

VIBRATION WELDING OF CARBON NANOTUBE REINFORCED POLYOXYMETHYLENE: MORPHOLOGY AND MECHANICAL PROPERTY

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Abstract

In the present work, carbon nanotube/polyoxymethylene nanocomposites with different filler loadings were melt-compounded on a co-rotated twin-screw extruder using a masterbatch dilution process. Optical microscopic images of the bulk materials present a good dispersion quality of CNTs even at a high filler loading of 4 vol.%, but some agglomerates on micro-scale can also be observed. The results of the tensile tests demonstrate that the tensile strength of the polyoxymethylene matrix was improved by 7% on the addition of 4 vol.% CNT. The weld strength of the composites was observed to be not significantly impacted by the weld pressures and filler loadings. The weld strength of the nanocomposites with 4 vol.% CNT content welded at 2.0 MPa was 4% higher than the matrix strength. Possible reasons for this high weld strength are discussed based on the morphological investigations.

1. Introduction

As carbon nanotubes (CNTs) were firstly discovered by Iijima in 1991 [1], they have stimulated the development of CNT-filled polymer nanocomposites for a variety of applications according to their outstanding mechanical properties with low density and high thermal as well as electrical conductivity, for instance electrically conducting polymers [2], structural [3] and photovoltaic [4] applications. Their diameters locate in nano-scale, whereas they are up to ten microns long, and can be single- and multi-walled (SWNT and MWNT), respectively. The extremely high aspect ratio and intrinsic properties of CNTs are expected to enhance the reinforcement efficiency at lower filler loadings compared to their competitors, such as carbon black and carbon fibers. The reinforcing efficiency of carbon nanotubes has been found to be strongly dependent on the choice of polymer matrix [5], the type of CNT [6] and particle/matrix interphase [5, 7] as well as processing methods and the corresponding parameters [5, 8]. However, their tendency to agglomerate owing to van der Waals and electrostatic forces makes it challenging to generate good CNT dispersion and distribution in the polymer matrix [9].

CNT/thermoplastic nanocomposites are usually manufactured by using melt compounding process due to its simplicity and adaptability for large-scale industrial production. To achieve optimum dispersion and distribution of CNTs using melt extrusion optimized processing parameters such as screw configuration, screw speed, melt temperature and residence time are imperative. It is commonly accepted that high stress are the ideal scenario for achieving better dispersion state of CNTs in the polymer matrix. Li et al. [10] observed that high shear stress resulted in homogenous MWCNT dispersion in poly(styrene-b-butadiene-co-butylene-b-styrene) (SBBS) matrix, and as a result, much better mechanical properties were obtained. Villmow et al. [11] have reported that an increase in the screw speed from 100 to 500 rpm can lead to better MWCNT dispersions on MWCNT-filled polycaprolactone (PCL) due to higher energy input. Similar observations were also found by Villmow et al. [12] on the examination of the influence of extrusion parameters on masterbatch dilution to manufacture MWCNT/poly(lactic acid) (PLA) composites using a twin-screw extruder.

As advanced materials, CNT reinforced thermoplastics exhibit superior mechanical and thermal properties. However, no information is available on the vibration welding of such materials which is important for designers to construct complex structural assemblies from simpler injection-molded components. Vibration welding is a mechanical welding technique that does not require any external heat sources; it is one of the most commonly used methods to join thermoplastic parts from simpler injection-molded parts to complex assemblies. The two components to be welded are first fixed in the welding fixture and driven together. One part is then vibrated relative to another at designed frequency and amplitude under pressure. Heat is initiated from friction and viscous dissipation that causes the melting of the polymer at the weld interface. The molten polymer is squeezed out under weld pressure. After accomplishing of the target welding time or meltdown the vibration is stopped, and the molten material cools under pressure to form a solid weld. The relative reduction of the displacement is referred to meltdown. According to meltdown, the welding process demonstrated four characteristic regimes: solid fraction, unsteady state of melt generation, quasi-stationary melt generation and the solidification [13]. It was found that the steady state of melt generation was a crucial factor to ensure high weld quality. Without reaching of this regime poor weld strength was obtained, and a further increase in the duration of this steady state had no influence on the weld strength. High welding pressure generally has a negative impact on weld quality [14]. This can be attributed to the thin molten-film resulted unfavorable molecular and fiber orientations parallel to interface at high welding pressure. Other welding parameters such as vibration frequency and amplitude have not been observed to have significant impact on the weld strength. On the vibration welding of thermoplastic-based nanocomposites, Bates et al. [15] have presented that the weld strength of PP significantly decreased on the addition of nano-sized organoclay. Increasing filler content led to a further decrease in the weld strength. According to the authors, this was caused again by the unfavorable alignment and accumulation of organoclay in the weld. However, no work has been reported on the weld strength attainable with CNT reinforced thermoplastics. This work will assess the impact of welding pressure and filler content on the weld quality and morphology of CNT/POM nanocomposites.

2. Experimental

2.1 Materials and sample preparation

POM (ULTRAFORM® N 2320 003) with a density of 1.4 g/cm³ and CNTs filled POM compound (ULTRAFORM® N 2320 C BK120 Q600) with a density of 1.42 g/cm³ that

contained approximately 4 vol.% CNTs were supplied by BASF SE (Ludwigshafen, Germany). All the raw materials were pre-dried at 80 °C for 4 hours before preparation of compounds. In order to investigate the influence of filler loading on the weld quality the composite with 4 vol.% CNTs was diluted to 2 vol.% using a co-rotating twin-screw extruder (TSK-N 030, Theysohn Extrusionstechnik GmbH, Salzgitter, Germany) with a temperature profile as hopper/190/190/195/195/195/195/195/195/195 °C. The screw speed was set at 150 rpm. The 4 vol.% CNT filled masterbatch was re-processed at the same processing conditions to gain the same thermal history. The prepared granulates were then injection molded into sheets with a dimension of 50x50x4 mm³ for welding experiments using an Arburg Allrounder 420 C injection molding machine (Arburg GmbH & Co.Kg., Loßburg, Germany).

2.2 Vibration Welding

Welding of the nanocomposites was performed on a fully automatic Branson Ultraschall Lab.-Vibration welding machine M112H (Dietzenbach, Germany). The sheets were butt-welded along the molded edges, as shown in Figure 1. The weld pressure was varied from 0.4 to 2.0 MPa, while the peak amplitude and vibration frequency were kept at constant values of 0.7 mm and 240 Hz, respectively. All the welding processes were reached the steady state for ensuring the best weld quality according to Schlarb et al. [13]. A special Butt-welded fixture integrated with a force sensor (the details were described in [16]) was used to secure the two sheets to the fixture during welding process. After welding, the welded samples were sawed into sheets with dimensions of 50x50x4 mm³ for preparation of the mechanical testing specimens, and to be ensured that the weld area was in the middle of the sheet.

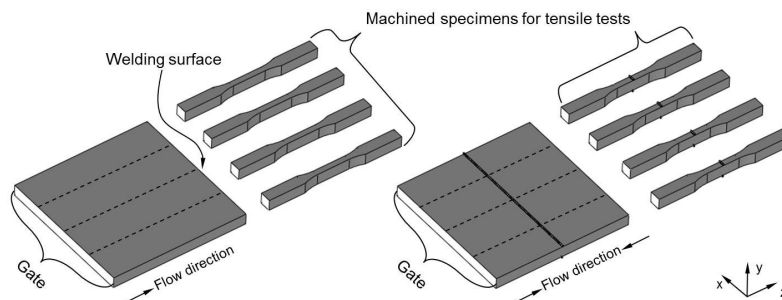


Figure 1. Schematic drawing of test bars from injection molded and welded plaques: (a) injection-molded sheet and (b) the welds.

2.3 Characterization

The dispersion state of CNT nanoparticles in the POM matrix and weld region were investigated using a Nikon ECLIPSE LV100POL optical microscope (Tokyo, Japan) operated in transmission mode. Thin slices with a thickness of approximately 5 µm cut parallel to the injection molding direction on the yz-plane (Figure 1) using a rotary microtome HYRAX M25 (Carl Zeiss MicroImaging GmbH, Göttingen, Germany) were deposited between two transparent, flat glass slides, which were pressed together using an immersion oil (Merck KGaA, Darmstadt, Germany). The images were taken with a micro-cam using a 10x magnification objective lens. Processing of the recorded images was performed with the software MATLAB R2011a corresponding to a total area of ca. 1.2 mm². The area fractions of the CNT agglomerates were calculated using certain thresholds of gray level. The morphology of the welds was analyzed in polarized transmission light using the same optical microscope with a microtomed thin section of about 10 µm. A Focused Ion Beam (FIB)

system (FEI Altura 875 Dualbeam, FEI, Hillsboro, USA) was also employed to assess the fracture surfaces for the welded assemblies. Referring to Figure 1, they were examined in the xy-plane.

For determination of the tensile performances of the bulk materials and different welds, the injection molded and the welded sheets were directly machined to the tensile specimens according to DIN EN ISO 527-2/1BB (dog-bone-shaped specimens with a cross-section of $2 \times 4 \text{ mm}^2$). All the samples were aligned along the flow direction (see Figure 1). The specimens were tested on a universal testing machine (Zwick 1446, Zwick GmbH & Co. KG, Ulm, Germany). The crosshead speed was set at 50 mm/min to determine the tensile properties at room temperature. All the data presented correspond to an average of at least ten measurements.

3. Results and discussions

The morphology of the compounds was examined by transmission optical microscope and the results obtained are presented in Figure 2. As is shown, visible CNT agglomerates with different sizes can be clearly observed in the compounds. The bright holes observed on the thin sections indicate the debonding of the agglomerates during the sample preparation. An increase in the CNT content tends to cause an increase in both the agglomerate counts and area fractions. Increasing filler loading from 2 to 4 vol.% results in an increment of the mean agglomerate area fraction from 0.005 ± 0.003 to 0.007 ± 0.001 . As described above, although an optimized extrusion process was utilized according to Knör et al. [17], there are still potentials to obtain better dispersion state of CNTs in the polymer matrix.

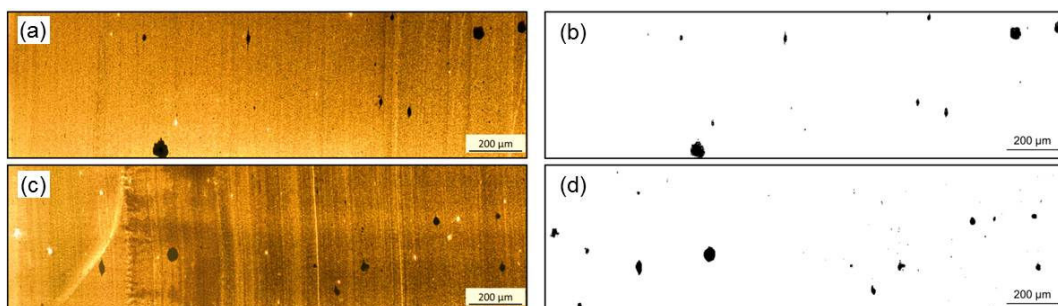


Figure 2. Micrographs of CNT/POM nanocomposites with different filler loadings: (a) and (b) POM filled with 2 vol.% CNT before and after image processing; (c) and (d) POM filled with 4 vol.% CNT before and after image processing.

The mechanical properties of the nanocomposites are mainly dependent on the CNT type, the dispersion state of CNTs in the matrix and the surface modification of nanoparticles as well as the filler loading etc.. In this work, all the materials were used as received; the mechanical performances should be therefore a function of the dispersion state of CNTs and the filler loadings. The tensile properties of non-welded CNT/POM nanocomposites are summarized in Figure 3. It is noticed that the addition of CNTs into polymer matrix leads to an improvement in the tensile strength which is defined as the maximum strength in the stress-strain curve (Figure 3a). The tensile strength of POM increases by approximately 5% on the addition of 2 vol.% CNT. Increasing CNT content further results in improvement in the tensile strength with 4 vol.% filler addition leading to a strength increase by 7%. Since the load bearing capacity of the CNTs strongly depends on the level of their dispersion in the POM matrix, the inherent strength of agglomerated CNTs is clearly not sufficient to create substantial reinforcement. Such studies of slight improvement or deterioration of tensile strength of

CNT-filled polymers were reported very commonly [18]. However, as expected, the addition of carbon nanotubes significantly impairs the ductility of the polymer matrix. As is seen from Figure 3b, a pronounced drop of strain at break was observed as CNT was incorporated into POM matrix. The strain at break of POM decreases by around 60% and 70% on the incorporation of 2 and 4 vol.% CNT, respectively. As is well known that the rigid fillers have contrast effects on the polymer matrix, on one hand, they reinforced the matrix due to their high stiffness and strength, on the other hand, the presence of individual CNT and CNT agglomerates restricts the motion of molecular chains [19, 20], and as a consequence, the ductility of the polymer matrix is decreased.

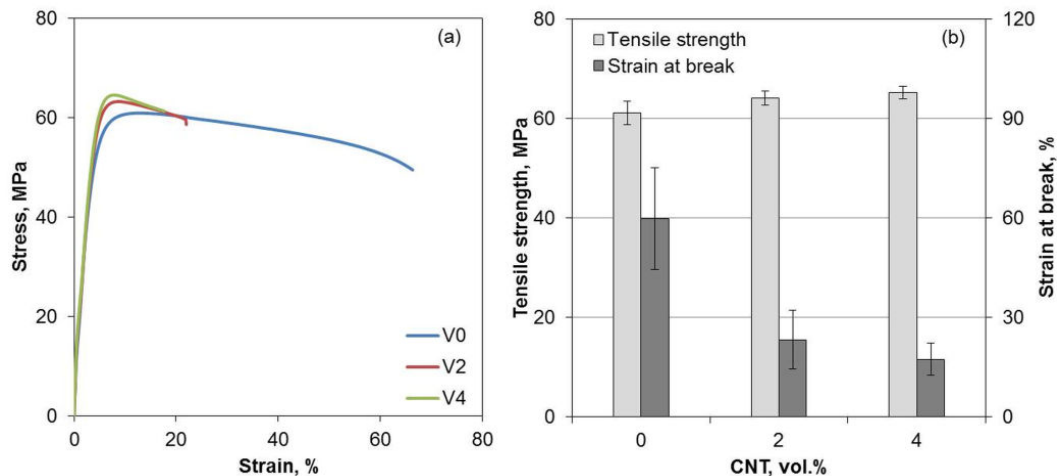


Figure 3. Tensile properties of the bulk materials: (a) stress-strain curves and (b) tensile strength and strain at break.

Concerning the weld strength of the polymer matrix, it is observed from Figure 4a that the weld strength of unreinforced POM welded at 0.4 MPa reaches the matrix strength. Increasing the weld pressure to 2.0 MPa results in a slight lowering of weld strength by about 2.5%. This is consistent with most previous welding studies [14-16] where high pressures were observed to cause lower weld strength of unreinforced thermoplastics. Narrower weld region (Figure 5a and 5c) caused by high weld pressure can be attributed to the impairment of the weld strength. Small weld region restricts the dissipation of the stress imposed during the mechanical testing due to different structure compared to the bulk materials, and therefore reduces the load bearing capacity of the joints. However, when considering the results of the weld strength of the nanocomposites, some interesting results were observed in this work. Both nanocomposites present improved or comparable tensile strength at different weld pressures as comparing the matrix strength. The weld strength of POM filled with 4 vol.% CNT at a weld pressure of 2.0 MPa is 4% higher than the matrix strength. The 64 MPa weld strength obtained with POM filled with 4 vol.% CNT is almost equal to the bulk material strength of dog-bone specimens machined in the same direction. These results are inconsistent with the report on the organoclay (nano-size) reinforced PP compounds [16] where the weld strength of PP was significantly lowered on the incorporation of organoclay. It is also of great interest from Figure 4 to note that the weld strengths of CNT/POM nanocomposites seem to be independent on the weld pressure in the studied range, an increase in weld pressure causes almost no change on the weld strength of POM filled with 2 vol.% CNT and a slight increase in the strength of the POM contained with 4 vol.% CNT. Even though the weld region manufactured at higher weld pressure is thinner than that at low pressure (Figure 5b and 5d), no impairments of weld strength were observed. The strain at break of various welds is present in Figure 4b. As one can see that the welding process leads to a further decrease in the ductility

of the nanocomposites. This drop of the strain at break is usually attributed to the addition of rigid particles into polymer matrix and the increased molecular orientation parallel to the weld induced by the vibration welding process.

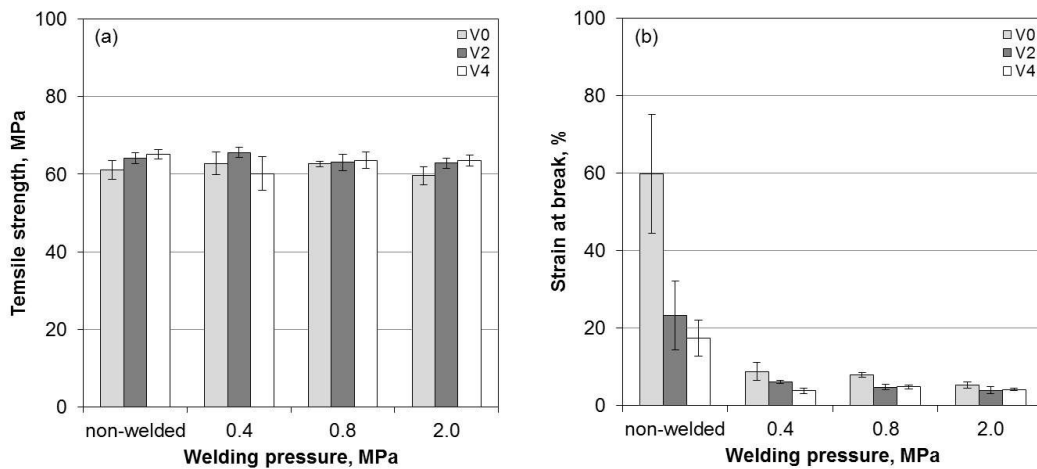


Figure 4. Tensile properties of various welds: (a) tensile strength and (b) strain at break.

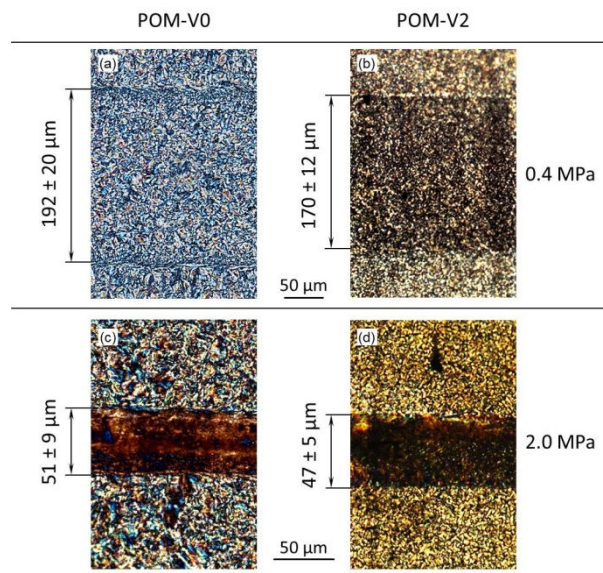


Figure 5. Microstructure of different joints welded at 0.4 MPa and 2.0 MPa.

The high resolution SEM micrograph in Figure 6 shows the weld fracture surface of POM filled with 2 vol.% CNT at a weld pressure of 0.8 MPa in xy-plane. Two different alignments of CNTs can be clearly observed from the fracture surface. Some of the CNTs (marked by A) align parallel to the fracture surface, and some of them are perpendicular to the fracture surface (marked by B) which are also parallel to the tensile testing direction. The perpendicular orientation of individual CNTs may be attributed to the fact that, due to their length and high stiffness, they are harder to align in the weld region during the welding process. This favorable orientation in the testing direction is responsible for the high weld strengths observed with POM nanocomposites owing to the fracture of the CNTs during the mechanical tests. Although the thickness of the weld region and the favorable orientation of CNTs have contrary effect on the weld strength, high weld strengths of CNT nanocomposites in this case point out the fact that the parallel orientation of CNTs in the testing direction plays a dominant rule in effecting weld strength of the nanocomposites.

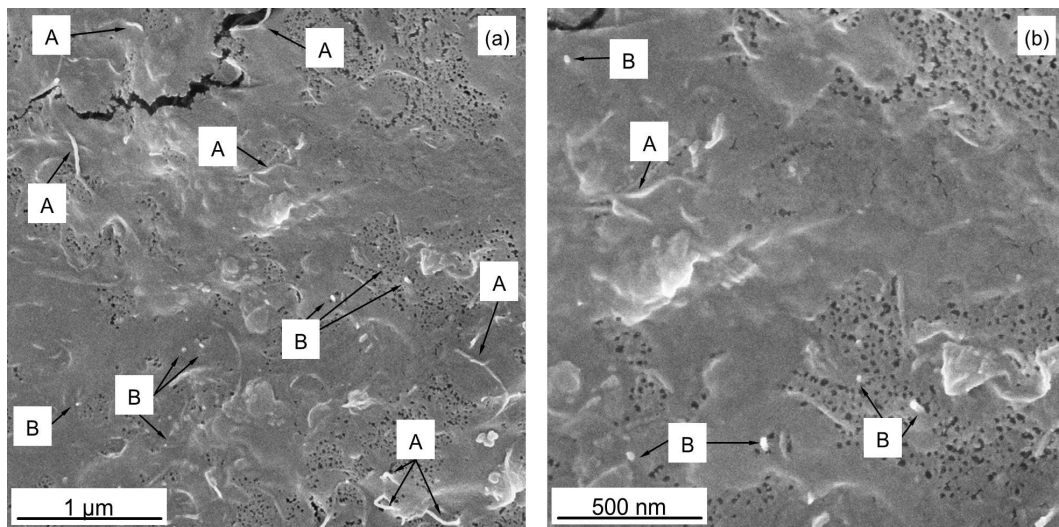


Figure 7. SEM Fractographs of POM filled with 2 vol.% CNTs welded at 0.8 MPa after tensile test with magnifications of (a) 50kX and 100kX (b). Item A indicates the carbon nanotubes parallel to the weld plane and Item B indicates the carbon nanotubes perpendicular to the weld plane, which were fractured during the mechanical test.

Conclusions

The influence of the filler contents and weld pressures on the weld strength and morphology of CNT reinforced POM has been studied. The results of the tensile tests of the non-welded bulk materials indicated that the addition of 4 vol.% CNT into POM matrix caused an improvement in the matrix tensile strength by 7%, and on the other hand, a significant decrease in the matrix ductility. As considering the tensile strength of various welds made of CNT/POM nanocomposites, it was of great interesting to observe that the weld strength of nanocomposites is comparable to the tensile strength of the corresponding bulk materials and slightly higher than that of the polymer matrix in the testing range of weld pressures. The examination of the fracture surface revealed that the high weld quality of CNT reinforced POM can be attributed to the favorable orientation of the partial CNTs in the tensile testing direction.

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