Thermo-Mechanical Characterization of MWCNTs-Modified Epoxy Resin

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Abstract-An industrial epoxy adhesive used in Carbon Fiber Reinforced Polymer (CFRP) strengthening systems was modified by dispersing multi-walled carbon nanotubes (MWCNTs). Nanocomposites were fabricated using the solvent-assisted dispersion method and ultrasonic mixing. Thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile tests were conducted to study the effect of nanotubes dispersion on the thermal and mechanical properties of the epoxy composite. Experimental results showed a substantial enhancement in the decomposition temperature and tensile properties of epoxy composite, while, the glass transition temperature (Tg) was slightly reduced due to the solvent effect. The morphology of the epoxy nanocomposites was investigated by SEM. It was proved that using solvent improves the nanotubes dispersion. However, at contents higher than 2 wt. %, nanotubes started to re-bundle in the epoxy matrix which negatively affected the final properties of epoxy composite.

Keywords—Carbon Fiber Reinforced Polymer, Epoxy, Multi-Walled Carbon Nanotube, Glass Transition Temperature.

I. INTRODUCTION

EPOXY resins are now extensively used in various industries such as automotive, aerospace, and construction applications, due to their unique characteristics such as high stiffness and adhesion strength and low shrinkage in cure [1], [2]. The epoxy resin used in this study is an industrial adhesive used in the Carbon Fiber Reinforced Polymer (CFRP)-strengthening systems applied on the old or damaged civil structures. CFRP sheets/laminates are attached to the structure using the epoxy adhesive to increase the load resistance of the structure. As a bonding agent, epoxy adhesive has the key role of transferring the applied load to the CFRP layer, meaning that, when the adhesive layer fails to transfer the load, the attached fibers fails to reinforce the structure [1]. Therefore, to have an effective strengthening system, the adhesive layer needs to be modified.

During the last years, tremendous efforts have been made to modify epoxy resins for particular applications in highperformance industries by adding rubbers [3], fillers/nanofillers [4], [5] and also using different mixing facilities like ultrasonic processor [6] or more sophisticated methods such as continuous mixing process [7], resin transfer moulding (RTM) [8], extrusion [9], continuous mixing process, three-role mill [10].

Owning to their exceptional properties, carbon nanotubes (CNTs) are considered ideal reinforcing agents for polymers and they have been widely used to enhance the mechanical, thermal, and electrical properties of epoxy polymers [11]-[13]. Carbon nanotubes are expected to offer major enhancements to the polymer properties by their excellent stiffness and strength, unique thermal stability, and specially, their high surface to volume ratio [11], [14]. Many researchers have observed substantial improvements in the epoxy composite properties as a result of introducing single-walled (SWCNTs) and/or multi-walled carbon nanotubes (MWCNTs) [15]-[17]. Noteworthy to mention that, to take advantage of carbon nanotubes excellent properties, a uniform dispersion of nanotubes in the polymer matrix together with an effectively strong interaction between the tubes and the polymer matrix must be achieved [6], [18], and [19]. There have been various approaches in the literature to meet these two critical issues which could be divided into mechanical approach such as ultrasonic mixing [20], [21] and mechanical stirring [22], [23], and chemical approach via the creation of covalent or noncovalent bond between the nanotubes and the polymer molecules. The non-covalent approach includes the solvent and surfactant-assisted dispersion [14], while the covalent approach includes the surface functionalization of nanotube [6]. Mechanical approach is known to reduce the reinforcing effect of nanotubes by damaging their physical structure [16]. The covalent approach also is reported to retard the mechanical and electrical properties of nanotubes by creating defects on the surface of tubes [6], [24]. However, the noncovalent approach is proved to have no negative effect on the physical and chemical structure of nanotubes [25].

In this study, MWCNTs were infused in epoxy resin using solvent-assisted dispersion method employing the ultrasonic mixing. Ultrasonication has been proved to effectively debundle the nanotube aggregates and uniformly disperse them in the polymer network. Authors have reported improvement in the CNT dispersion in the polymer matrix by using the solvent-assisted dispersion method [26], [27]. Acetone was picked up as a solvent in this study to improve the nanotube dispersion due to its relatively high polarity, compared to THF, and also its low boiling point compared to DMF. The other purpose of using acetone for CNT/epoxy nanocomposite fabrication was to dilute the epoxy resin to reduce the viscosity of the CNT/epoxy mixture, since the epoxy resin used in this study was highly viscous. The effect of solventassisted dispersion of MWCNTs on the properties of epoxy resin was investigated by conducting thermal and mechanical tests. The nanotubes dispersion status in the polymer matrix

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was interpreted by SEM test and the effect of the polymer homogeneity on the thermo-mechanical properties of the resulted epoxy nanocomposites was discussed.

II. EXPERIMENTAL

A. Materials

The epoxy resin used in this study is the commercially available Araldite-420 (Huntsman, Melbourne, Australia) which is a bisphenol A (DGEBA). Araldite-420 is the mostly used resin in construction applications. The Araldite-420 resin used for the experiments had a glass transition temperature (T_g) of ~65°C, a tensile strength of 26.8 MPa, and an elastic modulus of around 1.85 GPa, with the factory-recommended mixing ratio of 100:40.

The multi-walled carbon nanotubes were purchased from NTP Company, Beijing, China. Nanotubes had a diameter range of 90-130nm, length range of 20 to 45 μ m, and special surface area of 100-300 (m²/g). MWCNTs had >95 % purity containing ash content of >0.2 wt%, an amorphous carbon content of >2 wt%. High purity acetone and ethanol were supplied by Sigma Aldrich (Sydney, Australia). Ethanol was used for carbon nanotubes treatment before nanocomposite fabrication.

B. Composite Fabrication

The as-received MWCNTs were left in a high purity (99%) ethanol solution (1:10 concentration) for 2 days in a vacuum chamber to remove the amorphous carbon and deagglomeration of the tubes. After the adequate curing, nanotubes were dried in a vacuum oven for an hour at 80°C and then were cooled down to the ambient temperature in a desiccator to be used for the nanocomposite fabrication. Epoxy nanocomposites were prepared by dispersing specified weight percentage of treated MWCNTs (1%, 2%, and 3%) in acetone and sonicating (VCX-500, Sonic. Vibracell, Newtown, USA) for 15-20min (40 KHz) to get a homogeneous suspension. The next step was the addition of epoxy resin to the mixture and sonicating for another 50min (at 55% energy). Sonication was performed in 30s out of every 50s to prevent increasing the mixture temperature over the limit. Besides, the mixing beaker was submerged in a mixture of ice and water to avoid rise in temperature during sonication and keep it below 55°C. After homogeneously mixing MWCNTs suspension with the resin, mixture was heated on a hot plate for 1h at 65°C to evaporate the solvent followed by degassing in a vacuum oven for at least 4h. After cooling down the mixture to the room temperature in a desiccator, hardener was added and hand-mixing was carried out for 3-5 min. The optimum mixing ratio (resin: hardener) for Araldite-420, to get the maximum degree of curing, is 100:45 which was achieved in the author's previous work [28].

Reference nanocomposites were also prepared without using solvent. The treated multi-walled carbon nanotubes were dispersed directly into the curing agent, since the curing agent had a much lower viscosity than the resin. Sonication was performed for an hour at 55% energy, followed by the addition of epoxy resin and hand-mixing for 3-5 minutes.

After the mixing was finished, nanocomposites were poured into an engraved shaped Teflon mould, designed following the ASTM standard D3039, and were placed on a vibrating table (BTWT, Dynamic Solutions, Polson, USA) for 5min to settle in the mould properly. Finally, samples were cured by placing the moulds in an oven for 3 hours at 60°C. Then, samples were cooled down to the ambient temperature prior to testing.

III. CHARACTERIZATION

A. Scanning Electron Microscopy (SEM)

The micro structural analysis was conducted on the impact cross section of the specimens using SEM machine, Supra 40VP, manufactured by Carl Zeiss (Munich, Germany). The Scanning electron microscopy images were analysed to study the MWCNTs alignment in the epoxy matrix. A comparison was carried out between the images to investigate the effect of solvent and mixing order on the homogeneity of the nanotube dispersion.

B. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were measured using a dynamic mechanical analyser (DMA 2980, TA Instrument, New Castle, US). Cured samples were de-moulded and cut in a form of rectangular to the dimensions of 20mm ×5mm ×2 mm to fit inside the machine. A temperature scan was conducted from ambient to 150°C with a heating ramp rate of 5°C/min. Temperature scans were made using a strain of 0.05%, and a frequency of 1 Hz in a single cantilever mode. Five replications were done for each sample. The loss modulus (E[°]), the storage modulus (E[°]), and the tan δ (E[°]/E[°]) was obtained from the DMA analysis. The T_g was obtained for each sample.

C. Thermogravimetric Analysis (TGA)

Cured epoxy samples were de-moulded and were cut into small pieces (~10mg) to be scanned by the thermo-gravimetric analyzer (SDT 2960 TGA, TA Instruments, New Castle, US). During the analysis, the temperature was increased from ambient to 500°C at a rate of 10°C/min. Nitrogen gas was applied as a purge gas at the flow rate of 20mL/min. The decomposition temperature is achieved from the heat scans, which is the temperature at which the composite starts to decompose. The decomposition temperature is also determined as the maximum temperature range for the differential scanning calorimetry (DSC) analysis for in future experimental works. Five replications were done for each sample

D. Tensile Test

Tensile tests were conducted using a zwickinstron (TEST EQUIP, Ulm, Germany). The cured epoxy samples were demoulded and fixed between the grips with initial separation of 80mm. Specimens were pulled apart at cross head speed of 2 mm/min, using a 10 kN load cell. The tests were carried out at room temperature. Tensile strength and tensile modulus were

achieved using the tensile curves. The area under the tensile curves was also determined as the material toughness. Five replications were performed for each sample.

IV. RESULTS AND DISCUSSION

A. SEM

Fig. 1 shows the SEM image of the reference nanocomposite. A poor distribution of nanotubes in epoxy matrix was observed due to bundling. Owning to the van der Waals forces between the nanotubes, carbon nanotubes tend to create agglomeration in the polymer matrix [13], [24]. The other reason for the nonhomogeneous dispersion of nanotubes could be the extremely high viscosity of epoxy resin which limited the movement of the tubes and prevented the proper distribution of them throughout the network.

SEM images of the nanocomposite fabricated with solvent are given at Fig. 2. According to the Fig. 2 (a), relatively homogeneous distribution of nanotubes (2 wt. %) was achieved as a result of using solvent. Dispersing CNTs into the solvent helped the de-bundling of nanotubes which led to a more uniform dispersion. Besides, adding solvent considerably dropped the viscosity of the system which resulted in the more homogeneous distribution of CNTs in the epoxy resin. Fig. 2 (b) shows the MWCNTs dispersion status in the epoxy system, at a higher level of magnification.



Fig. 1 SEM image of the fracture surface of the reference nanocomposite containing 2 wt. % MWCTs (Mag. 10,000X)

As presented in Fig. 3, at the contents higher than 2 wt. %, nanotubes started tore-bundle, even in case of using solvent. Nanotubes agglomerations will negatively affect the mechanical properties of the polymer by creating empty spaces in the polymer matrix and reducing the density and rigidity of the polymer [12], [29]. The nanotubes aggregates also deteriorate the glass transition behavior of polymer by giving rise to the thermal motions in the polymer matrix [1]. The effect of nanotube dispersion status on the epoxy properties will be further discussed in the following sections.



<u>трт</u> WD = 6 mm

(b)

Fig. 2 SEM images of fracture surface of epoxy nanocomposites prepared with solvent (Mag. 12,000X) (a) S.1 sample containing 2 wt. % MWCTs (b) S.2 sample containing 2 wt. % MWCTs

B. DMA

The DMA plots of the epoxy nanocomposites are illustrated in Figs. 3 and 4. The glass transition temperature is determined from the peak position of tan δ . Fig. 3, shows the DMA diagrams for the reference samples. Adding 1 wt. % of Nanotube did not change the T_g of epoxy resin. While, adding 2 wt. % of nanotubes caused a slight increase the T_g. This was due to the presence of nanotubes in the system. Nanotubes were attached to the matrix molecular chains and limited their motions, which subsequently, increased the Tg of the composite.

Adding 3 wt. % of MWCNTs caused a drop in the T_g . It further proves the fact that with the CNT contents higher than 2 wt. %, nanotubes will agglomerate in the epoxy network. The nanotubes agglomeration creates a large number of empty spaces between the matrix molecules and lead to an increase in the segmental motions in the polymer network, which accordingly, lowers the T_g [23]. Increasing the nanotubes content will increase the number of agglomerations and thus the empty spaces in the polymer network, which results in a lower T_g values.

The other possible reason for the T_g reduction is the fact

that nanotubes bundles attract as many epoxy functional groups as they can in their local vicinity and prevent them from reacting with the amine groups of the hardener during the cure process. This is known as non-stoichiometric balance between the epoxide rings of the resin and hardener amine groups, which could lead to an un-complete cure and reduced glass transition temperature [12], [30].



Fig. 3 DMA diagram of reference CNT/epoxy nanocomposites

DMA plot of the epoxy nanocomposites prepared with solvent is shown in Fig. 4. Adding 1 wt. % and 2 wt. % of MWCNTs to S.1 nanocomposites caused a moderate reduction in the Tg of epoxy composite. This behavior could be explained with the solvent effect. Nanotubes were dispersed into the epoxy matrix and restricted the segmental motions which led to an increase in the Tg. However, the residual amount of the solvent remains in the network, even after long evaporation process. The remaining solvent in the network acts as impurity gives rise to the thermal motions of the molecular segments of the polymer and results in the reduction of glass transition temperature [31]. According to Fig. 4, adding 3 wt. % of MWCNTs dropped the Tg of epoxy resin by ~ 10 °C, compared to the neat epoxy. This huge drop could be explained by the agglomeration of nanotubes and the residual solvent in the network, both of which negatively affect the glass transition behavior of epoxy resin by increasing the thermal motions in the composite matrix.

TABLE I	
TGA RESULTS OF CNT/EPOXY NANOCOMPOSITES	

Sample	Tonset
Neat epoxy	334 ± 0.31
REF1%CNT	337 ± 0.09
Ref 2%CNT	341 ± 0.26
Ref 3%CNT	344 ± 0.18
Solv 1%CNT	344 ± 0.24
Solv 2%CNT	341 ±0.21
Solv 3%CNT	341 ±0.15

REF: Reference epoxy nanocomposites prepared without solvent. Solv: Epoxy nanocomposites prepared with solvent.

 T_{ONSET} denotes the decomposition temperature of the nanocomposite $T = {}^{\circ}C$



Fig. 4 DMA diagram of CNT/epoxy nanocomposites prepared with solvent

C. TGA

Thermogravimetric analysis results are presented in Table I. A slight improvement in the initial decomposition temperature of the reference nanocomposites was observed as a result of introducing MWCNTs. Due to the poor dispersion; nanotubes could not create an effective interaction with the epoxy molecular chains and failed to enhance the network rigidity. Nanotubes reinforced the epoxy system by interacting with the matrix molecular chains. Adding 3% of nanotubes caused a considerable retardation in the thermal behavior of the epoxy composite. This was attributed to the creation of nanotube bundles in the epoxy network which decreased the density of the system by producing empty spaces.

Aconsiderable enhancement in the thermal behavior of epoxy nanocomposites was observed as a result of solvent-assisted infusion of MWCNTs. According to Table I, the initial decomposition temperature of epoxy composite containing 2 wt. % of MWCNTs was heightened by 15° C, compared to the neat epoxy composite. This enhancement was due to the improvement in nanotube dispersion. This led to a stronger interaction between the nanotubes and matrix molecules and led to a highly rigid network.

The addition of 3wt. % of nanotubes to the epoxy resin dropped its decomposition temperature to 324°C. This was attributed to the agglomeration of nanotubes due to the high content, as well as the residual amount of solvent remaining in the system, both of which decreased the network density. This led to the decomposition of the epoxy composite at a lower temperature.

D. Tensile

The stress-strain curves of the CNT/epoxy composites are demonstrated in Figs. 5 and 6. The tensile strength of epoxy composites was enhanced by nanotubes dispersion. When nanotubes are dispersed in the polymer matrix, they attract the molecular segments with their high active surface area and create a large number of CNT/polymer films which act as reinforcements [12]. In this way, nanotubes prevent the crack propagation through the polymer network and enhance the tensile strength of the composite. Fig. 5 shows the stress-strain diagrams of the reference composites. The tensile strength was increased from 26.8 MPa for neat epoxy to 30.9 MPa for the reference nanocomposite containing 2 wt. % of MWCNTs. While, by adding 3 wt. % of nanotubes, the composite strength was dropped to 25.7 MPa. It was due to the aggregation of nanotubes which eased the crack propagation through the system. Another possible reason is the stress concentration in the agglomeration areas which initiates crack in the composite system.



Fig. 5Tensile diagrams ofreference epoxy nanocomposites

According to the Fig. 6, solvent-assisted dispersion of nanotubes increased the tensile properties of the epoxy resin. Adding 3% of nanotubes increased the tensile strength of epoxy composite by \sim 26%. This was due to the more uniform dispersion of nanotubes, compared to reference nanocomposite.



Fig. 6 Tensile diagrams of epoxy nanocomposites prepared with solvent

V.CONCLUSION

Epoxy composite was modified by infusing multi-walled carbon nanotubes, with and without solvent. It was proved that using solvent improves the morphology of the CNT/epoxy system by uniformly dispersing the nanotubes into the epoxy matrix. This led to a substantial improvement in mechanical properties of the epoxy composite. Adding 2 wt. % of MWCNTs to the epoxy resin using solvent-assisted dispersion method increased the tensile strength by 26%. Thermal decomposition temperature was also improved due to the reinforcing role of nanotubes in the polymer matrix. However, the glass transition temperature was either reduced or remained unchanged. While dispersing 2 wt. % of MWCNTs without using solvent increased the Tg of epoxy due to the presence of nanotubes in the system. Two mechanisms were competing to affect the Tg (a) the residual solvent in the system acting as impurity and giving rise to the thermal motions in the matrix and (b) carbon nanotubes limiting the segmental motions in the matrix by strongly attaching to the molecular chains of the polymer. Improving the thermal properties as well as maintaining the achieved enhancements in the mechanical properties is the author's future work.

REFERENCES

- O. Sindt, "Molecular architecture mechanical behaviour relationships in epoxy networks," *Polymer*, vol. 37(14), pp. 2989-2997, 1996.
- [2] O. Buyukozturk, "Progress on understanding debonding problems in reinforced concrete and steel members strengthened using FRP composites," *Construction and Building Materials*, vol. 18(1), pp. 9-19, 2004.
- [3] N. Chikhi, "Modification of epoxy resin using reactive liquid (ATBN) rubber," *European Polymer Journal*, vol. 38(2), pp. 251-264, 2002.
- [4] M. Harsch, "Influence of fillers and additives on the cure kinetics of an epoxy/anhydride resin," *European Polymer Journal*, vol. 43(4), pp. 1168-1178, 2007.
- [5] S. Saber-Samandari, "An experimental study on clay/epoxy nanocomposites produced in a centrifuge," *Composites Part B-Engineering*, vol. 38 (1), pp. 102-107, 2007.
- [6] L. Guadagno, "Effect of functionalization on the thermo-mechanical and electrical behavior of multi-wall carbon nanotube/epoxy composites," *Carbon*, vol. 49(6), pp. 1919-1930, 2011.
- [7] G. Subramanian, "Preparation of SWNT-reinforced composites by a continuous mixing process," *Nanotechnology*, Vol. 16(6), pp. 836-840, 2005.
- [8] Q.F. Cheng, "Carbon nanotube/epoxy composites fabricated by resin transfer molding," *Carbon*, vol. 48(1), pp. 260-266, 2010.
- [9] M. Abdalla, "Cure behavior of epoxy/MWCNT nanocomposites: The effect of nanotube surface modification," *Polymer*, vol. 49(15), pp. 3310-3317, 2008.
- [10] L.C. Tang, "Fracture mechanisms of epoxy filled with ozone functionalized multi-wall carbon nanotubes," *Composites Science and Technology*, Vol. 72(1), pp. 7-13, 2011.
- [11] J.D. Fidelus, "Thermo-mechanical properties of randomly oriented carbon/epoxy nanocomposites," *Composites Part a-Applied Science and Manufacturing*, vol. 36(11), pp. 1555-1561, 2005.
- [12] J.F. Shen, "The reinforcement role of different amino-functionalized multi-walled carbon nanotubes in epoxy nanocomposites," *Composites Science and Technology*, vol. 67(15-16), pp. 3041-3050, 2007.
- [13] E. Ivanov, "Effects of Processing Conditions on Rheological, Thermal, and Electrical Properties of Multiwall Carbon Nanotube/Epoxy Resin Composites," *Journal of Polymer Science Part B-Polymer Physics*, vol. 49(6), pp. 431-442, 2011.
- [14] Y.H. Liao, "Investigation of the dispersion process of SWNTs/SC-15 epoxy resin nanocomposites," *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, vol. 385(1-2), pp. 175-181, 2004.

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- [15] Y.X. Zhou, "Experimental study on the thermal and mechanical properties of multi-walled carbon nanotube-reinforced epoxy," *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, vol. 452, pp. 657-664, 2007.
- [16] K.Q. Xiao, "Effective separation and alignment of long entangled carbon nanotubes in epoxy," *Journal of Materials Science*, vol. 40(24), pp. 6513-6516, 2005.
- [17] Q.P. Feng, "Synthesis of epoxy composites with high carbon nanotube loading and effects of tubular and wavy morphology on composite strength and modulus," *Polymer*, vol. 52(26), pp. 6037-6045, 2011.
- [18] H. Miyagawa, "Thermo-physical and impact properties of epoxy nanocomposites reinforced by single-wall carbon nanotubes," *Polymer*, vol 45(15), pp. 5163-5170, 2004.
 [19] M. Dehghan, "Effect of fabrication methods on the glass transition
- [19] M. Dehghan, "Effect of fabrication methods on the glass transition temperature of CNT/Epoxy composites: state-of-the-art review," in Proc. 6th Int Comp Conf (ACUN-6), Melbourne, 2011.
- [20] M. Kim, "Processing, characterization, and modeling of carbon nanotube-reinforced multiscale composites," *Composites Science and Technology*, vol. 69(3-4), pp. 335-342, 2009.
- [21] D. Puglia, "Effects of single-walled carbon nanotube incorporation on the cure reaction of epoxy resin and its detection by Raman spectroscopy," *Diamond and Related Materials*, vol. 12(3-7), pp. 827-832, 2003.
- [22] L.J. Ci, "The reinforcement role of carbon nanotubes in epoxy composites with different matrix stiffness." Composites Science and Technology, vol. 66(3-4), pp. 599-603, 2006.
 [23] K.W. Putz, "Effect of cross-link density on interphase creation in
- [23] K.W. Putz, "Effect of cross-link density on interphase creation in polymer nanocomposites," *Macromolecules*, vol. 41(18), pp. 6752-6756, 2008.
- [24] C. Park, "Dispersion of single wall carbon nanotubes by in situ polymerization under sonication," *Chemical Physics Letters*, vol. 364(3-4), pp. 303-308, 2002.
- [25] S. Ghorabi, "Effects of three surfactant types of anionic, cationic and non-ionic on tensile properties and fracture surface morphology of epoxy/MWCNT nanocomposites," *Iranian Polymer Journal*, vol. 21(2), pp. 121-130, 2012.
- [26] S. Prolongo, "Effects of dispersion techniques of carbon nanofibers on the thermo-physical properties of epoxy nanocomposites," *Composites Science and Technology*, vol. 68(13), pp. 2722-2730, 2008.
- [27] A. Montazeri, "Viscoelastic properties of multi-walled carbon nanotube/epoxy composites using two different curing cycles," *Materials & Design*, vol. 31(7), pp. 3383-3388, 2010.
- [28] M. Dehghan, "Effect of Fabrication Method on Thermo-mechanical Properties of an Epoxy Composite," *The Journal of Adhesion*, 2013.
- [29] Y. Zhou, "Fabrication and characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes," *Materials Science and Engineering A*, vol. 475(1), pp. 157-165, 2008.
- [30] H. Faleh, "Fabrication and Characterization of Nano-Particles-Enhanced Epox," *Composites Part B: Engineering*, 2012.
- [31] A. Allaoui, "How carbon nanotubes affect the cure kinetics and glass transition temperature of their epoxy composites? - A review," *Express Polymer Letters*, vol. 3(9), pp. 588-594, 2009.