Synthesis of Carbon Nano Fibers: Fabrication and Characterization of Carbon Nano Fibers/rea-formaldehyde resin

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ABSTRACT--- ***This paper addresses fabrication of carbon nano fibers by pyrolysis of wood fibers and their dispersion in urea formaldehyde with an aim to optimize a stable carbon nano fibers/urea formaldehyde resin. All the resin hybrids were characterized with Fourier transform infrared spectroscopy (FTIR) and powder X-ray diffractometry (XRD), while the dispersion of carbon nano fibers particles was studied with Field Emission scanning electron microscopy (FESEM). Thermo gravimetric analysis (TGA) revealed that carbon nano fibers have little high effect in the thermal stability of the UF resin. From the TGA graph, it is observed that the thermal stability of the UF based carbon nano fibers is higher than UF only. The scanning micrographs provided evidence of the smoother surfaces in the UF resin made with carbon nano fibers. This was attributed to the better encapsulation of fibers by the matrix polymer.***

Keywords--- Wood Fibers, Urea-Formaldehyde, Carbon Nano Fibers.

1. INTRODUCTION

Urea–formaldehyde resins have been broadly used by the wood-composite industry for more than 100 years, due to their good concert in the production of wood-composite panels, as they have high reactivity and low cost. Their disadvantages are low water resistance and formaldehyde emission from the wood panels, resulting from the low stability of the amino-methylene bond.

To deal with this problem, many struggles have been made, like to alter the resin synthesis methods and applying various types of additives or hardeners, etc. [1–3]. The main object of the modern adhesive industry is to settlement these needs and produce effective UF resins with very low, if not zero, formaldehyde emissions. Besides, a drastic reduction in the formaldehyde emission with a significant improvement in the durability–stability of UF bonded wood composite could extend the applications and markets for these products. One preferably effective approach in order to reduce formaldehyde emission is to lower F/U molar ratio of the synthesized resin [4–6]. However, this leads to a reduced crosslinking and thus, inferior performance of the resin, regarding to its water resistance and mechanical strength [4]. In addition to lowering the F/U molar ratio, a number of studies have focused on modifying the synthesis parameters of UF resins by control parameters such as reaction pH [7–9], introduction of second urea addition [10] and the use of additives [11,12].

Additives in general, have reform effects on the properties of the UF resins [13]. The most effective and common methods that have been used so far include the addition of small quantities of melamine in the case of more demanding applications. The use of other additives, like formaldehyde catchers has also been tested [14]. Also, the addition of trimethoxymethylmelamine and dimethoxymethylmelamine as cross-linking agents were found to be favourable for durability [15]. At the present time, technology offers the possibility of using additives with dimensions in the nano scale. Such materials seem favorable because nanoparticles have large surface areas and can bring on new properties or even modify important properties of the resins that they are persuade to, like reactivity. Especially the addition of carbon Fibers in UF resins has been reported to enhance the mechanical properties of the medium density fiber board [18]. Few researchers have also tried high conductive nano particles such as multiwalled carbon nano tubes to enhance the rate of heat transfer and to increase the mechanical strength [19, 20] and therefore, needs to be studied in depth.

This work is aimed at analyzing the influence of using carbon nano fibers in UF resin with an aim to optimize a stable carbon nano fiber/urea formaldehyde resin. Therefore, this study was conducted in order to investigate the influence of carbon nano fibers on the thermal behavior of UF resins, using TGA. Also, a thorough characterization of the new hybrids was performed using FTIR, FESEM and XRD. The novelty of this work is the use of carbon nano fibers in UF resin for the first time.

2. EXPERIMENTAL

2.1 Materials

Urea-formaldehyde (UF) liquid resin used for this study was received from Dynea Malaysia Sdn. Bhd. The viscosity of the UF resin at 300 ^{o}C was 170 centipoises, pH 8.27, density 1.286 kg/m3 and gel time at 100 ^{o}C is 36s.

2.2 Carbon Nano Fibers

The carbon nano fibers particles were synthesized using a furnace in an inert condition at 350-450 ^{o}C for 2-4 hours, after that the fibers were grinded by Retsch Chemtical Grinder ZM 200 at 18000 rpm for 30 to 40 seconds. The purity of carbon in carbon nano fibers was found to be 74.09% using elemental analysis system (CHNS analyser).

2.3 UF resin/carbon nano fibers hybrids synthesis

The urea–formaldehyde (UF) resins prepared by Dynea Malaysia Sdn. Bhd. had final mole ratio F: U = 1.07 and resulted from the reaction of urea (U) with formaldehyde (F). Carbon nano fibers were added in the UF resin at the levels of 1, 2.5, 3.5 and 5% (w/w). The UF/ activated carbon particles mixtures were mechanically stirred for 30 min before use. The pure UF resin sample was given the name CF-0 while the mixtures were named CF-1, CF-2.5, CF-3.5 and CF-5 respectively.

2.4 FTIR spectroscopy

The hybrids were studied with FTIR in two different polymerization states: (i) as partially cross-linked polymers in liquid form, which is the usual condition that the UF resins are available on the market and (ii) as partially cured polymers in solid form. The partially cured resins were prepared by drying the liquid resins in a convection oven at 105 ^{o}C for 2 h. During the drying process, the curing of the resin is progressed and a three-dimensional network is built up corresponding to that developed during the production of wood-based panels. This process is irreversible and results in an insoluble resin. The FTIR transmittance spectra were obtained with a Spectrum 1000 Perkin-Elmer spectrometer in the spectral area of 400–4000 cm−1, with a resolution 2 cm−1 and 50 scans. For the resins in liquid form, the sandwich preparation method was used, in which a drop of hybrid is placed between two KBr pellets of 110 mg each. For the FTIR measurements of solid samples, KBr pellets with 1 wt. % of the powdered material were produced.

2.5 Field Emission scanning electron microscopy (FESEM)

The morphology structure prepared samples was investigated in a JEOL JSM-7500F Field Emission Scanning Electron Microscopy (FESEM) provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. The samples were carbon coated in order to provide good conductivity of the electron beam. Operating conditions were accelerating voltage 20 kV; probe current 45 nA, and counting time 60 s.

2.6 X-ray diffraction (XRD)

X-ray Diffraction (XRD) measurements of solid UF containing carbon nano fibers and without carbon nano fibers were studied. The X-ray diffraction (XRD) was performed in a XRD analyzer. The samples were scanned in 2θ ranges 3-80° at a rate of 1deg/min. The generator was operated at Cu/30 kV/15 mA. The inter layer spacing (d002) of carbon nano fibers was calculated in accordance with Bragg equation: $2d \sin\theta=\lambda$.

2.7 Thermogravimetric analysis (TGA)

Thermo gravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. The Standard Practice for Calibration of Temperature Scale for Thermogravimetry follows the ASTM 1582 method.

The thermal stability was investigated by non-isothermal Thermogravimetry (TG, DTA) using a TA Instruments. Samples (6 ± 0.2 mg) were placed in alumina crucibles. An empty alumina crucible was used as a reference. The samples were heated from 30 to 600°C in a 50ml/min flow of Nitrogen with a heating rate of 10°C/min.

3. RESULTS AND DISCUSSION

3.1 Characterization of resins, interactions with carbon nano fibers

The chemical structure of UF resins can be specified as poly (methylene methylene ether hydroxymethylureas) which is resulted by the condensation reactions of urea with aqueous solution of formaldehyde. Carbon nano fibers have surface carbon and some hydrogen and nitrogen which can react with macromolecular end groups and mainly with hydroxyl groups via condensation reactions [21]. During the first step of addition reactions between urea and formaldehyde 1, 3-bishydroxymethyl urea (dimethylolurea) is produced, which has 2 hydroxyl groups and could interact with carbon and

making C–OH stretching mode. In order to verify this during the formation of UF/carbon nano fibers hybrids all samples were studied with FTIR spectroscopy and the recorded spectra are shown in Fig. 1.

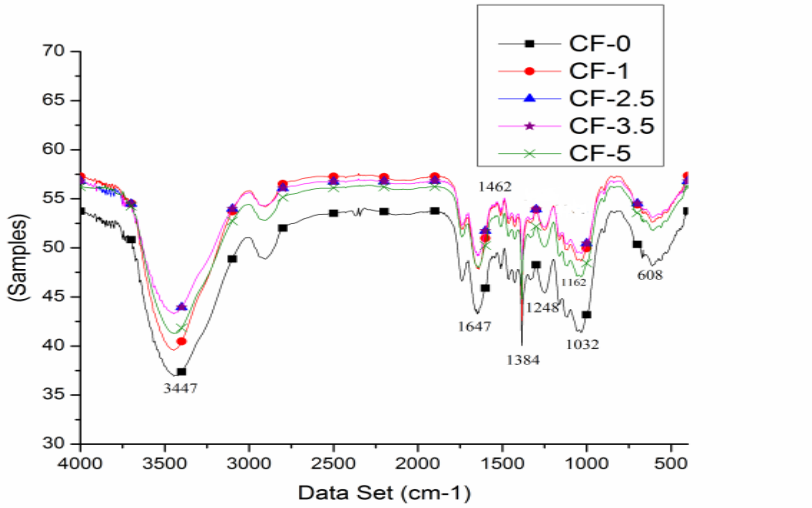

Fig. 1. FTIR transmittance spectra of CF-0, CF-1, CF-2.5, CF-3.5 and CF-5.

The multiple and broad peaks on the CF-0 resin's spectra are mainly due to the entanglement of the polymer structure. In the spectrum of the liquid UF resin, the broad peak around 3350–3450 cm−1 can be attributed to the hydrogen bonded O–H and N–H. The C–OH stretching mode and the bending mode can be found at 3447 cm-1 and 1509 cm-1, respectively. The peak occurs at 1161 cm-1 is characteristics of C–O is stretching in lactonic, alcoholic groups and carboxylate moieties [22] In the area of 1600–1650 cm−1 multiple and some overlapped peaks appear in the spectrum of pure UF resin. These peaks are assigned to the C O stretching of amide I and II, as well as the –N–H scissors of amide I. The overlapped peaks at the area 1500–1600 cm−1 are attributed to –N–H bending vibrations of amide II. The multiple peaks at 1460–1470 cm−1 may be attributed to C–H bending vibrations of CH2–N group, while the small peaks at the area of 1320–1450 cm−1 can be assigned to stretching C–N vibrations of amide I and II, while it has also been assigned to C–H stretching and –O–H bending vibrations of alcohol [23]. The strong but broad peak at 1250 cm−1 is assigned to C–N stretching vibrations of amide II [24]. The 1162 cm−1 peak is attributed to both the asymmetric stretch of N–CH2–N and the asymmetric stretch of –C–O–C– of ether linkages [25]. The FTIR spectra of UF and UF/CF resins are shown in Table 1.

Table 1. FTIR peaks observed for UF resin and UF/CF resins.

Chemical Assignment	UF and UF/CF resins Wavenumbers/cm^{-1}				
	CF-0	CF-1	CF-2.5	CF-3.5	CF-5
(NH) 2° amine and OH	3447.34	3446.99	3447.98	3447.97	3447.98
(C=O) in –$CONH_2$ (amide I)	1648.01	1639.08	1647.98	1647.99	1640.75
(NH) in NH-CO in 2° amine (amide II)	1508.56	1509	1509.06	1509.08	1509.10
CH- deformation; asymmetric in –CH3- and -CH2-	1459.30	1459.10	1459.11	1462.92	1462.92
(CH) in CH_3/CH_2OH/N-CH_2-N)	1384.42	1384.40	1384.45	1384.43	1384.34
(C-C-O)	1247.92	1249.12	1248.11	1249.12	1250.85
(N-CH_2-N), ν(C-O-C) of ether linkage	1115.66	1161.92	1161.14	1162.69	1162.69
(H-N-H-CH_2-CH_3) 1° amine	1032.19	1031.66	1032.67	1033.67	1034.17
(-CH)	609.76	608.39	608.23	608.61	608.61

The spectrum of UF/activated carbon particles resins shows a strong absorption band between at 3446-3448 cm-1 region and 3421 cm-1 for pure sample. These are the characteristics absorption bands of hydrogen bonded N-H of – NH2, formed due to the methylenization reaction happen during cross-linking [24].

The strong absorption band is observed in the spectra, near 1648, 1639,1647, 1647 and 1640 cm-1 for CF-0, CF-1, CF-2.5, CF-3 and CF-5 respectively, assigned to the stretching C=0 (amide-I) in –CONH2 group. The very strong absorption bands around 1508.56, 1509, 1509.08 and 1509.10 for CF-0, CF-1, CF-2.5, CF-3 and CF-5 respectively, it may be due to –NH (amide II) is assigned. The stretching vibrations around 1350-1400 cm-1 for resin samples, represent by the C-H

bending mode in CH2/CH2OH/N-CH2-N. The intermediate absorption band in the around 1115-1162cm-1 may appear due to stretching vibrations of –N-CH2-N- group of the ether linkage. The weak absorption bands near 608-609 cm-1 ascribed the –CH bending mode.

3.2 X-ray diffraction (XRD)

The powder X-ray diffraction profiles of all studied hybrids in solid form, as well as UF are presented in Fig. 2.

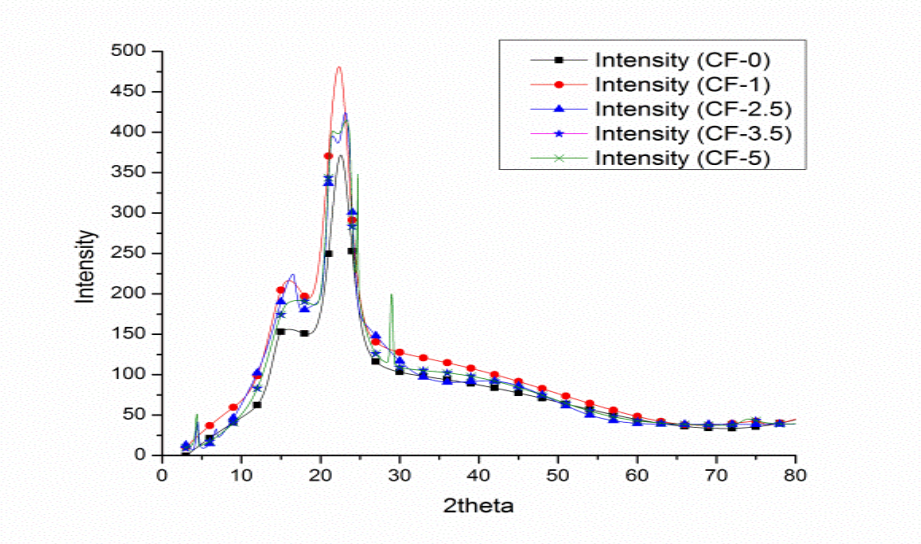

Fig. 2. XRD pattern of UF containing different ratios of carbon nano fibers.

The XRD patterns of all samples, confirm the fact that all the resins are mainly amorphous with a small degree of order, while the presence of carbon nano fibers cannot change the appearance of the patterns. Only in CF-1 and UF-3.5 patterns, the peak at 22^{o} seems to be slightly broader than in UF-0, which can be due to the presence of carbon nano fibers and the higher degree of amorphisation of the material. These show that they all contain disordered graphite micro crystallites, with inter crystallite and intra crystallite voids forming the pores. In fact, sharp narrow diffraction peaks show crystalline structures, while the broad peak is an amorphous structure. XRD pattern of UF containing different ratios of carbon nano fibers indicate that changes in the network structure occurred in the amorphous region of the UF resin.

3.3 Field Emission Scanning Electron Microscopy (FESEM) Analysis

The surface morphology of the resins was studied with FESEM. All the pictures were taken with 8000× magnification. In the case of the resins, some characteristic microphotographs of the samples CF-0, CF-1, CF-2.5 and UF-5 are presented in Fig. 3.

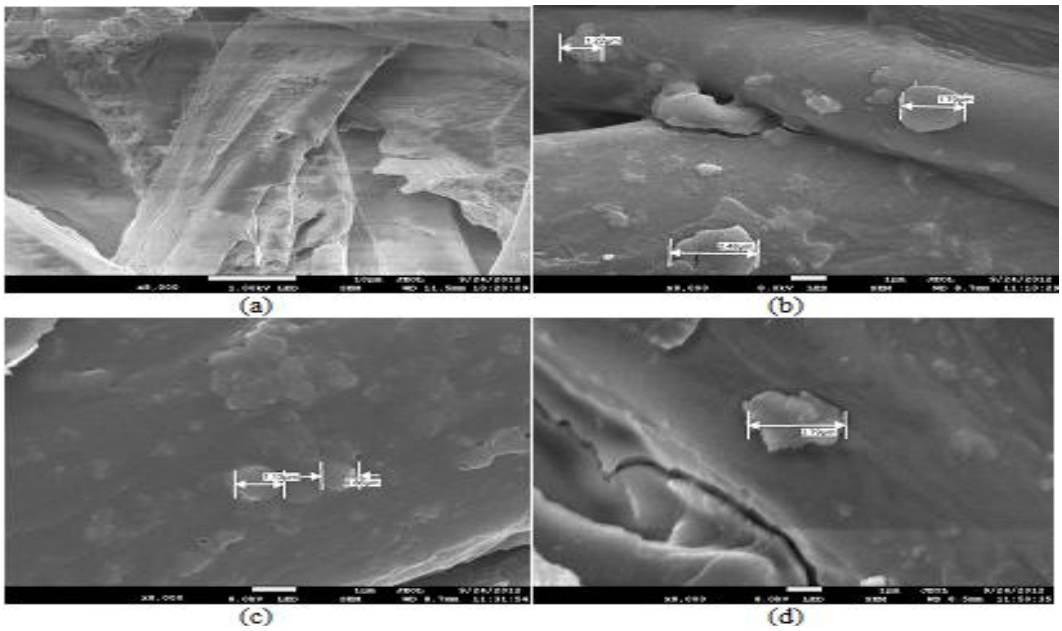

Fig. 3. FESEM microphotographs of (a) CF-0, (b) CF-1, (c) CF-2.5 and (d) CF-5 samples.

These pictures show that as the carbon nano fibers concentration increases, greater number of small bright areas appear on the samples. These micrographs on comparison clearly show the difference in the morphology of the polymer composites when compared with the morphology of the CF-0, CF-1, CF-2.5 and CF-5 (Figures 3a-3d). It is shown that when UF resin matrix is reinforced with the different loadings of carbon nano fibers, some morphological changes take place depending upon the bonding between the varying loading of fibre and the UF resin. In case of lower carbon nano fibers loading (1 or 2.5%) when the content of polymeric resin being higher there is lower bonding between the matrix and the reinforcement.

3.4 Effect of carbon nano fibers on the thermal stability of the resins

Carbon fibers when added in a polymer matrix have as result to enhance the thermal stability of different polymers [18]. This was also expected in the present study and in order to evaluate this thermogravimetric analysis was used. In Fig. 4 the TG curves for all samples are presented, revealing that the addition of carbon nano fibers to the UF resin affects little to its thermal stability.

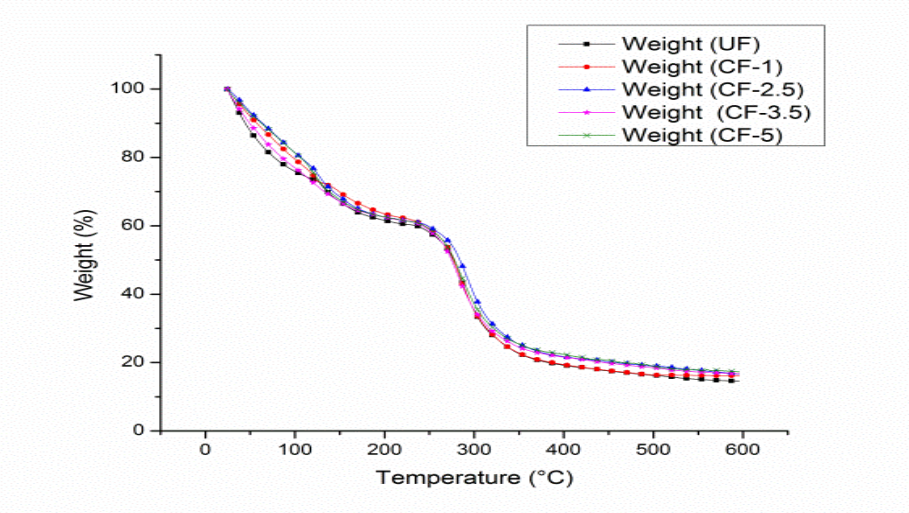

Fig.4. TG curves of all samples: (1) CF-0, (2) CF-1, (3) CF-2.5, (4) CF-3.5, and (5) CF-5. Heating rate 10 ^{o}C/min.

From the TG curves it is clear that the study can be divided into two regions [26]. The first mass loss step that corresponds to 3–4.5% losses in every case occurs for all samples between 50 and 100 ^{o}C. This step corresponds to water evaporation of the samples. Slow formaldehyde emissions at temperatures 100–200 ^{o}C result in small mass losses, in every sample. Above 200 ^{o}C, the main degradation step is initiated when chain scissions begin and the radicals formed induce the formation of cyclic structures in the polymer chain. This process results in the extensive polymer fragmentation. Degradation of cured resins begins with release of formaldehyde from dimethlene ether groups [25] and the maximum degradation rate happens when the stable methylene ether linkages deconstruct [26]. Comparing the mass loss curves of all samples above 200 ^{o}C, it can be seen that the hybrids affect the thermal stability of the resin. The resins with lower carbon nano fibers content have intermediate values between those of CF-1 and UF-2.5, which are in all cases slightly higher than UF-0. However, at higher temperatures, UF resin with carbon nano fibers performed better in thermal stability than without activated carbon particles.

4. CONCLUSIONS

The ultimate goal of the carbon nano fibers addition was with aim to optimize a stable and also to improve the properties carbon nano fibers/urea formaldehyde resin. The degree, to which this is done, strongly depends on the dispersion of the additive into the resin and the resin–wood adhesion. In this work, it is verified from FTIR spectroscopy that carbon nano fibers can create hydrogen bonds with UF resins. However, this is not effective in order to have a fine dispersion of carbon nano fibers as individual particles in the polymer matrix and some aggregates are also formed. Furthermore, carbon nano fibers as an additive in UF resins was found to affect many of the hybrids' properties, when they can be applied to adhesive based composite. From the TGA graph it is observed that the thermal stability UF based carbon nano fibers, was higher than only UF. The scanning micrographs provided evidence of the smoother surfaces in the UF with carbon nano fibers.

5. ACKNOWLEDGMENTS

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