J Wood Sci (2014) 60:263–268
DOI 10.1007/s10086-014-1406-2

ORIGINAL ARTICLE

Mechanical properties of kenaf fiber–cement composites containing kenaf gamma-ray grafted with acrylamide

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Received: 17 December 2013 / Accepted: 19 March 2014 / Published online: 5 June 2014

Abstract Kenaf fibers have excellent properties and possess the potential to be outstanding reinforcing fillers in cement. The grafting of acrylamide to kenaf fibers is important in improving the compatibility between the fibers and the cement. Acrylamide was grafted onto kenaf fibers using gamma-ray radiation. The radiation dose ranged from 20 to 100 kGy, and the dose rate was 10 kGy/h. The degree of grafting increased with increased radiation doses. FT-IR analysis revealed an increase in amide content after gamma-ray-radiation-induced grafting, further evincing the attachment of acrylamide to the kenaf fibers. SEM images showed evidence of acrylamide grafting to the fiber surface. Contact angle measurements on individual fibers taken before and after grafting demonstrated changes in wettability. The mechanical properties of the gamma-ray-grafted kenaf fiber–cement composites were superior to those of the ungrafted kenaf fiber–cement specimens.

Keywords Gamma-ray · Irradiation · Grafting · Kenaf · Cement composite

Introduction

Kenaf has attracted considerable attention as a renewable resource. Kenaf can be grown under a wide range of weather conditions. Moreover, kenaf grows to more than 3 m within 3 months [1, 2]. During the past decades, kenaf exhibiting low density, specific mechanical properties, and biodegradability has been widely studied. The stalk of the kenaf plant is composed of an outer layer (bark) and a core. The core possesses an isotropic and complex porous structure. However, the bark exhibits an orientated, highly crystalline fiber pattern [3]. As a fiberglass alternative, kenaf fiber can be utilized as a reinforcement material for polymeric and cement composites. Kenaf fiber possesses many desirable properties; however, for some applications, the fiber lacks critical attributes available in synthetic alternatives [1]. The internal adhesion between fibers and cement paste can be improved by modifying the surface process of fibers by a suitable pre-treatment. Thus, the surface modification of kenaf fibers by graft polymerization allows its surface hydrophilicity to be increased resulting in the higher internal adhesion between them [4, 5]. Cement, as being widely used in construction, is hardened in the process of hydration reaction. The calcium silicate hydrate gel (C–S–H) is the dominant hydration product resulting from normal hydration (curing) of Portland cement [6]. To improve the fiber-cement adhesion and to utilize the properties of the fiber efficiently, an intimate interaction is needed between the fiber and matrix. Therefore, fiber surface modifications have become particularly important process before these fibers will be successful components in cement composites. Gamma-ray-induced graft polymerization is a fascinating method for polymeric material processing due to its several advantages such as a high reactivity, unnecessary of initiator, deep penetration ability, and good controllability [7, 8]. For these reasons, gamma-ray radiation has been widely employed for polymer surface modification. The gamma-ray-radiation grafting process proceeds through a radical-based mechanism [9].

In this study, we adopted acrylamide as a hydrophilic polymer because of its high wettability. The grafting of

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acrylamide onto kenaf fibers was conducted using gamma-ray radiation in different doses. The ability to modify the surface of the fibers can be controlled easily by varying the irradiation dose. The effect of irradiation doses on the graft yield of kenaf fibers was investigated. The grafted copolymer was characterized using Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) and contact angle measurements. The mechanical properties of kenaf fiber–cement composites were also examined.

Experimental details

Materials

Five-month-old kenaf was obtained from the Advanced Radiation Technology Institute and the Korea Atomic Energy Research Institute. The kenaf's core and bark were separated by hand. The bark was chopped into 3 cm lengths for this experiment. Ordinary Portland cement from Asia Cement Co. (Seoul, Korea) was used. Acrylamide (98 %) was obtained from Aldrich (St. Louis, MO, USA).

Kenaf fiber preparation

The kenaf was separated into bark and core by hand. Kenaf bark was soaked in ethanol at room temperature for 10 h. The epidermis of the kenaf bark was removed by washing with ethanol. The bark was dried at 60 °C for 48 h and then milled for 2 min to produce the fibers. The kenaf fibers were separated until they could pass through a 2 mm screen.

Gamma-ray-radiation-induced grafting of acrylamide onto kenaf fibers

Acrylamide was grafted to the surface of the kenaf fibers using gamma-ray irradiation (Fig. 1). The kenaf fibers were dried to a constant weight in a vacuum oven at 60 °C and were then placed in closed polyethylene bags that contained 20 wt.% acrylamide in ethanol. The immersed kenaf fibers were treated at room temperature with a 100 kGy dose of gamma-ray radiation at a rate of 10 kGy/h. After the gamma-ray graft reaction, the acrylamide-grafted kenaf fibers were repeatedly washed with ethanol and water until they were pH-neutral in order to remove any residual unreacted acrylamide monomers, as well as homopolymers that may have been produced during the irradiation process. The fibers were subsequently dried again for 12 h in a vacuum oven at 60 °C.

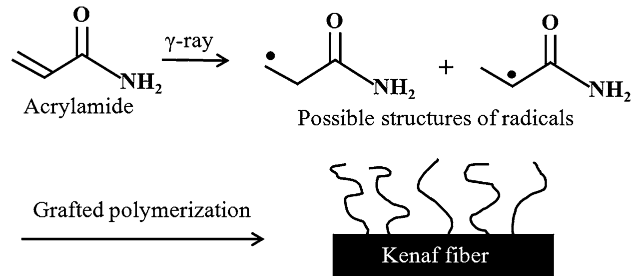


Fig. 1 Schematic illustration of the grafting of acrylamide onto the kenaf fibers

Preparation of the cement composites

The mortars were prepared, stored, and tested with dimensions of 40 mm × 40 mm × 160 mm according to the method described in standard KSL ISO 679 [10]. Cement, sand, water, and kenaf fibers were mixed in a mass ratio of 450:1,354:225:5.36 (22.1:66.5:11.1:0.3 wt.%), respectively. The prepared mortars were cured in water at 20 °C.

Characterization

The degree of grafting was calculated using the following equation

$$\text{Degree of Grafting } (\%) = (W_g - W_0)/W_0 \times 100$$

where W_g is the fiber weight after grafting, and W_0 is the fibers' weight before grafting. The surface morphologies of the acrylamide-grafted kenaf fibers were observed using a scanning electron microscope (SEM, JEOL JSM-6390). Fourier-transform infrared/attenuated total reflectance spectra of the ungrafted and acrylamide-grafted kenaf fibers were collected with a Bruker (Germany) Tensor 37 spectrometer. The contact angles were measured using the Wilhelmy plate method with a Kruss K100SF tensiometer (Germany) to determine the change in wettability after the gamma-ray irradiation. Figure 2 shows a schematic of the technique used. Distilled water was used at room temperature as the contact angle solution. The immersion depth was 5 mm, and the deionized water was moved up (advancing) and down (receding). Each contact angle given is the average value of 10 measurements, and the standard deviation is of the order of 0.5° or less. The interfacial forces between single kenaf fibers and the deionized water were recorded. These values were used to calculate the contact angles through the equation

$$F = L d \cos\theta$$

where L is the deionized water surface tension, d is the circular cross-section diameter of the fibers, and θ is the contact angle.

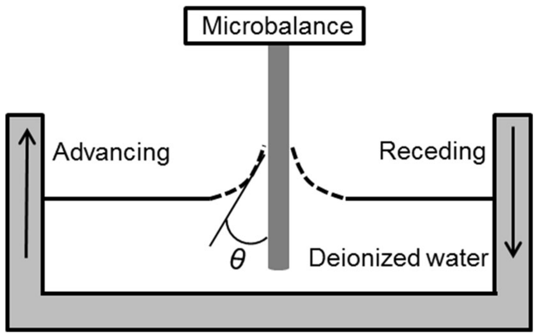


Fig. 2 Schematic diagram of the Wilhelmy plate method used to measure the contact angles on the fibers

The flexural and compressive strengths of the kenaf fiber–cement composites were measured using a universal testing machine (Heung Jin, Korea) and were performed according to the standard strength test for cement described in standard KS L ISO 679 [10]. The specimens were prepared with dimensions of 40 mm × 40 mm × 160 mm. Five replications were used for the flexural and compressive strengths. All specimens were tested immediately after being removed from the curing chamber. The tests were performed on specimens cured for 1, 7 and 28 days.

Results and discussion

Degree of grafting

The effects of the gamma-ray irradiation dose on the degree of acrylamide grafting were investigated, and the results are shown in Fig. 3. The degree of grafting gradually increased as the irradiation dose was increased. This result was attributed to the greater degree of radicalization at higher irradiation doses: a greater concentration of radicals led to increased grafting [9].

FT-IR

The graft polymerization of acrylamide onto the kenaf fibers was confirmed by FT-IR analysis. The FT-IR spectra of the grafted and ungrafted kenaf fibers were analyzed and are presented in Fig. 4. Bands between 1,200 and 1,000 cm^{-1} are typical of cellulose and hemicellulose (C–O–H stretching of primary and secondary alcohols at 1,043 cm^{-1}, C–O–C stretching at 1,164 cm^{-1}). The peak at 1,310–1,370 cm^{-1} was found to originate from syringyl, and the peak at 1,225–1,270 cm^{-1} was found to originate from guaiacyl. The peak at 1,510–1,610 cm^{-1} was related to vibrations of aromatic rings in the lignin. The peak at 1,740 cm^{-1} in the raw kenaf core sample was due to the C=O stretching vibration of in acetyl groups in

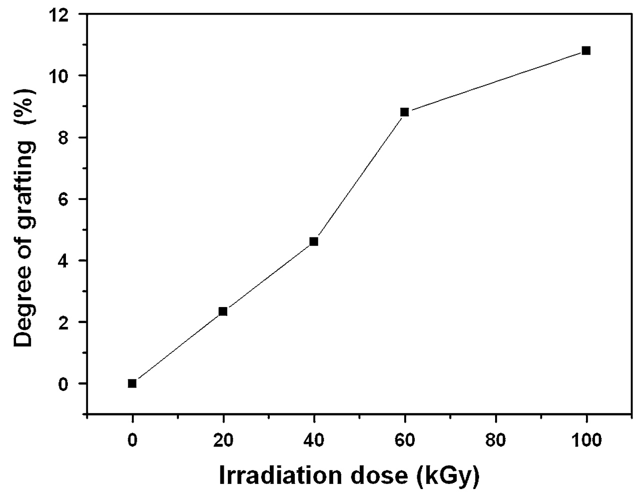


Fig. 3 Degree of grafting as a function of the radiation dose

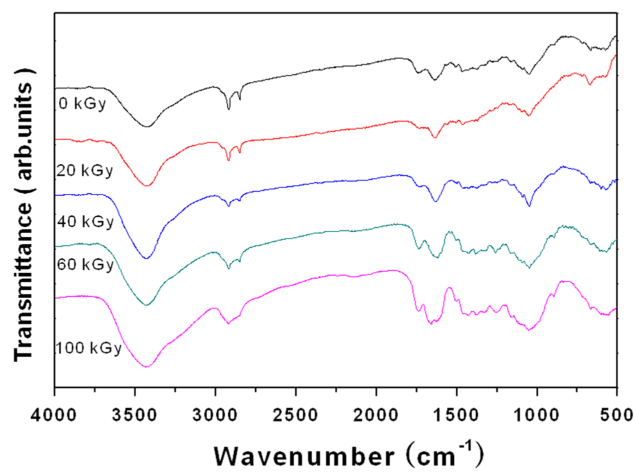


Fig. 4 Infrared spectra of the kenaf fibers after acrylamide graft polymerization at various gamma-ray radiation doses

hemicelluloses or the ester linkage of carboxylic group in the ferulic and *p*-coumaric acids of lignin or hemicellulose [11, 12]. The spectra of the acrylamide-grafted kenaf fibers revealed double peaks at 1,670 and 1,630 cm^{-1} resulting from amide I and II absorptions, respectively [13]. In addition, the intensity of these absorption bands increased with increased irradiation doses. A broad band was observed between 3,600 and 3,100 cm^{-1}, which corresponded to overlapping asymmetrical OH and NH stretches. The signal observed at 1,610 cm^{-1} corresponded to an amide II absorption [14]. Again, the FT-IR spectra of the irradiated kenaf fibers showed the presence of acrylamide on the fiber surface.

Contact angles

Contact angle measurements were conducted to determine the changes in wettability resulting from acrylamide grafting. Measurements were performed on single kenaf fibers. The contact angle results are plotted in Fig. 5. A decrease in both advancing and receding contact angles occurred because of the grafting; however, the contact angles increased slightly as the irradiation dose was increased. All receding angles were smaller than the advancing angles. This observation was attributed to both the material's heterogeneity and the roughness of the material surface [15, 16]. A lower contact angle indicates hydrophilicity and the potential for strong adhesiveness [17, 18]. The gamma-ray-radiation-induced acrylamide grafting enhanced the wettability of kenaf fibers.

Morphology

To elucidate the morphological changes induced by the grafting, we investigated the surface morphologies of grafted and ungrafted fibers using a JEOL JSM-6390 scanning electron microscope. The grafted kenaf fibers exhibited different structural features compared with the ungrafted kenaf fibers. Notably, after acrylamide grafting, an obvious coating layer was observed on the kenaf fibers (Fig. 6). These results indicate that grafting had occurred.

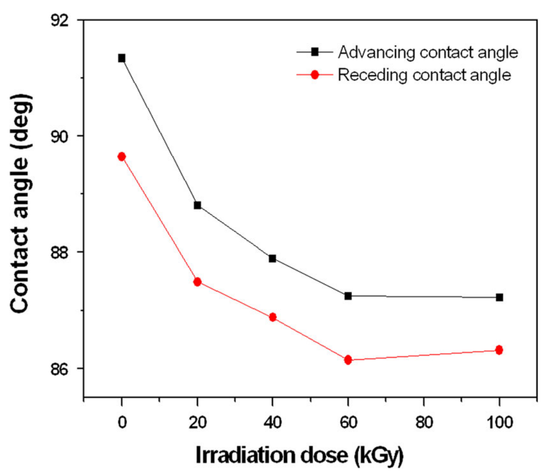


Fig. 5 Contact angle variation resulting from different radiation doses

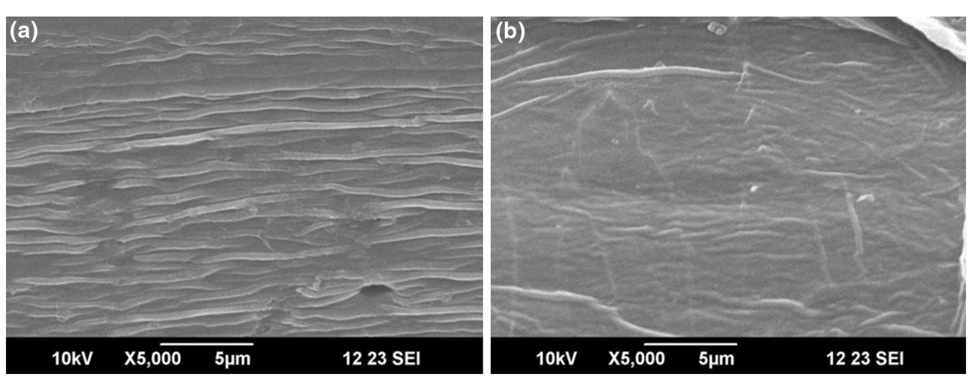
Flexural strength

After 1 day of curing, the flexural strengths of kenaf fiber–cement composites that contained kenaf grafted at various irradiation doses were measured; the results are shown in Fig. 7. The flexural strength increased as the irradiation dose was increased up to 40 kGy but decreased when the irradiation dose was 100 kGy. At higher irradiation doses, such as 100 kGy, radical generation increases. The increase in radicals increases grafting but also degrades the cellulose within the kenaf fibers. High irradiation doses have been reported to weaken kenaf fibers through cellulose degradation and thereby negatively affect the mechanical properties of the fibers [19, 20]. At 3 days, the flexural strength exhibited similar trends (Table 1); however, the strength values increased because of the additional curing. At 28 days, the flexural strength of the grafted kenaf fiber–cement composites remained higher than that of the ungrafted kenaf fiber–cement composites.

Compressive strength

The results of the flexural strength tests appeared to be comparable to the results of compressive strength tests. The compressive strengths after day 1 of curing are graphed in Fig. 8. Compared with the ungrafted samples, the composites containing fiber grafted at 40 kGy exhibited 17.5 % greater compressive strength and 14.6 % greater flexural strength. Table 2 illustrates the compressive strengths of mortar at different curing times and for different grafting irradiation doses. At any given point in time, the compressive strength of the grafted kenaf fiber–cement composites was greater than that of the ungrafted composites. After 28 days of curing, the grafted kenaf fiber–cement composites had an 18.7 % greater compressive strength

Fig. 6 Scanning electron micrographs of the surface of **a** ungrafted kenaf fibers and **b** kenaf fibers grafted with acrylamide at a gamma-ray radiation dose of 100 kGy



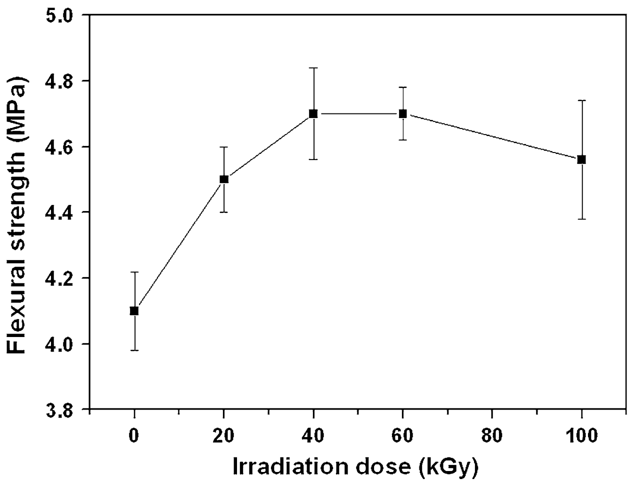


Fig. 7 The flexural strengths after 1 day of curing of kenaf fiber–cement composites that contain kenaf grafted using different irradiation doses

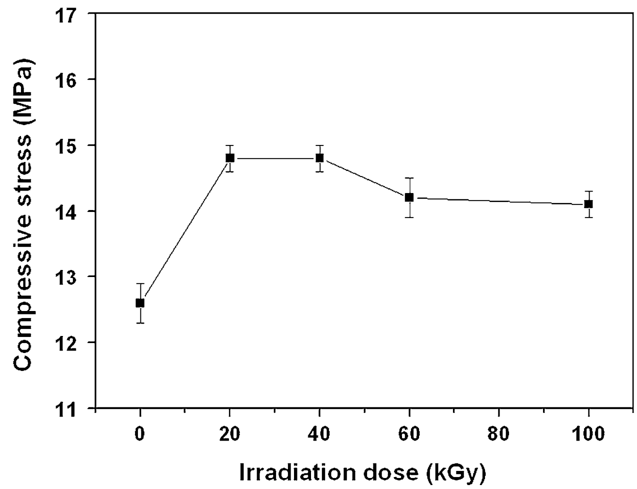


Fig. 8 The compressive strengths after 1 day of curing of kenaf fiber–cement composites that contain kenaf grafted at different radiation doses

Table 1 Effects of the irradiation-induced grafting and curing time on the flexural strength of the kenaf fiber–cement composites

Irradiation dose (kGy)	Flexural strength (MPa)		
	Day 1	Day 3	Day 28
Non-irradiated	4.10 ± 0.12	6.40 ± 0.12	8.42 ± 0.10
20	4.50 ± 0.10	7.14 ± 0.15	8.66 ± 0.07
40	4.70 ± 0.14	7.25 ± 0.12	9.24 ± 0.04
60	4.70 ± 0.08	6.90 ± 0.12	9.59 ± 0.08
100	4.56 ± 0.18	7.14 ± 0.08	9.24 ± 0.08

Table 2 Effects of the irradiation-induced grafting on the compressive strength of the kenaf fiber–cement composites

Irradiation dose (kGy)	Compressive strength (MPa)		
	Day 1	Day 3	Day 28
Non-irradiated	12.6 ± 0.3	26.4 ± 0.4	42.8 ± 0.3
20	14.8 ± 0.2	28.6 ± 0.2	50.7 ± 0.3
40	14.8 ± 0.2	28.7 ± 0.3	50.7 ± 0.3
60	14.2 ± 0.3	28.1 ± 0.2	50.7 ± 0.2
100	14.1 ± 0.2	27.1 ± 0.3	50.8 ± 0.2

than the ungrafted kenaf fiber–cement composites. In contrast, after 28 days of curing, the differences in irradiation doses did not appear to affect the compressive strengths. Hydrophilic polymers, such as acrylamide, grafted to fibers are believed to improve the bond between the fibers and the cement paste [17, 21]. In summary, gamma-ray-radiation-induced acrylamide grafting increased the hydrophilicity of kenaf fibers. A strong interfacial adhesion between the grafted fibers and the cement paste influenced the mechanical properties of the kenaf fiber–cement composites. Where strong bonds existed, the kenaf fiber–cement composites exhibited high flexural and compressive strengths [22, 23].

Conclusion

In this study, kenaf fiber surfaces were grafted with acrylamide using gamma-ray radiation. The FT-IR and degree-of-grafting results confirmed that acrylamide was successfully grafted onto the kenaf fibers. This study also demonstrated that the extent of grafting can be controlled by the irradiation dose. Contact angle measurements confirmed that the grafted kenaf fibers were more hydrophilic than the unmodified kenaf fibers. At a given point in time, the flexural and compressive strengths of the kenaf fiber–cement composites that contained grafted kenaf fibers were higher than those of the composites that contained ungrafted kenaf fibers. This pattern was observed for all radiation doses. In conclusion, kenaf fiber–cement composites that contained kenaf grafted with acrylamide through gamma-ray irradiation improved the flexural and compressive strengths compared with their ungrafted counterparts.

Acknowledgments Korea Science and Engineering Foundation, which is funded by the Ministry of Science, ICT and Future Planning, Korea.

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