Carbon Nanotube/Polypropylene Composite Particles for Microwave Welding

Tongfei Wu, Yongzheng Pan, Erjia Liu, Lin Li

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Received 4 August 2011; accepted 17 January 2012
DOI 10.1002/app.36832
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Multiwalled carbon nanotube (MWCNT)/polypropylene (PP) composite particles with various compositions were prepared by mechanical grinding of PP microparticles and MWCNT powders in a mortar at room temperature. Scanning electron microscopy (SEM) revealed that PP particles were coated by MWCNTs, forming a core-shell structure. The electrical resistivity versus temperature behavior of MWCNT/PP composite particles and the changes in phase structures before and after melting were studied. Furthermore, MWCNT/PP composite particles with 4 wt % MWCNT were used to weld PP substrates under microwave irradiation. The effects of the irradiation duration and the compression pressure on the welding strength were examined. Here, we have demonstrated a simple and economic method for polymer welding. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: carbon nanotube; composites; electrical properties; microwave-assisted; welding/joining

INTRODUCTION

The research and development of carbon nanotube (CNT)/polymer composites have been growing extremely rapidly in recent years owing to remarkable properties of CNTs. CNTs theoretically have exceptional mechanical properties such as elastic modulus and strengths of 10–100 times higher than the strongest steel.[1] CNTs also show unique electrical properties and electric-current-carrying capacity of 1000 times higher than copper wire.[2] This combination of electrical and mechanical properties makes CNTs potentially ideal candidates for the preparation of polymer composites with improved mechanical properties and high electrical conductivity. CNT/polymer composites have a multitude of potential applications ranging from ultrastrong materials for bullet-proof vests, flexible displays, and electronic papers. [3] CNTs have already given rise to new industrial products with excellent mechanical properties. For example, sports products, such as tennis racquets and golf clubs containing CNTs, have been produced and marketed. With CNTs becoming easier to produce and cheaper to buy, the CNT industry could potentially overtake that of the carbon fiber industry and become one of the major additives for fabrication of advanced polymer composites. [4]

Besides the remarkable electrical and mechanical properties, several studies have been conducted to investigate the interaction between microwave radiation and CNTs over the past few years. [5–10] It has been found that CNTs could absorb microwave energy to release a large amount of heat. The intense heat release from single-walled CNTs under microwave irradiation leads to temperatures close to 2000°C, as measured by a pyrometer. [11] The term "microwave" refers to electromagnetic radiation with frequencies ranging from about 300 MHz–300 GHz. Indeed, microwave radiation is extensively used in many fields. In materials processing, microwave irradiation (heating) is a well-known process that directly couples electromagnetic energy with a material through molecular interactions, and enables energy dissipation through the release of heat.[12–14] Microwave heating offers several advantages over conventional heating methods such as the use of a remote source, the relatively high speed of the process, and volume- and material-selectivity.[15] Owing to these advantages, microwave processing has received much attention for the sintering of ceramics and the treatment of minerals, among other applications.[16]

Polymer welding is a long-established technology in the thermoplastic industry where the strength of the welded joint can approach to the bulk properties of the adherends. [17,18] Polymer welding techniques have often been classified according to the

Correspondence to: L. Li (mlli@ntu.edu.sg).
Contract grant sponsor: A*STAR SERC, Singapore; contract grant number: 0721010018.

technology used for introducing heat, such as bulk heating, frictional heating, electromagnetic heating, and two-stage techniques. [19–21] Taking the advantages of microwave processing and the vigorous response of CNTs to microwave irradiation, Zhang et al. demonstrated the feasibility for multiwalled carbon nanotubes (MWCNTs) to weld plastic materials under microwave irradiation.[10] Wang et al. devoted their efforts to the microwave heating of MWCNTs for real applications and developed ultrafast microwave welding of MWCNTs and plastic materials such as polycarbonate and polyethylene terephthalate.[9] Furthermore, they prepared a flexible field emitter made of CNTs microwave-welded onto a polymer substrate within a few seconds. [22] Recently, Wang et al. prepared two kinds of core-shell MWCNT/polymer composite particles.[23] One consisting of a UHMWPE core and a MWCNT shell was used for the microwave assisted fast fixation of heavy mineral oil. The other was MWCNT/poly (methylmethacrylate) (MWCNT/PMMA) composite particles, which were used for the formation of MWCNT/PMMA hollow cylinders under microwave irradiation.

Our purpose of this work here is to develop a simple method for welding thermoplastic materials using MWCNTs and microwave irradiation. We prepared MWCNT/polypropylene (MWCNT/PP) composite particles by mechanical grinding of PP particles with MWCNTs and used them as a solder to weld PP substrates. Because of the low loading of MWCNTs and the flexibility of operation, polymer welding based on this method is simple and economic. Before the welding experiments, we characterized the MWCNT/PP composite particles for their morphological properties and electrical conducting behaviors as functions of composition and temperature.

EXPERIMENTAL

Materials

PP with a melt index of 4.0 g/10 min (230°C/2.16 kg) and poly(ethylene glycol) (PEG) with an average M_n of 10,000 g/mol were purchased from Aldrich. MWCNTs were purchased from Iljin Nano Tech (Korea) with a diameter ranging from 10 to 15 nm and a length ranging from 10 to 20 μm and used as received.

Preparation of PP particles

PP particles were prepared by removing the continuous and water solvable phase of PEG from a PEG/PP (80/20 in weight) composite. The PEG/PP (80/20) composite was prepared by melt mixing at 200°C in a HAAKE MiniLab (Thermo Scientific) at a screw speed of 100 rpm. A 100 g of the PEG/PP (80/20) composite was dispersed in 1 L deionized water for 6 h. PP particles were collected using vacuumized filtrating and then air-dried at room temperature for 24 h. PP particles with a size below 38 μm were selected using a sieve (400 mesh).

Preparation of MWCNT/PP composite particles

The solid-state preparation of MWCNT/PP composite particles with different MWCNT contents was carried out in a continuous mechanical mortar at room temperature. To prepare composite particles containing 1 wt % MWCNTs, 0.99 g PP particles with a white color was mixed with 0.01 g MWCNT with a black color in a mortar. By continuously grinding the two powders using a pestle for 60 min, a uniform black powder was obtained, indicating that MWCNTs were uniformly dispersed on the surface of the PP particles. MWCNT/PP composite particles of different compositions are referred to as MWCNT/PP0.25, MWCNT/PP0.5, MWCNT/PP1, MWCNT/PP2, and MWCNT/PP4, where the numbers indicate the weight percentages of MWCNTs in the composite particles.

Characterization and microwave welding

The PP particles and MWCNT/PP composite particles were coated with a thin layer of gold and observed using a scanning electron microscope (SEM, JEOL, JSM-5600LV). Optical images for the phase structure of the MWCNT/PP4 composite were obtained on an optical microscope (Nikon YS100). The samples for electrical test were pill-like with a diameter of 2.5 mm and a thickness of 1.0 mm. Pill-like samples were prepared by compressing under a controlled pressure. A metal/(MWCNT/PP composites)/metal configuration was used to test the volume electrical resistivity by a digital multimeter (Fluke, Fluke 110). The bonding strength of the microwave-welded bonds was examined using a PP/(MWCNT/PP composite particles)/PP configuration. For this test, a dumb-bell shaped PP specimen designed according to ASTM D638 test method was cut at the middle of the narrow neck into two parts with the same size, and used as PP substrate plates. A 5 mg of MWCNT/PP4 was loaded between two PP plates and the plates were pressed together by various weights. Microwave welding was performed in a commercial microwave oven (2.54 GHZ) without any further modification at 850 W for various irradiation durations. The mechanical tests were carried out on a universal testing machine (Instron, INSTRON 5569) at room temperature and with a test speed of 5 mm/min.

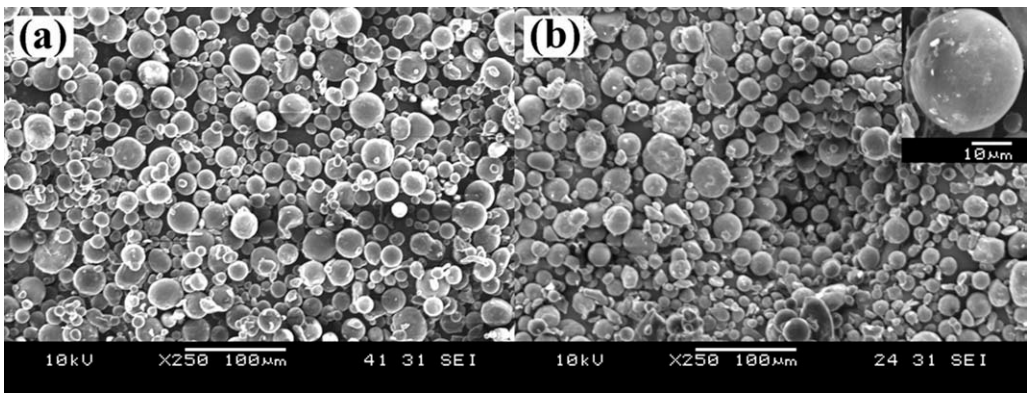

Figure 1 SEM images of PP particles (a) and MWCNT/PP1 composite particles (b).

RESULTS AND DISCUSSION

Microstructure and electrical resistivity of MWCNT/PP composite particles

PP particles were prepared by removing the continuous and water solvable phase of PEG from the PEG/PP (80/20) composite. PP particles with a size below 38 μm were collected using a 400 mesh sieve. Figure 1(a) shows SEM micrographs of typical PP particles. It can be seen that PP particles are spherical with an average size of about 25 μm in diameter. Figure 1(b) shows SEM micrographs of MWCNT/PP1 composite particles, which are significantly different from the neat PP particles. MWCNTs are observed to cover the surface of the PP particles. The similar core-shell structures were also found for MWCNT/PP0.25, MWCNT/PP0.5, MWCNT/PP2, and MWCNT/PP4 composite particles.

Figure 2 shows electrical resistivity of MWCNT/PP composites with various MWCNT contents. From Figure 2(b), it can be seen that the electrical resistivity of MWCNT/PP composites decreased with increasing the compressing pressure, because they became more compact under higher compressing pressure. The electrical resistivity of MWCNT/PP composites decreased slowly with the compressing pressure getting higher. After removing the compressing pressure (30 MPa), compacted pill-like samples were used to test the electrical resistivity of MWCNT/PP composites as a function of the composition, which is shown in Figure 2(a). The electrical resistivity decreased from 10^5 to 10 Ω·cm with increasing the MWCNT content from 0.25 to 4 wt %. Their conducting network is schematically proposed in Figure 4(c). With increasing the MWCNT content, the MWCNT layer on the surface of PP particles would become thicker and the conducting network would become stronger, which contributed to the increase of electrical conductivity.

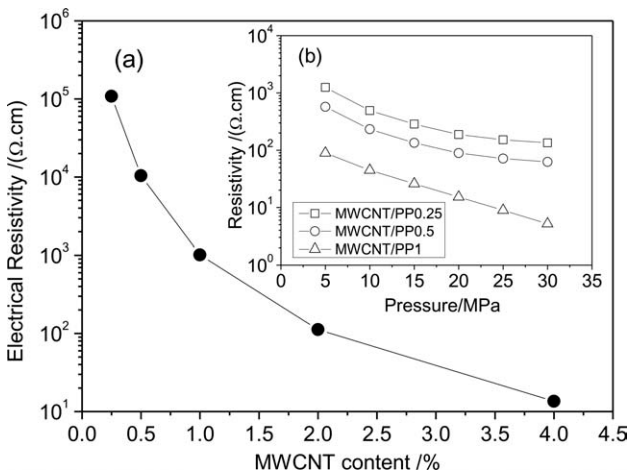

Figure 2 (a) Electrical resistivity of MWCNT/PP composites prepared at 30 MPa and (b) electrical resistivity as a function of the compressing pressure.

Electrical resistivity-temperature behavior of MWCNT/PP composites

Figure 3(a) shows the resistivity of the MWCNT/PP composites as a function of temperature. It can be seen that the electrical resistance of MWCNT/PP1 almost did not change at lower temperatures, but increased shapely at around 165°C before reaching to a plateau at higher temperatures. This resistance transition with a positive temperature coefficient (PTC) was observed for all composite particles with various MWCNT contents of interest. The location of the PTC transition temperature was closely related to the melting point of PP (about 165°C). For the application as a temperature sensor, an essential parameter of the PTC effect is the PTC intensity [$\log(\rho_{200}/\rho_{50})$], which reflects how sensitive and to what extent the resistance response will be after being stimulated by the change of temperature or electrical current. The effect of MWCNT content on the PTC intensity is shown in Figure 3(b). As shown in Figure 3, the PTC intensity increased slightly with increasing the MWCNT content. The very interesting phenomenon is that there is no evidence for

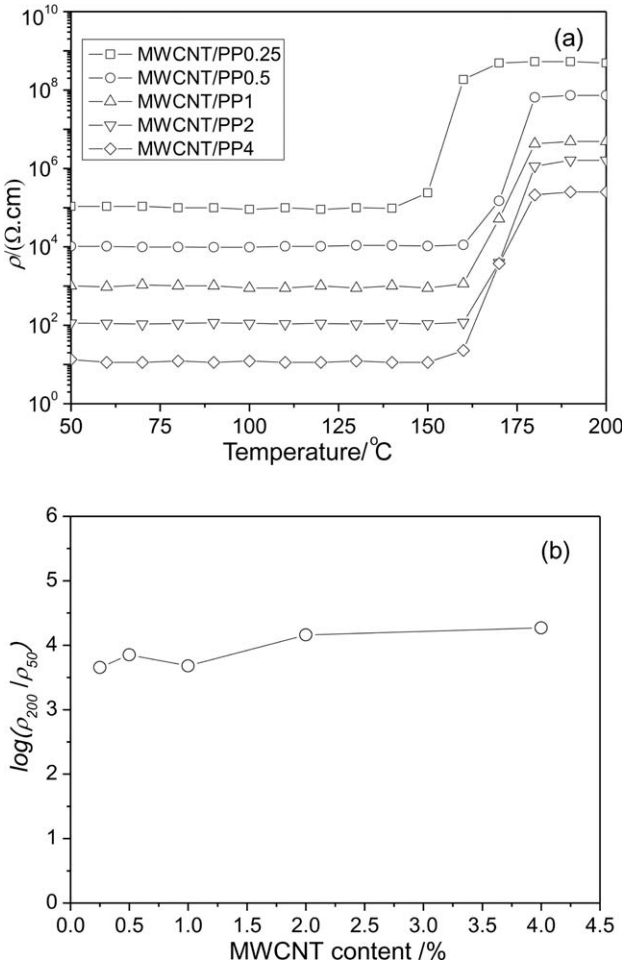

Figure 3 (a) Temperature dependence of electrical resistivity of MWCNT/PP composites and (b) $\log(\rho_{200}/\rho_{50})$ as a function of MWCNT content, where ρ_{200} and ρ_{50} are the resistivity at 200°C and 50°C, respectively.

decreases in the PTC intensity with increasing the MWCNT content, which is common for the conducting particle-filled polymer composites. [24]

As the PTC transition occurs near the melting point of PP particles, the change of the thermal state of PP particles should be responsible for this PTC transition. A PTC transition for a mixture of conducting particles and a polymer matrix usually arises from the difference in the thermal expansion coefficients between the polymer matrix and conducting particles. [25,26] However, the PTC transition of MWCNT/PP composites originates from the unstable conducting network in the PP melt. Figure 4(a,b) shows optical microscope images of MWCNT/PP composite particles (MWCNT/PP4) before and after melting. It can be seen that MWCNTs coated on MWCNT/PP composite particles were dispersed randomly in the PP matrix after melting of PP particles. As illustrated in Figure 4(c), MWCNTs coated on MWCNT/PP composite particles formed a conducting network, which resulted in a lower resistivity below the melting point of PP particles. After melting of PP particles, MWCNT/PP composite particles merged together and the conducting network collapsed, which caused the increase of electrical resistivity and the PTC effect. This process was irreversible.

Microwave welding of MWCNT/PP composite particles

In the section above, we have demonstrated that the phase structure of MWCNT/PP composite particles changed upon heating MWCNT/PP composite particles to a temperature above the melting point of PP and PP particles would merge together. Here, MWCNT/PP composite particles were used as a "solder" (binder) to weld polymer substrates by microwave irradiation. Two PP plates were welded together using MWCNT/PP4 with the aid of microwave irradiation. The bonding strength of the welded PP plates was examined by the mechanical test, as shown in Figure 5. Figure 5(a,b) show the sandwich structure with the configuration PP/(MWCNT/PP composite particles)/PP which was prepared for the tension test.

The effect of the duration of microwave irradiation on the bonding strength has been studied. The power of microwave irradiation and the pressure of compression were kept as 850 W and 4 MPa, respectively. It was found that MWCNT/PP composite particles with the MWCNT content below 4 wt % could not be used as the solder, because the heat released from MWCNTs could not melt PP particles at 850 W within 1 min. The MWCNT/PP4 could not weld two PP plates together at 850 W when the duration of microwave irradiation was less than

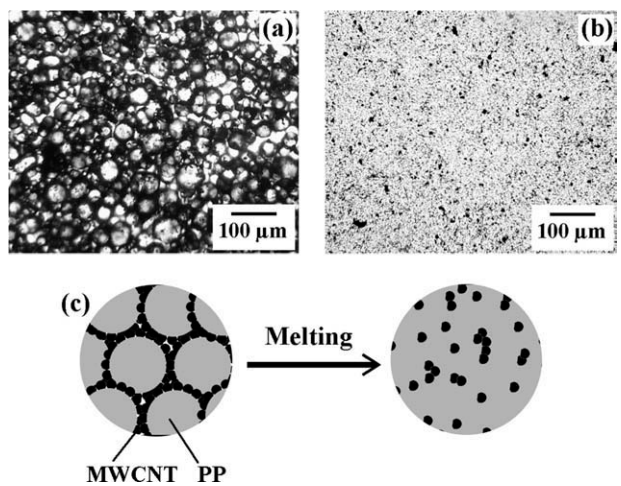

Figure 4 Optical microscope images of MWCNT/PP4 composite particles prepared at 30 MPa before (a) and after (b) melting of PP and (c) a schematic for the PTC transition.

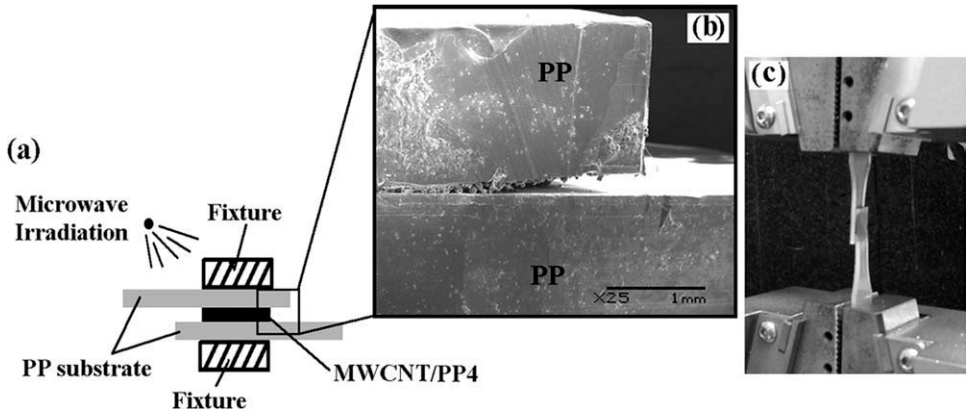

Figure 5 (a) A schematic for microwave welding for a sandwich structures of PP/(MWCNT/PP composite particles)/PP. (b) SEM image of a sandwich structure before microwave irradiation. (c) Photograph of the PP plates welded together by microwave irradiation at 850 W and 4 MPa for 30 s before tension test.

30 s. Figure 6 shows the results of the tension test for sandwich structures that were microwave welded for 30, 40, and 50 s. For the 30 s-welded sample, with increasing the load, a sudden fracture occurred with a tensile strain of about 1% at a load of 85 N, which is used to represent the bonding strength of the welded junction. This bonding results from the intercalation between the surfaces of PP plates and MWCNT/PP composites. With increasing the irradiation duration from 30 to 50 s, the bonding strength increased from 85 to 170 N. It was because those MWCNTs could release more heat within a longer irradiation duration to let more PP be melted at the interfaces between PP plates and the MWCNT/PP composite layer, resulting in a stronger bonding.

It was observed that all the fractures occurred at one of the two interfaces between PP plates and the MWCNT/PP composite layer. The fractured surfaces of MWCNT/PP composite layers are shown in Figure 7. From Figure 7(a), it can be seen that for the 30 s-welded sample, all MWCNT/PP composite particles were melted and most areas of the surface were smooth, which indicated a poor bonding between PP substrate and the MWCNT/PP composite because of the short duration of microwave irradiation. With increasing the irradiation duration, the bonding between PP substrates and the MWCNT/PP composite layer became stronger and the fractured surface became tougher, which was caused by the stronger bonding at the interface. For the 50 s-welded sample, the fracture load reaches a maximum value of 170 N. From the morphology of the fractured joint, there exist cracked regions in the PP plates, as shown in Figure 7(d). This cracking denoted that although the total strength of the sandwich structures was still weaker than that of neat bulk PP samples, the bonding strength between PP substrate and the MWCNT/PP composite layer was close or comparable to the intrinsic strength of the polymer substrates. The effect of the compressing pressure on the bonding strength is shown in Figure 8. The load at fracture for the sandwich structures increased with increasing the compressing pressure. It was true that a higher pressure could force more PP in the MWCNT/PP composite layer to flow after they were melted and improve the intercalation between PP plates and the MWCNT/PP composites.

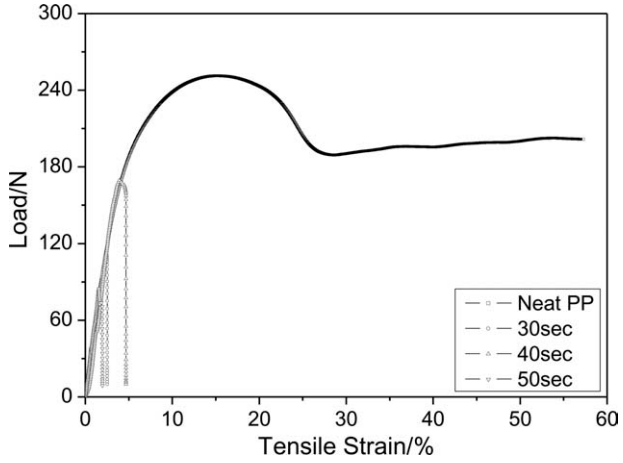

Figure 6 Load-strain curves of the sandwich structures PP/(MWCNT/PP composite particles)/PP microwave welded at 850 W and 4 MPa for various times.

CONCLUSIONS

MWCNT/PP composite particles with various compositions were prepared by mechanical grinding of PP particles and MWCNT powders in a mortar at room temperature. SEM revealed that MWCNTs coated the surface of PP particles, forming a core-shell structure. The electrical resistivity of MWCNT/PP composites obtained by compression under 30 MPa decreased from 10^5 to 10 Ω·cm with increasing

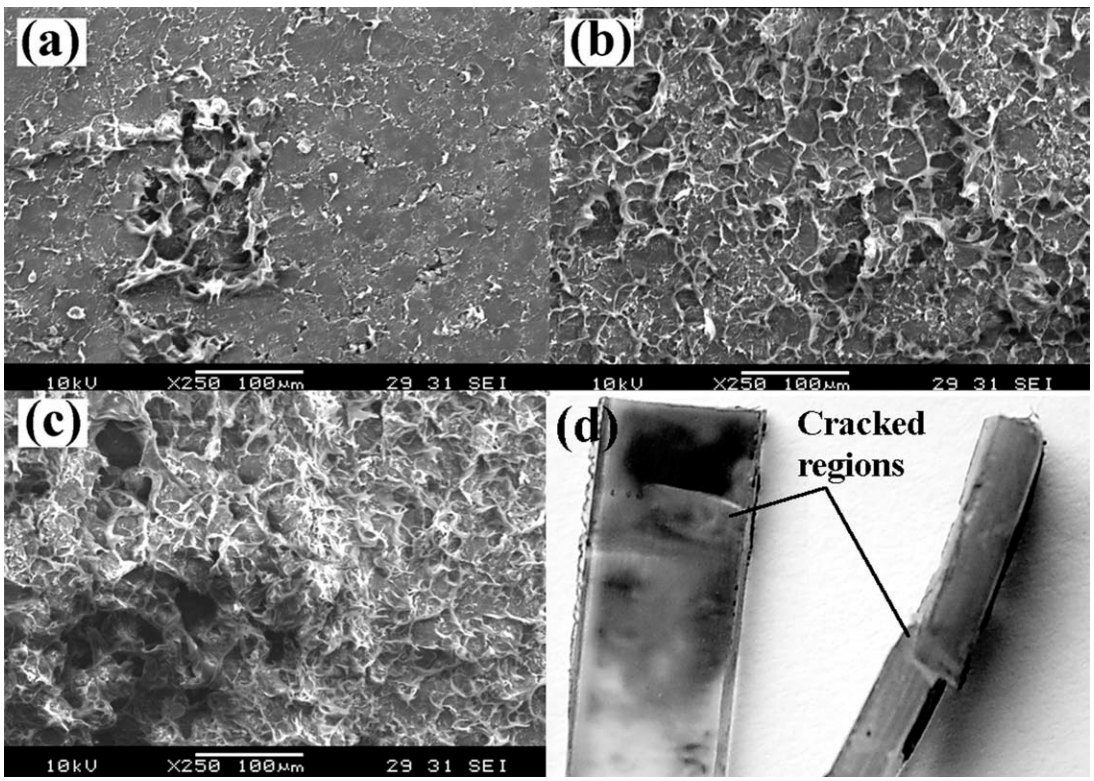

Figure 7 SEM images of fractured surfaces of MWCNT/PP composite layers microwave welded for (a) 30 s, (b) 40 s, (c) 50 s, and (d) photograph of the cracking morphology of the joint of the 50 s-welded sample.

the MWCNT content from 0.25 to 4 wt %. Their conducting network could be ruined during heating to a temperature above the melting point of PP, which resulted in a PTC transition for MWCNT/PP composites. MWCNT/PP composite particles with 4 wt % MWCNT were used to weld PP substrates under microwave irradiation. The effects of the irradiation duration and the compression pressure on the welding quality were examined. It was found that increasing the irradiation duration and the compression force both can improve the bonding strength between PP substrates and the MWCNT/PP composite layer.

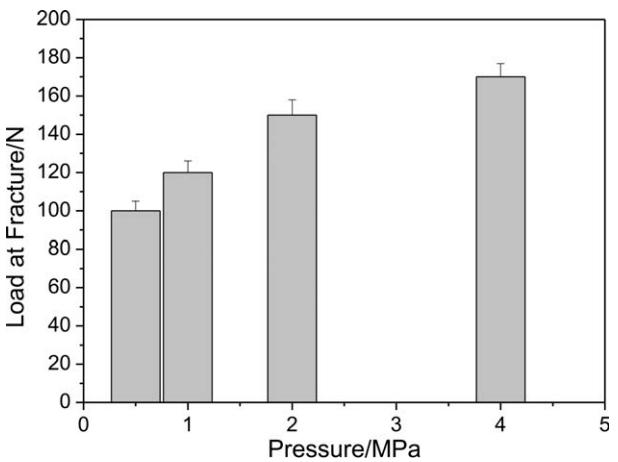

Figure 8 Fracture load of the sandwich structures prepared under various pressures.

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