel fabrication process is presented for enhancing the machineability in terms of higher ductility of PC without significant loss of transparency by mixing with cobalt/carboxyl multi-walled carbon nanotubes (Co/COOH-MWCNTs) . Carboxyl worked as a bridge between Co and PC chain, under a magnetic field, Co caused the movement of PC chains, and connect better with polymer chains. Experimental investigations show that a low concentration of Co/COOH-MWCNTs can increase the ductility of PC by fibre reinforcing effects. The experimental results provide promising guidance for enhancing the machinability of PC by appropriate concentration of the additive.

1.**Introduction**

The precision machining of optical plastic has been well explored. Among all industrial optical polymer materials, polycarbonate (PC) is one of the wildly used plastic for optical applications due to its low

cost, high toughness, high refractive index, and light weight [2]. According to the requirements of PC application, high-quality micro-structures are necessary with a smooth surface finish [3]. However, during the machining, PC faces lots of challenges to obtain good surface finish due to its low machineability. It is known that ductility is directly related to microstructure and material compositions. Although many technologies attempt to adjust the surface properties of PC according to various machining technologies, the study and adjust of PC microstructure is far from complete. In this paper, the relationship between additive and mechanical properties of PC composites were investigated. Firstly, cobalt/carboxyl multi-walled carbon nanotubes (Co/COOH-MWCNTs) was synthesized through chemical reaction. Then, Co/COOH-MWCNTs/PC was fabricated by thermocompression. In the composites, COOH-MWCNTs was used to connect Co and PC like a bridge through carboxyl. The magnetic property of Co could help the chain movement and arrangement under a magnetic field. As a result, the relationship between ductility and machinability could be balanced.

2.**Experimental Methodology**

The functionalized Multi-Wall Carbon Nanotubes (MWCNTs) were fabricated through acid treatment by a mixed acid of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) with a ratio of 3:1[4]. Through a reduction process by sodium borohydride ($NaBH_4$), Co^{2+} was reduced and captured by the functionalized MWCNTs. Then Co/COOH-MWCNTs mixed with the dilute solution of PC under a magnetic field, followed by drying under the magnetic field.

2.1. Materials

Raw multi-walled carbon nanotubes (99.9%, inner diam: 5-10nm, outer diam: 1-20nm, length: 50-30 μm), 1,2-dichloromethane (99.8%), and cobalt nitrate hexahydrate (98%) are from FineLab Scientific Limited. Hydrochloric acid (≥37%) is from Honeywell Fluka. Nitric acid (68%) is from Avantor VWR Chemicals. Sulfuric acid (95-97%) is from International Laboratory USA. Sodium borohydride (≥98%) is from Sigma-Aldrich.

2.2. Functionalization of MWCNTs

Purchased raw MWCNTs were placed in a silica crucible and were heated at 500℃ to 520℃ for 3 hours, followed by the acid treatment with 6.0M hydrochloric acid for 6 hours at 95℃. The treated MWCNTs were washed with deionized water for several times until the PH of the filtrate was neutral, following by overnight drying at 40℃.

The p-MWCNTs was dissolved in 75mL mixed acid (nitric acid: sulfuric acid 1:3) and refluxed for 6h at 80℃. COOH-MWCNTs were collected through suction filtration following by washing several times by deionized water until the PH of the filtrate was neutral. The collected COOH-MWCNTs was dried at 50℃.

2.3. Fabrication of Co/COOH-MWCNTs

2g $CoCl_2 \cdot 6H_2O$ were dissolved in 10mL deionized water. 0.1g COOH-MWCNTs were added into the $CoCl_2$ solution rapidly and ultrasonic mixed for 1 hour. In the meantime, a 5wt% NaBH4 solution was prepared. When the COOH-MWCNTs were homo-dispersed, the $NaBH_4$ solution was dropped into the solution under magnetic stirring for 1 hour. The mixture was then filtered and washed with deionized

water several times before vacuum drying at 100℃ [5][6].

2.4. Co/COOH-MWCNTs/PC Composites

15g PC particles were dissolved in 35mL dichloromethane by magnetic stirring. After PC dissolved in the solvent, 0.1wt%, 0.05wt%, 0.025wt% Co/COOH-MWCNTs were added into the solution, when the solution has been mixed uniformly, the solution was further dispensed through the ultrasonic mixer for 2 hours in an ice-bath. The solution was then transferred into Petri dishes for drying under a strong magnet (1TB) 2cm higher than Petri dishes. After drying, the composites were broken into very small pieces by a hammer. The pieces of composites were collected into a sample bottle. The whole scheme for the process is shown in Figure 1.

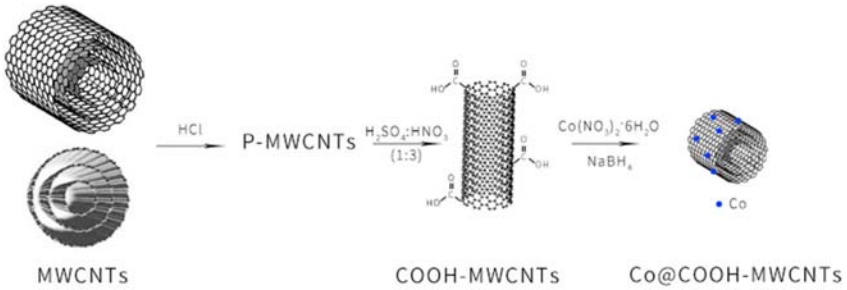

Figure 1. Scheme of experimental reactions.

2.5. Thermocompression of Co/COOH-MWCNTs/PC composites

1g Co/COOH-MWCNTs/PC pieces were put into pointing machine for pre-compression. The pieces were pressed at 180℃ under 40 atm for 20 minutes to form a round slice with a diameter of 30 mm. The pre-pressed composites slice was then put into the thermo-compression mold. The whole mold was put into an oven and was heated to 265℃. After keeping in the oven for 3 hours, the mold was quickly transferred to an FM-15A tablet press machine. The mold was then cooled by turning water.

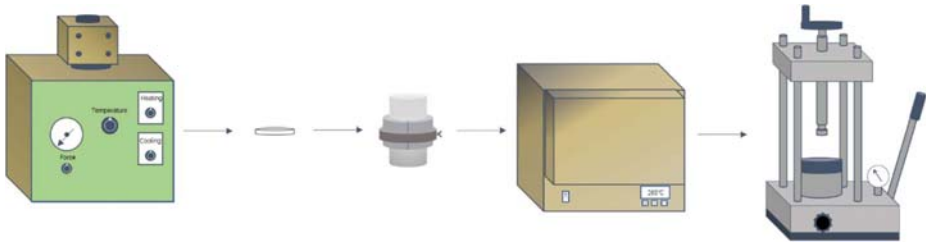

Figure 2. Scheme of experiments.

2.6. Characterization Methods

The morphologies of samples were tested by scanning electron microscope (SEM). Energy dispersive X-ray (EDS) was used to recognize elementary distribution. The phase composition was analyzed through X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). Data of XRD were collected by 2θfrom 0° to 80° with a scan speed of 10 (°)/min. The transparency of samples was tested through transparency measuring instrument TMS-II-VIS-NIR from Leapwise Dragon Industry Limited.

3. **Results and Discussion**

The morphologies of COOH-MWCNTs, Co/COOH-MWCNTs and PC/Co/COOH-MWCNTs were observed by SEM. Figure 3(a) shows the morphologies of COOH-MWCNTs. From Figure 3(b), it shows that Co covered the surface of COOH-MWCNTs. Figure 3(c) shows the smooth surface of PC/Co/COOH-MWCNTs and Figure 3(d) shows the edges of the sample. From the image, it is found that Co/COOH-MWCNTs were mixed with PC. Since the existing of carboxyl, Co/COOH-MWCNTs could connected with PC tightly through hydrogen bounds which lead to a better connection.

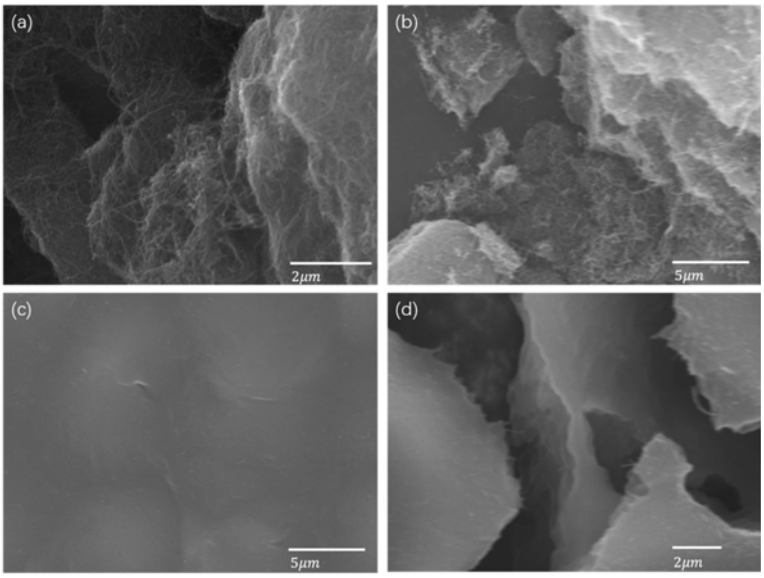

Figure 3. SEM images of (a) COOH-MWCNTs; (b) Co/COOH-MWCNTs; (c, d) PC/Co/COOH-MWCNTs.

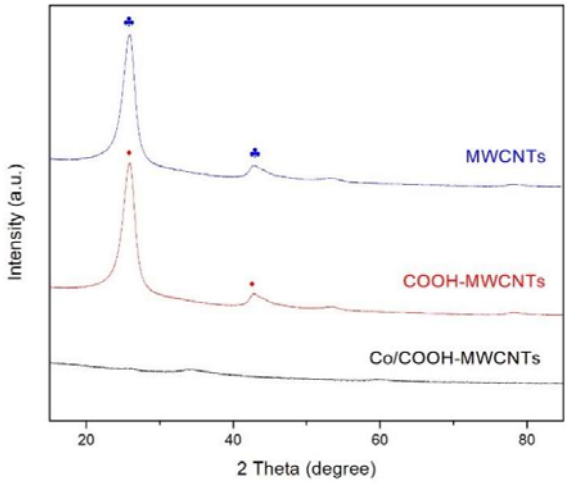

Figure 4. XRD patterns of p-MWCNTs, COOH-MWCNTs, and Co/COOH-MWCNTs.

X-ray diffraction patterns of raw MWCNTs, COOH-MWCNTs, and Co/COOH-MWCNTs were

shown in Figure 4. It is noted that p-MWCNTs and COOH-MWCNTs had similar patterns since their similarity in crystal structures as shown in Figure 3. The peak at around 26° shows the (002) refraction of MWCNTs.

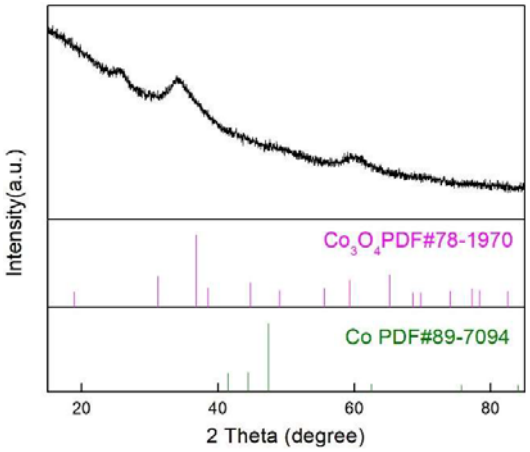

Figure 5. XRD patterns of Co/COOH-MWCNTs.

The Co-doped functionalized MWCNTs were investigated through XRD as shown in Figure 5. Although during the experiment, the magnet could attract part of the powder, compared with standard PDF cards of Co and Co_3O_4, it is found that most of Co were oxidated to Co_3O_4. The peak around 26° refers to MWCNTs is still there. The transparency of Co-doped COOH-MWCNTs/PC was tested. The results are shown in Figure 6. From the spectrum, it is found that the transparency of the PC composite significantly decreases when the concentration of Co/COOH-MWCNTs is greater than 0.025wt%. Samples with 0.012wt% Co/MWCNTs had similar transparency as compared with pure PC. Moreover, the lower PC transparency compared with commercial PC may be due to the micro-size bubbles in the samples which cannot be removed under such a condition.

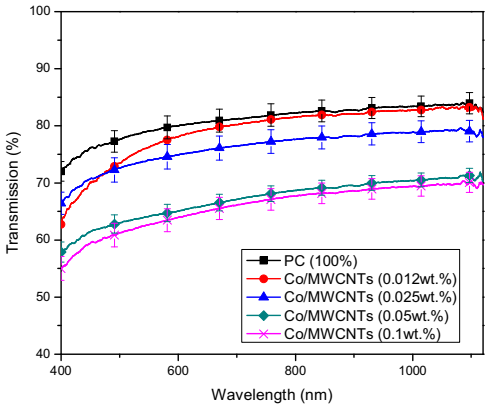

Figure 6. Transparency spectrum of samples.

The mechanical properties of composites were investigated through the tensile test, the results were shown in Figure.7. By adding additive, the strength of samples decreased. From the tensile test results, it is found that, when the concentration of Co/COOH-MWCNTs was 0.012%, the ductility of PC

composites increase in term of higher strain to failure and lower strength. When the concentration added to 0.025%, the ductility of composites was decreased. With the increase of Co/COOH-MWCNTs, carboxyl may connect with polymer matrix which increases the stiffness of PC composites. When the concentration was lower than 0.025%, the ductility was increased by the fibre reinforcing effects. The results provide guidance to strike a balance between optical properties and machineability of the PC composites. The main uncertainties of this measurement are from the micro-cracks generating from the cutting process and the residual micro-bubbles in the samples. The temperature, and skill of operator will also cause uncertainty of this measurement.

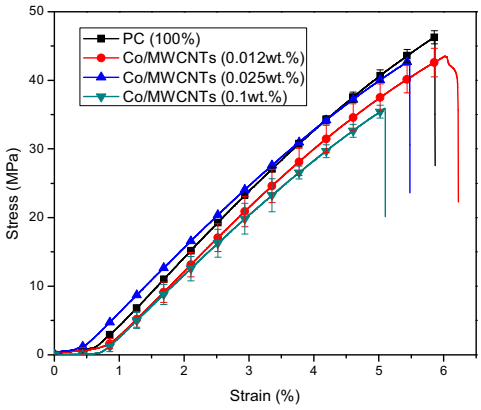

Figure 7. Tensile tests result of different PC composites samples.

Table 1. Tension test results of all PC composites with different Co/COOH-MWCNTs concentration.

Samples	Additive concentration	Strength (MPa)	Error (Standard Deviation)	Strain at failure (%)	Young Modulus (GPa)
PC	0	46.354	0.58	5.86	1.005
PC1	0.012%	43.521	0.94	6.21	0.960
PC2	0.025%	42.856		5.47	0.947
PC4	0.100%	35.920	0.78	5.10	0.908

4. **Conclusions**

This research investigated the effect of additive Co/COOH-MWCNTs, under a magnetic field, the magnetic additive Co/COOH-MWCNTs connect with PC, and in the dilute solution, carboxyl connected connect Co and PC chains, push the movement of PC chains. The additive reduced the strength leading to a better machinability compared with pure PC samples. It is evident that with the increase of concentration of additive, the stiffness of composites increased. When the weight concentration was 0.012%, the ductility of composites increased without a significant decrease in transparency. When the additive concentration increases, the strength of PC decreases with a slight decrease in transparency (about 5%) which is shown in Figure 6. By investigation of microstructure by SEM, it is found that the additive was dispersed well in the PC matrix. By balancing the optical property

and the mechanical property, it provides a useful guide for manufacturing optical devices with enhanced machineability without significant loss of transparency of the PC composites.

5. **Acknowledgement**

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