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Development of Fine-Celled Wood Fiber/PVC Composite Foams Using Multi-Walled Carbon Nanotubes

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Abstract: Recently, foaming wood plastic composites and using nano particles to form good foam cellular structures, has been considered by the researchers. In this study, Multi-Walled Carbon Nanotubes ($MWCNT_s$) were compounded with PVC, wood-flour and foaming agent in an internal mixer. Different levels of wood flour (40, 50, 60 phr), CNT (0, 1, 2 phr) and chemical foaming agent (0, 3, 6 phr) were considered. The samples were foamed via batch process using a compression molding machine at 180° C. Morphology, density and flexural properties of foamed were evaluated as a function of wood flour, CNT and chemical foaming agent contents. The experimental results indicated that, in the presence of CNT the cell density increased and the cell size decreased. When the wood flour content increased to more than 50 phr, the foam morphology and properties were destructed and the effect of CNT as the nucleating agents was not significant. Density of the foamed nano composites were not affected by chemical foaming agent contents. At the constant chemical foaming agent content, addition of CNTs to wood plastic foams led to more density reduction. The results revealed that the addition of CNTs led to the increase of the flexural strength and modulus of foamed nanocomposite up to 16% and 13% respectively.

Key words: Composite · Nano · Foam · Multi-Walled Carbon Nanotube · Wood flour

INTRODUCTION

The use of wood-flour (WF) as a filler and reinforcement in thermoplastic has been gaining acceptance in applications such as building, automotive and decking [1-4]. But wood plastic potential for use in many industrial applications has been limited because of their lower impact resistance and mainly higher density compared to neat plastics [5-7]. Creating a foam-like structure by chemical blowing agents in wood plastic composites (WPCs) can decrease their density, improve their specific mechanical properties and reduced material cost [8, 9]. There are however, several major challenges that remain in foamed wood plastic composite field that need to be solved. WPCs typically contain 30-70 wt% wood-flour. WPC foam manufacturers tend to keep the WF content as high as possible to obtain maximum reduction in material costs. Since chemical blowing agents have relatively high decomposition temperatures, WF will release volatiles under high processing temperature [10, 11]. Also high wood content usually increases melt viscosity and makes it difficult to distribute WFs uniformly in the polymer matrix. In order to minimize melt viscosity, the processing temperature should be kept to a maximum rate. But during high-temperature foaming process, WFs releases volatiles, which lead to deterioration of the cell structure of WPC foams [5, 15]. Today, research interest has shifted to producing foams with a smaller cell size and a higher cell density [13]. It was observed that the addition of nano particles generally decreases the cell size and increases the cell density; therefore facilitates the foam expansion [14].

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The presence of nano particles may enhance mechanical and physical properties of wood-polymer composites via the improvement of nucleation sites in WPCs, during the foaming process. Due to extremely small particle size, it is possible to generate a large number of nucleants with a relatively low particle loading [15]. Because of high flexibility, low mass density, large aspect ratio, high tensile modulus and great strength of carbon nanotubes (CNTs), these nano particles are the most promising candidates for the design of novel ultra high strength wood polymer composite foams [16, 17]. However the effect of CNTs on morphology improvement of WPC foams is closely related to their distribution in WF and polymer interface. In addition to the challenges which previously mentioned about the using high wood flours in WPC foams, increasing the wood content may affect the nucleating effect of CNTs in WPC foams.

Study the effect of adding wood-flours at different concentrations on the morphology and properties of the wood flour/PVC nano composites was the scope of this study. Investigating the effect of adding chemical foaming agents (CFA) and CNTs with different concentrations on the foam density, cell size and cell density of the wood/PVC composites was the other object of present study. Flexural properties of nano composites at different WF concentrations were evaluated and compared with the nano composite foams without CNTs.

MATERIALS AND METHODS

The polymer matrix used in this study was PVC with a K value of 66, (supplied by Bandare Imam company). Commercial wood flour of populus (70 mesh-sized) (Aria cellulose Co.) was used as a filler. The exothermic chemical foaming agent Azodicarbon amide (Anhui Huishang Co.) was used to foam WPCs. The multi-walled carbon Nanotube used in this study was supplied by Iran Research Institute of Petroleum Industry (RIPI). The outer and inner diameter of the MWCNTs were about 10 and 3.5 nm respectively and purity was 95 wt%.

The heat stabilizer (tin-based) was from Hammond group Inc. with Plasti stab trade name and Paraloid k-150 from Rohm and Haas Company was used as processing aid in the samples. Zinc oxide (from Tianjin First Chemical Co.) was used as a catalyst (kicker) to decrease the decomposition temperature of CFA. Its Content was fixed at 1.5 phr of chemical foaming agent content in each treatment. Formulations of samples are depicted in table 1. As can be seen the concentration of chemical foaming agent and CNT are 0, 3, 6 and 0, 1, 2 respectively. Wood flours varied from 40 to 60 phr.

Table 1: Formulations used for foamed and unfoamed composites

Ingredients	Concentrations (phr)
PVC	100
Tin-based heat stabilizer	2
Processing aid	5
Wood flour	40, 50, 60
Chemical foaming agents	0, 3, 6
Multi walled carbon nanotube	0, 1, 2

Sample Preparation: The oven-dried wood flour (at 105° C for 24h) was dry blended with the PVC, Zno and other additives listed in table 1 (except the CFAand CNTs) in a turbo mixer (Kim Engineering Machine Co.) for 5 mins. The above formulations were then mixed in 45 ml-electrically-heated-internal mixer (Brabender Plasti Corder Co.) with roller style mixing blades. The temperature of internal mixer was fixed at 150°C, below the decomposition temperature of CFA, throughout the experiments. Internal rotor speed was 60 rpm and a 5-kg dead weight was put on the top of the ram. Mixing of wood flour and rigid PVC and ingredients was started in internal mixer in order to follow the fusion curve. Melting started and after two minutes when the material reached a void free state and equilibrium torque was reached, CNTs were added to internal mixer. Mixing process continued and after 1 min (third minute of mixing), CFA was added to internal mixer. The mixing process took 7 minutes. The similar procedure has been reported by Faruk *et al.* for the preparation of PVC/CNT nano composites [18]. Melted mixtures of internal mixer at different treatments were put into a mold and then were compression-molded (Toyo Seiki Press) into test samples at 180°C and 25MPa constant pressure for 15 minutes. After 15 minutes, press temperature reduced to a degree below 100°C by circulating water around the press plates. After the cooling procedure, pressure released to the atmospheric pressure to induce a sudden thermodynamic instability in polymer/gas solution and the foams were formed.

Determinations: Foam morphology (cell size andcell density) was characterized using scanning electron microscopy (SEM, LEO Oxford). Nano composite foams were freeze-fractured in liquid nitrogen and the fracture surface was Sputter-coated with gold. The SEM pictures were analyzed by Corel DRAW software (version 12) to determine cell size and cell density.

Cell density (number of cells per cm^3), N_f can be expressed by Eq (1) [19]:

$$N_f = (nM^2/A)^{3/2} \quad (1)$$

Where A is the area (cm^2) of SEM micrograph, M is the magnification factor and n is the number of cells in the SEM micrograph. The densities of foamed and un-foamed composites were determined by averaging the mass/volume. Measurement results of five specimens per sample were obtained following the procedure described in ASTM-D 1622-98. Flexural tests were performed on a Zwick Z250 testing machine equipped with a computer according to ASTM standard method D-790. Statistical analysis was conducted using SPSS programming (version 12) method in conjunction with the analysis of variance (ANOVA) techniques. Duncan multiple range test (DMRT) was used to test the statistical significance $\alpha = 0.05$ level.

RESULTS AND DISCUSSION

To interpret of the results, it is useful to start by expressing the foam morphology. Typical SEM micrographs of wood flour/PVC composites without CNT are demonstrated in Fig. 1.

These figures show the effect of wood fiber content and chemical foaming agent on cell morphology of the samples. It was observed that in the composites contain more than 50 phr WFs, the cell morphology deteriorated. Table 2 shows the cell size and cell density of the samples.

Table 2: Cell size and cell density of rigid PVC/wood flour composite foams

Formulation(phr)	Cell Size (μm)	Average Cell Density (cell/cm^3)
40WF/0 CNT/3 CFA	11.01	1.1×10^7
40WF/0CNT/6 CFA	14.36	1.76×10^7
50WF/0CNT/3 CFA	10.1	1.9×10^7
50WF/0CNT/6 CFA	13.5	2×10^7
60WF/0CNT/3 CFA	16	6.9×10^6
60WF/0CNT/6 CFA	16.61	8.5×10^6

It is clear that at constant CFA concentration, with increase of wood flour content up to 50 phr cell size decreased and cell density increased. When the wood flour content increased to 60 phr, cell density decreased and cell size increased. It seems that when WF in composites increased to 60 phr, PVC matrix was significantly decreased. The more reduction of polymer probably resulted in somewhat vigorous cell coalescence, which increased the cell size and decreased the cell density. In other words, the presence of higher wood fiber ruptured the plastic matrix and deteriorated the cell morphology of the composite foams. At 6 phr CFA, gas concentration was enough to bubble growth, therefore the cell size increased and in some regions cell coalescence happened (Fig. 1b).

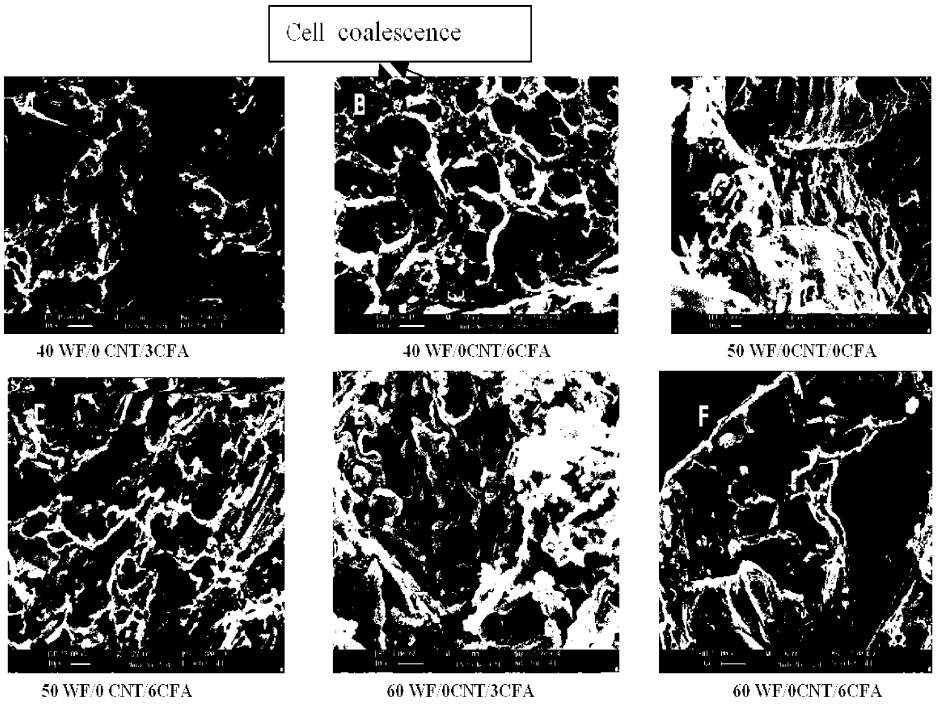

Fig. 1: SEM micrographs of foamed composites without CNT at different AZDC content.

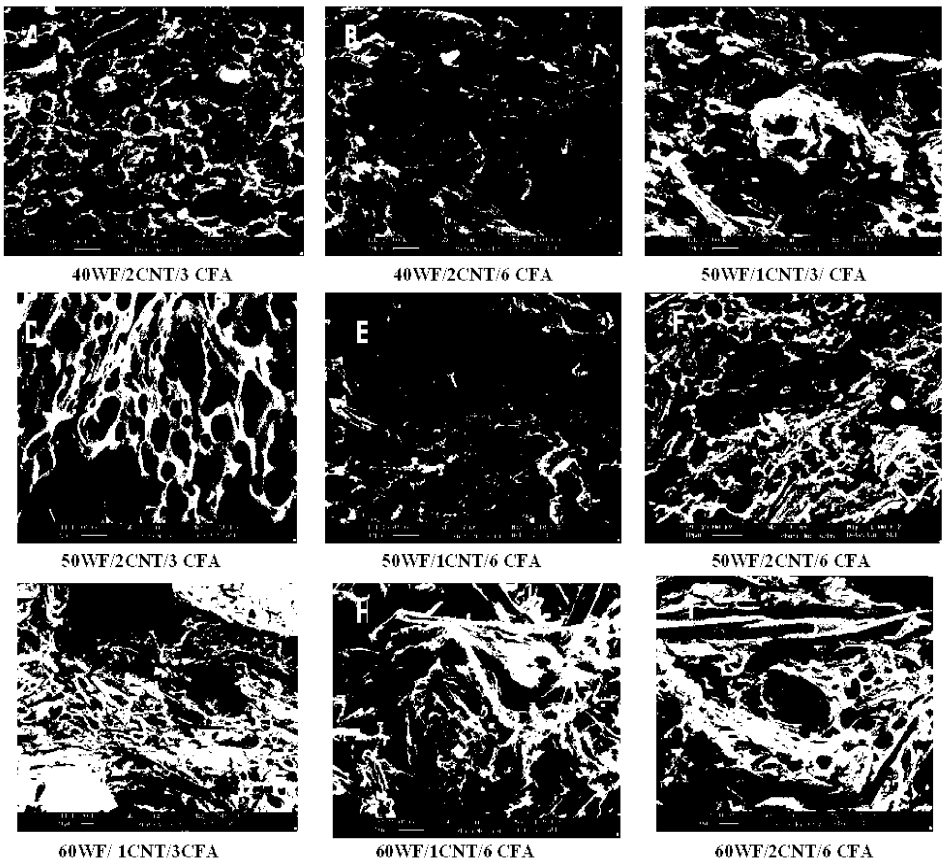

Fig. 2: SEM micrographs of foamed nanocomposites at different CNT and CFA content.

Figure 2 shows the morphology and the cell structures of wood/plastic nano composites as a function of CNT content. It was observed that the addition of CNT facilitated the foam expansion and improved the cell morphology. However, the content of the wood fibers strongly affected the distribution and nucleating effect of CNTs.

It was observed that the cell morphology of nanocomposites above the 60 phr WF, was visibly irregular and dispersed. The interfacial regions between the WF and polymer at this WF concentration were not completely wetted and this may affect the uniform gas and nano particles distribution. During processing, the WF typically, experiences the following changes: evaporation of volatile substance (95°-150°C or higher), superficial carbonization and slow exit of flammable gases (150°-200°) [20]. Also the amount of volatiles released from WFs is influenced by both wood flour content and the exposure time at the foaming temperature. Both incomplete wetting of wood flours by polymer and long exposure time at 180°C (15 min) may cause the release of volatiles from WFs and consequently deteriorated the cell structures.

Table 3: Cell size and cell density of foamed nanocomposites.

Formulation(phr)	Cell Size (μm)	Average Cell Density (cell/cm^3)
40% WF/1% CNT/3% AZDC	10	2.19×10^7
40% WF /1%CNT/6%AZDC	11.5	3.3×10^7
40% WF /2%CNT/3%AZDC	7.5	2.52×10^8
40% WF /2%CNT/6%AZDC	10	5.7×10^7
50% WF /1%CNT/3%AZDC	8.5	3.5×10^7
50% WF /1%CNT/6%AZDC	10.1	2.7×10^7
50% WF /2%CNT/3%AZDC	4	4.2×10^8
50% WF /2%CNT/6%AZDC	5.5	8×10^7
60% WF /1%CNT/3%AZDC	7.3	3×10^7
60% WF /1%CNT/6%AZDC	13	2.8×10^7
60% WF /2%CNT/3%AZDC	9.8	2.71×10^7
60% WF /2%CNT/6%AZDC	11.9	2.7×10^7

Table 3 shows the cell sizes and the cell densities of the foamed nano composites.

The results showed that, by incorporation of CNTs into the compound, cell sizes were decreased. In both cases, the presence of small amount of CNTs (1and2%) leads to a smaller cell size. Compared to the pure WPC foams, the addition of 2 phr of CNTs to nano composites

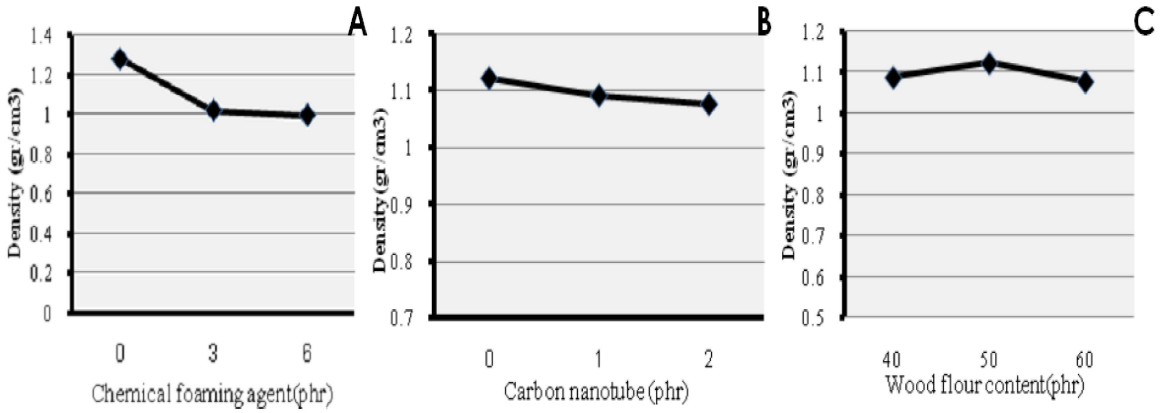

Fig. 3: Effect of CFA (a), CNT (b) and wood flour (c) concentration on the density of foamed composites

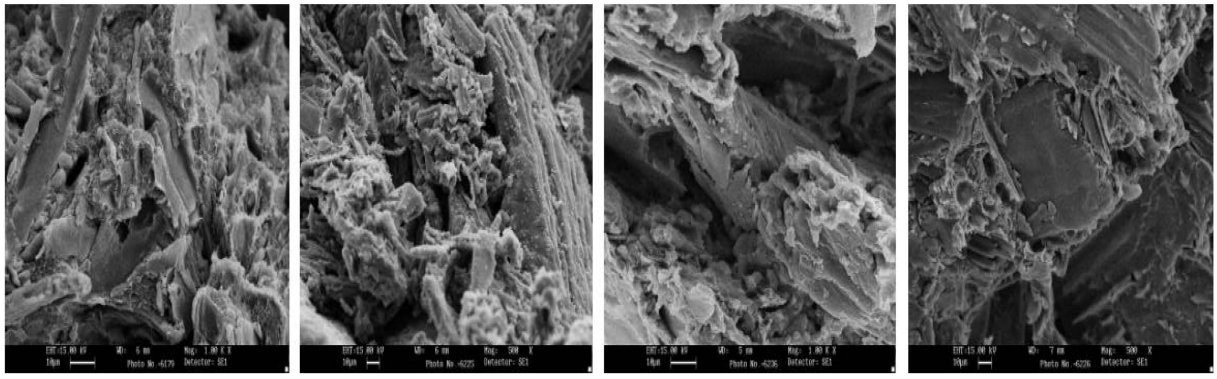

Fig. 4: SEM micrographs of foamed nanocomposites at 60 phr wood flour content

contain 40 and 50 phr WF, yielded an increase of the cell densities up to 2.52×10^{8} and 4.2×10^{8} respectively, while the cell sizes decrease to 7.5 and 4µm. In fact the extremely fine dimensions and large surface area of CNTs help to more nucleation centers creation in polymer and polymer/wood interface. Consequently, there is less amount of gas available for bubble growth in polymer which leads to cell size reduction and cell density improvement. It was observed that as the WF increased to 60 phr, the nucleation effect of CNTs on cell morphology of WPC foams became insignificant. When the solid WF particles were introduced into the polymer, the viscosity of the mixture was increased. This effect became increasingly significant as the WF content increased to 60 phr. The increased melt viscosity, makes the dispersion of WFs and CNTs in the polymer matrix more difficult. Therefore the potential nucleating effect of CNTs, was decreased.

Figure 3 illustrates the effect of CFA, CNT and wood flour concentration on the density of wood-PVC nano composite foams. CFA had significant influence on density reduction of wood/PVC composites according to analysis of variance. The addition of 3 phr CFA decreased the density up to 20% (from 1.282 gr/cm ^{3} to 1.019 gr/cm^3). Duncan test revealed that density of the foamed nano composites were not affected by CFA contents and both composite densities (3and6 phr CFA) were put in one group (Fig. 3a). At the constant CFA content, addition of CNTs to wood/PVC foams lead to more density reduction (Fig. 3b). In other words, by addition of CNTs to wood-PVC composites, cell density was increased (Table 2). This is because of more bubble nucleation by nano particles which causes to increase of cells and decrease of composite density.

Lower density of the foam composites contain 60 phr (Fig. 3c), could be probably due to the large voids which generates in WPCs as shown in Fig. 4. However low wetting may also affects the density of these composites.

The best density reduction and good morphology was achieved for the WPC having the wood content 40 phr, CFA content 3phr and carbon nanotubes content 2 phr.

Figure 5a shows the effect of CFA levels on the flexural strength of the WPCs. Overall, the flexural strengths decreased as CFA were increased from 0 phr to

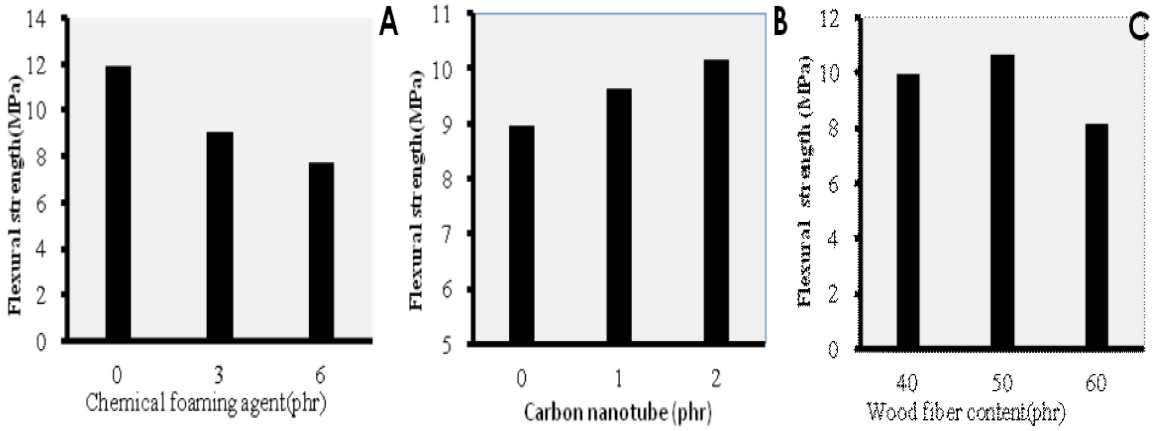

Fig. 5: Effect of CFA (a), CNT (b) and wood flour (c) concentration on the flexural strength of foamed composites.

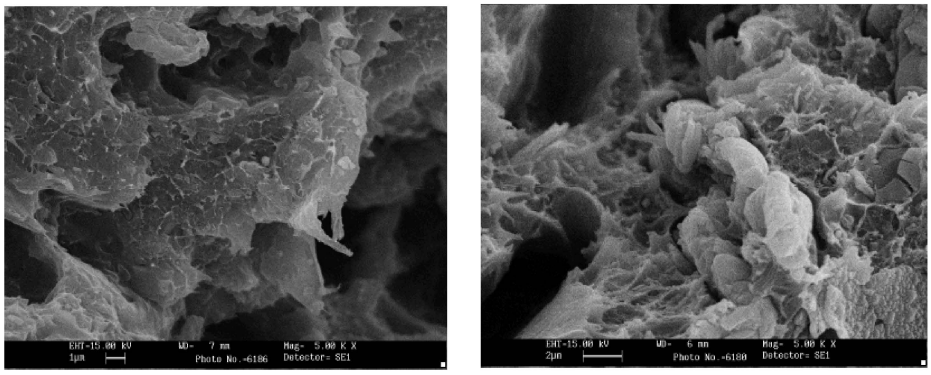

Fig. 6: SEM micrographs of foamed nanocomposites reinforced by CNTs.

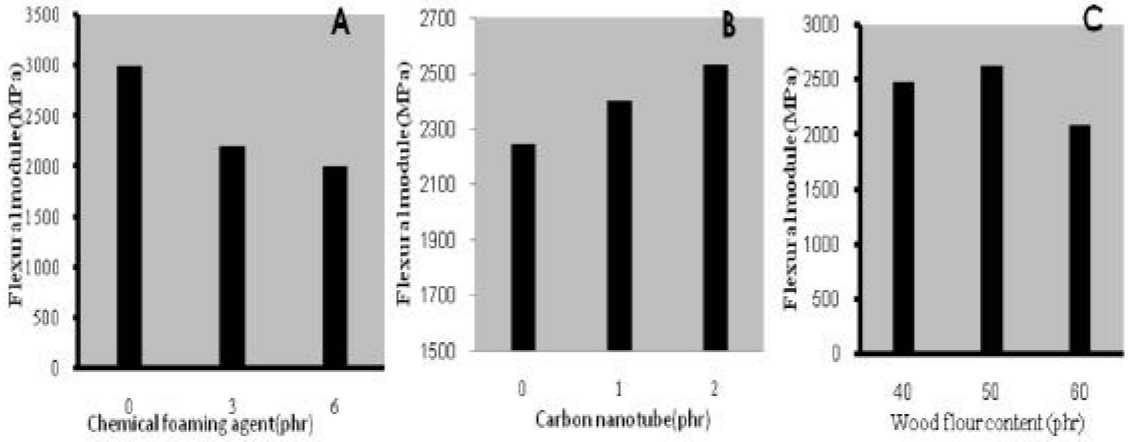

Fig. 7: Effect of CFA (a), CNT (b) and wood flour (c) concentration on the flexural strength of foamed composites.

6 phr (Fig. 5a). These trends may be due to the increased bubble nucleation and probably due to the cell coalescence happened by increasing foamin agent concentration.

Flexural strength of the WPC foams with different levels of CNTs was shown in Fig. 5b. The results revealed that the addition of CNTs to 2 phr leads to the increase of the flexural strength up to 16%. Typical SEM micrographs which show the status of dispersion of nano particles in the polymeric matrix are given in Fig. 6.

This trend for flexural strength can be explained as follows: CNTs can affectively induce the nucleation of a large amount of bubbles and consequently cell densities of foamed WPCs increased. As the cell

densities increased, cell sizes decreased to lesser than 5 microns. These too small microspheres can contribute to transfer the applied stress and can increase the flexural strengths.

Figure 5c shows the effect of the wood filler levels on the flexural strength of foamed composites. The flexural strength was increased as the level of wood increased from 40 to 50 phr. More increment of WF than 50 phr, had adverse effect on flexural properties. In fact, WF contents more than 50 phr could not produce a finer structure because of inhomogeneity of the materials. Consequently, the flexural strength was reduced with increasing the fiber content.

Flexural modulus of the WPCs at different level of CFA and CNT was shown in Fig. 7. Overall the modulus drops with the increasing of the CFA content (Fig. 7a). Flexural modulus, increased with the increasing level of CNTs as shown in Fig. 7b. As seen, at constant concentration of CFA, addition of the 1 and 2 phr CNTs to foamed composites led to the improvement of the flexural modulus up to nearly 7% and 13%, respectively. Optimum flexural modulus in foamed WPCs as a function of wood fillers was evaluated at 50 phr (Fig. 7c).

CONCLUSION

This study examined the use of multi-walled carbon nanotubes to reinforce rigid PVC/wood flour composites foams. First, the effect of WF, CNT and foaming agent contents on foam morphology (cell size, cell density) of composite foams was evaluated. Second, the influence of the addition of different levels of WF, CNT and CFA on foam density and flexural properties of nanocomposites was examined. The following conclusions can be drawn from the experimental results.

- The cell morphology of foamed composites above the 50 phr WFs content was visibly irregular and the nucleating effect of CNTs was insignificant.
- Compared to composites without CNTs, in the presence of CNTs, cell density of wood/plastic foams were increased and cell sizes were decreased.
- By using CNTs, it was possible to create very good cellular structures in wood-plastic contains 40 and 50 phr WFs, by compression molding technique.
- Density of the samples were not affected by CFA contents. As the CNT contents were increased to 2 phr, foams density decreased which implies to the effect of CNTs on increasing the bubble nucleation in the wood polymer foams.
- Compared to the pure WPCs, the addition of CNTs yields the increase of flexural strength. At foamed nano composite samples, addition of 2 phr CNTs led to the increase of the flexural strength up to 16% and the improvement of the flexural modulus up to nearly 13% compared to similar foamed samples without CNT.

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