The Manufacture and Mechanical Properties of 5 wt%. MWCNT/Epoxy Composites by Using 2-Aminoethanol Functionalization and Thermal Pre-curing Treatment

D. Abdullah[1,], B. Yahya[1] , H. Judawisastra[1], M. Siswosuwarno[1], M. Karina[2]*

[1]Faculty of Mechanical and Aerospace Engineering, Bandung Institute of Technology (ITB), Indonesia; dawamdullah@yahoo.com
[2]Research Center for Physics, Indonesian Institute of Sciences (LIPI), Indonesia

Abstract. Functionalization with 2-aminoethanol and/or pre-curing) treatment of multi-walled carbon nanotube (MWCNT) were performed in fabrication 5 wt.% MWCNT/epoxy composite. The effect of MWCNT treatment on interfacial properties were investigated by FTIR and SEM. Tensile tester was used to evaluate mechanical properties of composites : tensile strength and modulus of elasticity. FTIR spectrums show an effect of functionalization by a new peak as indication of formation of amin-primer (N-H). However, tensile test yield the result that precuring do a better improvement to the mechanical properties than amin-functionalization. SEM image confirmed these result by less fiber pull-out in the sampel with precuring as an indication of good mechanical properties.

Keywords: MWCNT; composite; functionalization; precuring; mechanical properties

Introduction

Multi-Wall Carbon Nanotube (MWCNT) is an important nano-material due to its structures and properties [1]. MWCNT has an excellent mechanical properties : tensile strength and modulus of elasticity. It was reported that the tensile strength of MWCNT could reach 200 GPa and it’s modulus of elasticity is up to 1.2 TPa [2-6]. Regarding to these properties, MWCNT has a good potential application as a fillers for reinforcing agent of polymer composite.

Many efforts have been done to utilize MWCNT as reinforcement of polymer matrix, especially for thermoset polymers such as epoxy [7-12]. Tensile strength and modulus of elasticity of epoxy tend to be increase when added with MWCNT. Unfortunately, it’s only occured when percent fraction of MWCNT is less than 2 wt.%. The situation is contrary when percent fraction is greater than 2 wt.%. According to the theory “rule of mixture”, the more reinforcement content should be resulted in good mechanical properties. But, the latest report says that it is still difficult to be achieved. So, the effort to add more MWCNT fraction on MWCNT/epoxy composite is still remain a problem.

The rule of mixture theory is derived from the assumption that load transfer between matrix (epoxy) and filler (MWCNT) is perfect (non-slip). However, such condition is difficult to be occured because of quality of interface. Theoretically there are three possibilities of the bond mechanism between polymer and MWCNT. They are micro-mechanical interlocking, chemical bonding and van der walls [13,14]. The most common interaction between MWCNT and epoxy is van der walls bond which is the weakest [14].

This research aimed to improve MWCNT-epoxy interface by amine functionalization and/or thermal precuring. Although several works have reported amine-functionalization of MWCNT, but using 2-aminoethanol as a precursor is still limited. Prolongo et.al. has conducted precuring of MWCNT but still involved low fraction of MWCNT (<0.4 wt %) and limited to the flexural properties evaluation [8]. Thus, our research conducted composite with high fraction of MWCNT (5 wt.%) and evaluation of mechanical properties by tensile testing. In this study, we also conducted combination treatments, functionalization and/or precuring, to investigate correlation of these effects to the mechanical properties of composites.

Experimental

Materials

MWCNT with outer diameter > 50nm was procured from Chengdu Alpha Nano Tech, Co, Ltd. The epoxy resin, Diglicydil Ether of Bhisphenol-A (DGEBA) and Polyamino Amide (PAMAM) as hardener, were from local manufacturer Justus epocshon®. The chemicals that used were 2-aminoethanol (Merck,Co) and Chloroform (Bratachem, Co). The later was as dispersant agent.

Functionalization

MWCNT as received were processed by purification prior to functionalization. The detail of purification is as published in the reference [15]. Functionalization MWCNT with 2-aminoethanol water based solution (1 M) was done at 80^{o}C, for 3 h. Functionalized or non-functionalized–MWCNT were dispersed into chloroform by using ultrasonic homogenizer before manufactured to become composite.

Fabrication of MWCNT/epoxy composites by precuring treatments

Precuring was done before pouring the MWCNT and resin into the compression molding. It was done by following the reference, by holding MWCNT and epoxy at 150°C, for one hour [8]. Then the composites were made by cold-pressing. Mixing of hardener was performed at temperature 100°C of epoxy resin. There were three samples variation that is made: non-functionalized and non-precuring; non-functionalized and precuring; functionalized and precuring sample.

Characterization and Testing

The effect of functionalization was characterized by FTIR (Shimadzu IR Prestige-21). It was used signal of absorbance to measure the intencity. Tensile test is performed by Universal Testing Machine (UTM, Orientec 5 T) to compare mechanical properties of composite samples. Modulus of elasticity was measured by additional apparatus "extensometer". Microscopy with SEM (JEOL) is aimed to reveal the bond condition of interface. It was conducted by magnification untill 30.000 x.

Results and Discussion

FTIR characteristics of amin-treated MWCNT

An FTIR characteristic of amine functionalization is presented in Fig. 1. These figure is consisted of two spectrums: before (blue) and after (orange) 2-aminoethanol functionalization. At blue spectrum, active site is identified as carboxylate group : C-CO (518 cm^{-1}) C-O (941 cm^{-1}; 1080 cm^{-1}) and O-H (2854 cm^{-1}; 2922 cm^{-1}) which are formed due to prior acid-treaments (H_2SO_4/HNO_3) [16,17]. Whereas for orange spectrum, weak intensity at wavenumber 518 cm^{-1} is addressed the annihilation of carboxylate group. On the other hand, the formation of new peak at 1622 cm^{-1} (N-H deformation vibration) is identified as an indication of amine primer as a yield of functionalization by esterification reaction [16,18]. However, there are another peaks which is identified as an alcohol (1072 cm^{-1}; 1165 cm^{-1} and 1382 cm^{-1}) [17]. Probably, it is an hydroxyl (O-H) of 2-aminoethanol which attach to the carboxylate site by secondary bonding. Though, the carboxylate could react to become alcohol by reduction reaction [18]. Alcohol is less reactive to the epoxy resin than carboxylate and amine, so the presence of such active site is unexpected for MWCNT/epoxy interfacial properties.

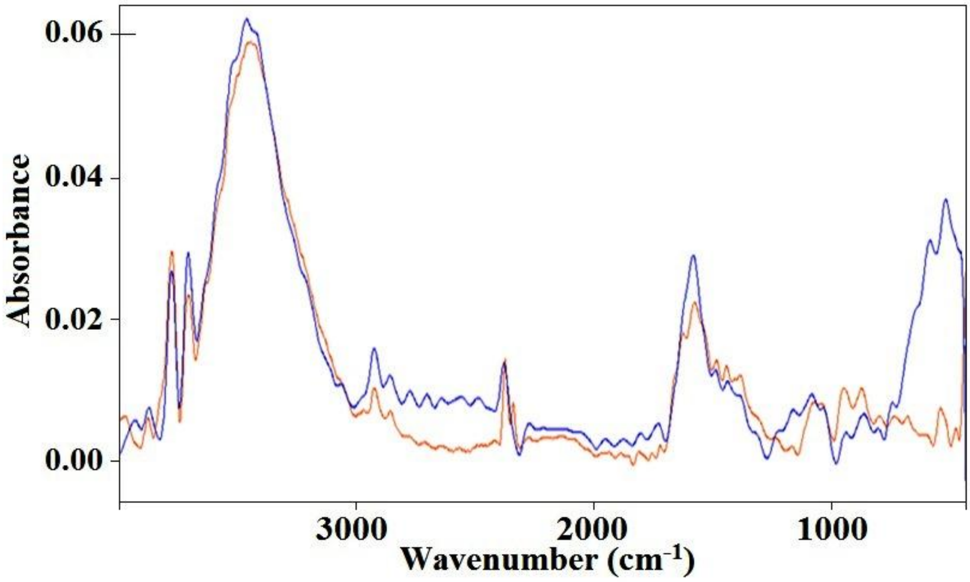

Figure 1. FTIR spectrum of MWCNT, before (blue) and after (orange) 2-aminoethanol functionalization.

Mechanical properties of MWCNT/epoxy composite

Tensile test was conducted to evaluate effect of functionalization and/or thermal precuring treatment of MWCNT/epoxy composite. The results are presented in Table 1. As mentioned in the table, thermal precuring has improved the mechanical properties of composites (modulus elasticity from 27 MPa to 2363 MPa; tensile strength from 2.9 MPa to 2.34.1 MPa). However, mix-treatment (functionalization and precuring) indicated a lower improvement in mechanical properties by value only a half before (modulus elaticity 1363 MPa, tensile strength 16.4 MPa). The result proved that individual precuring treatment was more effective than combined with 2-aminoethanol. These confirmed infrared evaluation as explained above.

Table 1. Mechanical properties of MWCNT/epoxy composites.

Properties	Non-functionalized Non-Precuring	Non-Functionalized Precuring	Functionalized Precuring
Modulus of Elasticity (MPa)	27	2363	1363
Tensile strength (MPa)	2.9	34.1	16.4

Fractography of MWCNT/epoxy composites

Achieving good MWCNT-epoxy interfacial bonding is critical challenge to get excellence mechanical properties especially for structural composite [4]. Good interfacial bonding will provide effective stress transfer among the MWCNT which act as load carrier.

Qualitative evaluation of interfacial strength could be conducted by image analysis such as TEM [4]. However, for this research the MWCNT-epoxy interface evaluation was performed by using SEM image.

Surface fractography of MWCNT/epoxy nanocomposites are presented in Fig. 2. Fiber-like structure is identification of MWCNT, whereas the dark area is identification of epoxy matrix [19]. The thin area surrounding fiber-like structure is called interface [13].

Fig. 2(a), surface fracture of non-functionalized and non-precuring MWCNT/epoxy composite, give the evidence that fiber pullout mechanism which represent the poor interfacial bond has poor-mechanical strength as mentioned in Table 1 [20] . Effect of precuring that caused an increase of mechanical properties is proven by Fig. 2(b) which show mechanism of fracture less fiber pullout. Fig. 2 (c) represent mild pullout which performed better mechanical properties than the first sample.

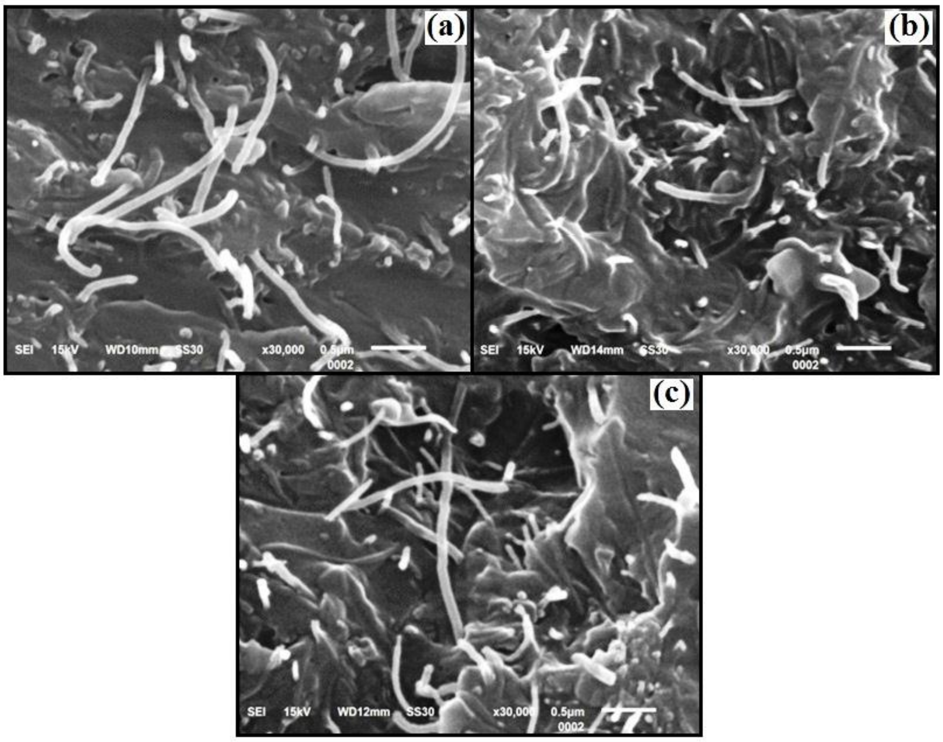

Figure 2. SEM images of surface fracture : (a) non-functionlized & non-precuring ; (b) non-functionalized & precuring ; (c) functionalized & precuring.

Conclusion

Precuring and amine functionalization treatments were succesfully improved the mechanical properties of MWCNT/epoxy composite. Individual precuring exhibited better improvement to the mechanical properties of MWCNT/epoxy composite than combined with 2-aminoethanol. SEM image showed less fiber pullout in the only precuring sample.

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