Construction of Cement Composite Using Walnut Shell Reinforced with Bacterial Nanocellulose Gel

Ali Hassanpoor Tichi,[a,*] and Meysam Razavi [b]

The effect of nanocellulose on mechanical, physical, and morphological properties of composites made of walnut shell and cement was investigated. The mixing ratio of walnut shell as a lignocellulosic material with cement at three levels (10:90, 20:80, and 30:70) and nanocellulose at three levels (0%, 1%, and 3%, based on dry weight of cement) were considered as the variables. Boards were prepared according to the ISO 11925-2 (2020) specifications for the fire resistance properties and according to the DIN EN 634-1 (1995) specifications for the mechanical and physical properties. Morphological properties of composites and nano distribute were evaluated by scanning electron microscopic (SEM) imaging. The results showed that boards containing nanocellulose increased the mechanical properties compared with cement board without nanoreinforcement. The modulus of rupture, modulus of elasticity, and internal bonding of the boards decreased with increased walnut shell amount, and its maximum value was obtained when using 10% walnut shell. Nanocellulose remarkably reduced the fire resistance of the boards. The results from SEM showed that nanocellulose can fill the pores of the composite and create a uniform structure, and thus improved the strength of the boards.

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Keywords: Walnut shell; Density; Modulus of rupture; Nanofiber cellulose

*Contact information: a: Department of Wood Industry, Technical and Vocational University (TVU), Tehran, Iran; b: Department of Civil Engineering, Technical and Vocational University (TVU), Tehran, Iran; *Corresponding author: hasanpoortichi@gmail.com*

INTRODUCTION

Today, the use of lignocellulosic materials in making cement composites is motivated by their advantages of being renewable, widely available, low price, lightweight, and suitable having physical and mechanical properties. These composites also are environmentally friendly. Such boards are widely used in flooring, interior covering of walls, ceilings, and partitions. Additionally, when exposed to fire, this composite has higher resistance than other wooden products, such as chipboard and medium-density fiberboard (MDF). Agricultural waste and fruit skin produce a large part of lignocellulosic materials that are useless and this has caused environmental concerns. Using these wastes in making wooden products, such as cement composites, can reduce this problem (Rowell *et al.* 1991; Hassanpoor Tichi *et al.* 2015; Golbabaei *et al.* 2017). The walnut shell is a byproduct of the fruit of the walnut tree. A spherical nut or egg inside is the fruit of the walnut tree. The walnut tree is cultivated all over the world (Xiao *et al.* 1998).

One of the main disadvantages of cement composites is the non-adherence of cement with lignocellulosic materials due to the presence of extractive materials. Today, this problem can be reduced to a great extent by washing lignocellulosic materials and also by using inorganic and organic nanomaterials. Such measures can help to increase the adhesion process of cement to lignocellulosic materials. Bacterial nanocellulose gel with the chemical formula $(C_5H_{10}O_5)_n$ is used in papermaking, textiles, medicine, medical engineering, pharmaceutical, cosmetic, food industry, agriculture, automotive, construction, sports containers, petroleum, paint and coating, and aerospace industries, among others. Zor *et al.* (2023) investigated the thermal, mechanical, and morphological properties of cellulose/lignin nanocomposites. They stated that the use of 2.5% nanolignin resulted in high thermal stability, mechanical strength, and suitable morphological structure compared to other samples. Effects of polyvinyl alcohol (PVOH) and silica were studied relative to the chemical, mechanical and electrical properties of cellulose nanocomposite. The results showed that the lowest crystallinity value was in the CNF-Si (nanocellulose-silica). Although the CNF-P (nanocellulose-PVOH) composite had mechanical advantages, the CNF-Si (nanocellulose-silica) composite displayed the best thermo-mechanical properties (Poyraz *et al*. 2017). Yildirim and Candan (2021) revealed that nanocellulose (NC) and boric acid (BA) reinforcement substantially affected the performance properties of the particleboard panels. It was determined that using 3% NC and 3% BA in the panels afforded the best results relative to thickness swelling, water absorption, moisture content, modulus of rupture, modulus of elasticity, and internal bonding strength. Beskopylny *et al*. (2023) evaluated the effect of walnut-shell additive on the structure and characteristics of concrete. The results from their study showed that physical and mechanical properties of boards decreased with increasing walnut-shell content. Balea *et al.* (2019) investigated the use of nanocellulose in cement composites. They stated that the use of nanocellulose improves the bending strength, modulus of elasticity, and internal adhesion, but the main disadvantages are the high price of this nanocellulose. Guo *et al*. (2020) investigated the effect of cellulose nanocrystals, cellulose nanofibers, and bacterial nanocellulose on cement composites. According to their findings, all three types of cellulose nanocrystals have increased density, decreased water absorption, delayed cement hydration, increased hydration degree, decreased porosity and shrinkage, improved mechanical resistance, and decreased penetration of sulfate and chloride ions in the composite. Mohammadkazemi *et al*. (2015) investigated the effect of bacterial nanocellulose on the properties of fiber-cement composites. In their research, the effect of bacterial nanocellulose in three levels (control, powder, and gel) as a reinforcement, as well as bagasse fibers in 6 and 7% were used to make composites. They concluded that boards made with nanocellulose gel had higher resistances than cellulose nano powder and blank. Lu *et al*. (2011) stated that cement composites made of bacterial cellulose had higher bending and compressive strengths. Additionally, bacterial cellulose increased the production rate of hydrated calcium silicate gel during cement hydration. Fu *et al*. (2017) stated in a study that by increasing the amount of cellulose nanocrystals in cement, the degree of hydration and flexural strength of cement increased 20%. In other work, the effect of nano wollastonite on cement composites made of kraft pulp fibers was investigated. The researchers concluded that the physical and mechanical resistance increased with the increase of nano wollastonite in cement mortar (Hassanpoortichi *et al*. 2016). The purpose of the current research is to investigate the effect of nanocellulose on the functional properties of several walnut-shell-cement structures and determine the optimal amount of nanocellulose in the construction of these panels. The goal was to determine whether nanocellulose can improve the bonding between cement and walnut shell.

EXPERIMENTAL

Materials and Methods

Panel production and specimen preparation

In this research, used walnut-shell was collected from the fruit of the walnut in Mazandaran province, Babol city (Fig. 1-A). The type of cement used was Portland 2, a product of Qazvin Abic Cement Company. Additives, including nanocellulose bacteria, were prepared in the form of a suspension from Nano Novin polymer, located in Gorgan University of Natural Resources (Fig. 1-B). Bacterial cellulose nanofiber (BCNF) was synthesized through bacterial synthesis, through building up glucose and cellulose chains by "*Acetobacter xylinus*" in aqueous culture media during a time period around two weeks. Naturally, bacteria is produced BCNF in the form of wet sheet containing nanofibers with diameter size of 30 to 60 nm and impurities originated from cultivation media components. The impurities were removed by treating the sheets with NaOH (3 wt%) at 70 °C for 1 h, which resulted in semi-transparent wet purified sheets. The purified sheets were then treated with sulfuric acid (5 wt%) at 50 °C for 1 h. The acid-treated sheets were washed with a proper amount of deionized water to get a pH value around 7. Finally, the neutralized BCNF sheets were passed one time through disk grinder (MKCA6-2; Masouko Co., Japan) to produce BCNF gel. The characteristics of cellulose nanogel are shown in Table 1.

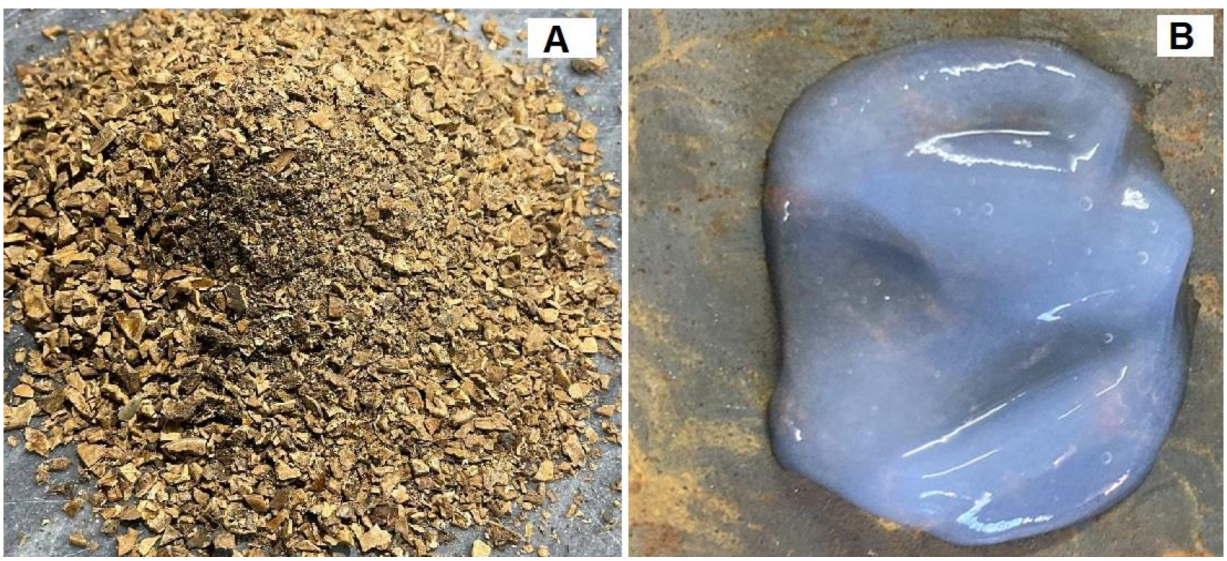

Fig. 1. Walnut-shell (A) and nanocrystal cellulose (B)

Table 1. Properties and Formula of Cellulose Bacterial Nano Gel

Formula	$(C_5H_{10}O_5)n$
State of matter	Gel (1%)
Color	White
Method of production	Chemical synthesis
Nanofiber diameter	Average 40 nm
Nanofiber length	800 to 200 nm
Degree of purity	99%≤
PH	7
Density	$1.5\ \frac{g}{cm^3}$

The variable factors in this study included the ratio of walnut-shell to cement in three levels (10:90, 80:20, and 70:30 %), and the amount of nanocellulose was in three levels of (0, 1, and 3% of the cement weight).

Fig. 2. A: mixer machine, B: Mixing cement with walnut shell and nanocellulose, C: The mold contains cement, walnut shell and nanocellulose, D: Board made of walnut shell and cement.

In the initial stages of making the boards, a wooden mold with dimensions of 12 × 270 × 350 mm^3 was made, and then according to the target density (1.1 g/cm^3), the mass of the raw materials in each treatment was calculated. In the next step using a digital scale, the ratio of water, cellulose nanogel, and calcium chloride was determined, and after combining them in a mixer, these materials were added to walnut-shell and cement, whose weight ratio was determined in advance.

The mortar obtained from the mixer was uniformly poured into a metal mold with dimensions of 1.2 × 270 × 350 cm^3 and under the press under cold conditions for 10 min with a pressure of 30 kg/cm^2 until it reached the final thickness of 12 mm and was compressed under constraint. After that, the boards were kept under confinement for 24 h. To finalize and minimize the drying speed, the boards were kept in a special chamber with a temperature of approximately 20 °C and relative humidity above 90% for 20 days. After this period, the boards were cut to the side using a circular saw and placed in an air-conditioned room with a temperature of 20 °C and a relative humidity of 65% for 28 days (Fig. 2).

Then, the test samples were prepared according to DIN EN 634-1 (1995) and their physical and mechanical properties including density, fire resistance, thickness swelling, modulus of rupture, modulus of elasticity, and internal bonding were measured.

Mechanical and physical tests

Testing of flexural strength (bending strength and modulus of elasticity) and internal bonding was completed using the universal device of Amol Rokesh laboratory located in Amol city with a loading speed of 10 mm/min.

Physical test

The physical properties include the apparent density and thickness swelling (TS) after 2 h and 24 h immersion in water (15 °C) were determined in samples with the dimensions of 50 mm × 50 mm × 16 mm.

Fire retardant testing device

Measurement of fire resistance (percentage of weight loss) was tested according to ISO 11925-2 (2020) standard with dimensions of 15 cm × 10 cm. From the preliminary weight of specim*ens before fire exposure (*W_1*, g) and second weight of specimens after fire exposure (*W_2, g), the mass loss (*ML*) was calculated as Eq. 1:

$$\text{ML (\%)} = \{(W_2 - W_1) / W_1)\} \times 100 \quad (1)$$

Scanning electron microscopy

To check the microscopic photography (SEM), first, the samples were cut into 1 × 1 cm dimensions, and then in the next step, the samples were covered with a round of gold, and their imaging was done with the help of an electron microscope. The scanning electron microscopy (SEM) analysis was performed using a Philips model AIS 2100 (Seoul, North Korea) at the School of Electrical and Computer Engineering, Amir Kabir University, Tehran, Iran.

Statistical analyses

To check and compare the physical and mechanical properties of the boards, one-way analysis of variance was used in the form of a completely random design using SPSS software (Dell Inc., Landolock, TX, USA) at the confidence level of 99 and 95%. Additionally, the grouping of the averages was performed with Duncan's multi-domain test (DMRT).

RESULTS AND DISCUSSION

Mechanical Properties

The effect of independent and mutual factors on the bending strength, modulus of elasticity, and internal bonding of the samples was significant at the 99% and 95% confidence levels. As shown in Figs. 3, 4, and 5, the highest amount of mechanical resistance was related to boards made with 3% cellulose nano gel and 10% walnut-shell with 90% cement, in which the values were respectively for bending strength, modulus of elasticity, and internal adhesion equal to 10.4, 4300, and 0.69 MPa. The lowest value of mechanical resistance was observed in boards without nanocellulose and 30% walnut-shell with 70% cement. Based on the obtained results, boards containing nanocellulose had higher bending strength, modulus of elasticity, and internal bonding. One of the reasons for the increase in mechanical strength with the increase of nanocellulose is that nanocellulose has many available OH groups and because the cement matrix and cellulose fibers are both hydrophilic, they tend to form chemical bonds with each other. Strong connections between cellulose and cement increase the mechanical resistance of boards. Because the hydroxyl groups of nanocellulose are abundant and available, it accelerated the production of hydrated calcium silicate gel, and the rate of cement hydration reactions increased (Mohammadkazemi *et al.* 2015). When nanocellulose is used in the boards, because it prevents the penetration of chlorine ions, sulfates, and destructive chemicals in the depth of the boards, it increases the durability and self-healing between cement and walnut-shell, and as a result, the mechanical resistance has increased (Guo *et al.* 2020).

Because of the structure of nanocellulose, it has a high specific surface area and increases the heat of hydration of cement. This caused a faster and better adhesion of walnut-shell with cement and as a result, the mechanical resistance of the board increased. These results are consistent with the studies conducted by Shayestehkia *et al.* (2020).

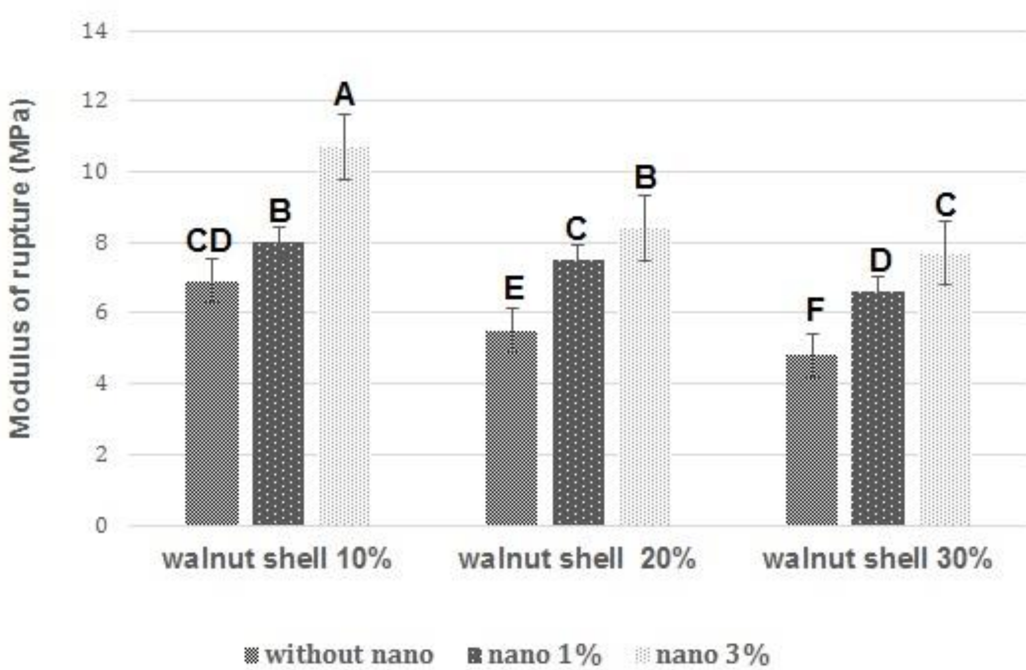

Fig. 3. Interaction of walnut shell mix ratio, cement, and cellulose nano gel on modulus of rupture of composites with Duncan's grouping

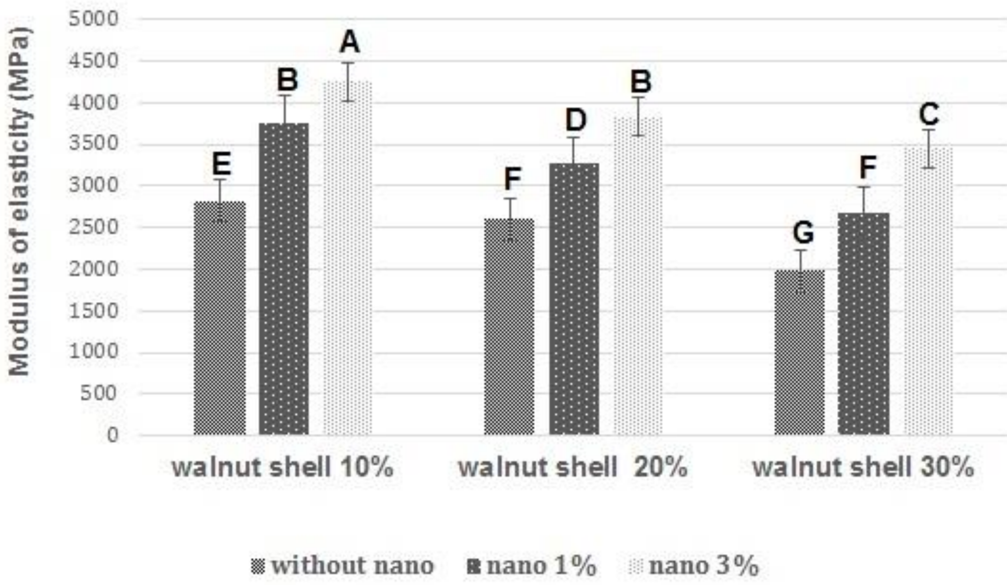

Fig. 4. Interaction of walnut shell mix ratio, cement, and cellulose nano gel on modulus of elasticity of composites with Duncan's grouping

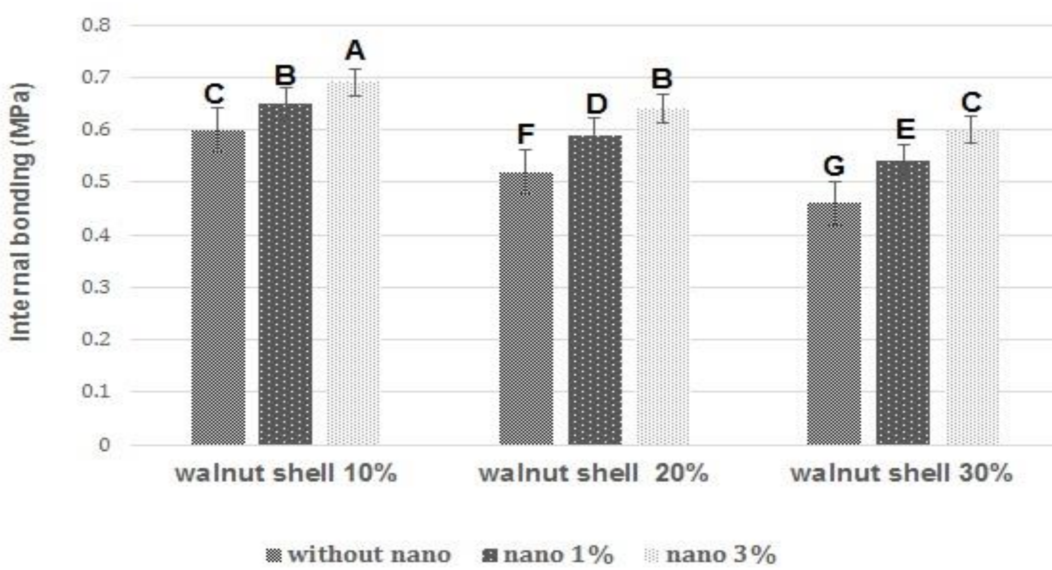

Fig. 5. Interaction of walnut shell mix ratio, cement, and cellulose nano gel on internal bonding of composites with Duncan's grouping

Physical Properties

The lowest amount of thickness shrinkage was observed in boards with a mixture of 10% walnut-shell, 90% cement, and 3% nanocellulose (Fig. 6). In relation to the density of the boards, it increased from 0% to 3% with the increase of cellulose nanogel. Boards with 3% nanocellulose and 10% walnut-shell have the highest density of 1.38 g/cm^3 (Fig. 7). In the composites containing 3% nanocellulose gel, the swelling thickness of the boards decreased compared to the boards without nanocellulose. In boards containing nanocellulose, due to the uniform distribution of nanocellulose in the cement matrix and walnut-shell, it causes more compaction of the composite, and as a result, less empty space is left for water to penetrate inside the board, reducing the thickness swelling. However, walnut-shell decreased the dimensional stability of the boards due to its hydrophilic properties. With the increase of nanocellulose, the fire resistance of the boards decreased (Fig. 8).

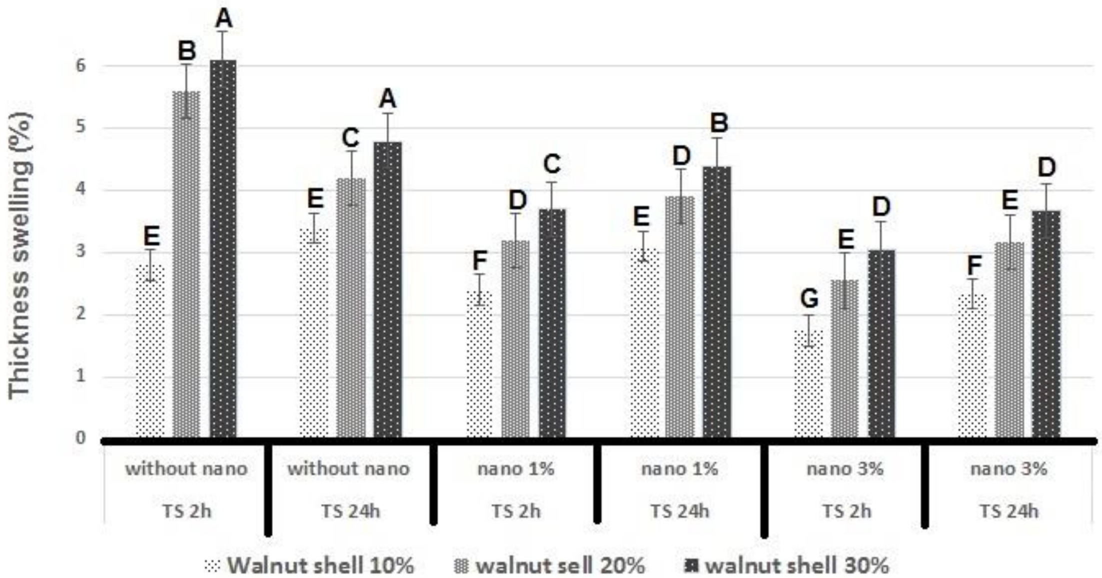

Fig. 6. Interaction of walnut shell mix ratio, cement, and cellulose nano gel on thickness swelling after 2 h and 24 h immersion in water of composites with Duncan's grouping

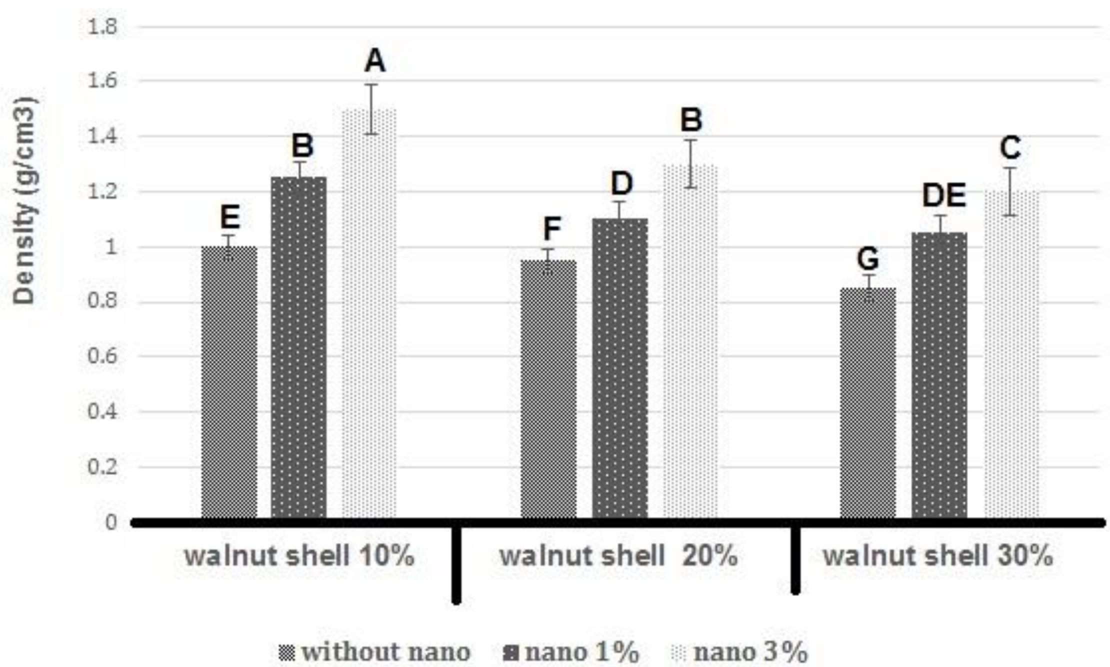

Fig. 7. Interaction of walnut shell mix ratio, cement, and cellulose nano gel on density of composites with Duncan's grouping

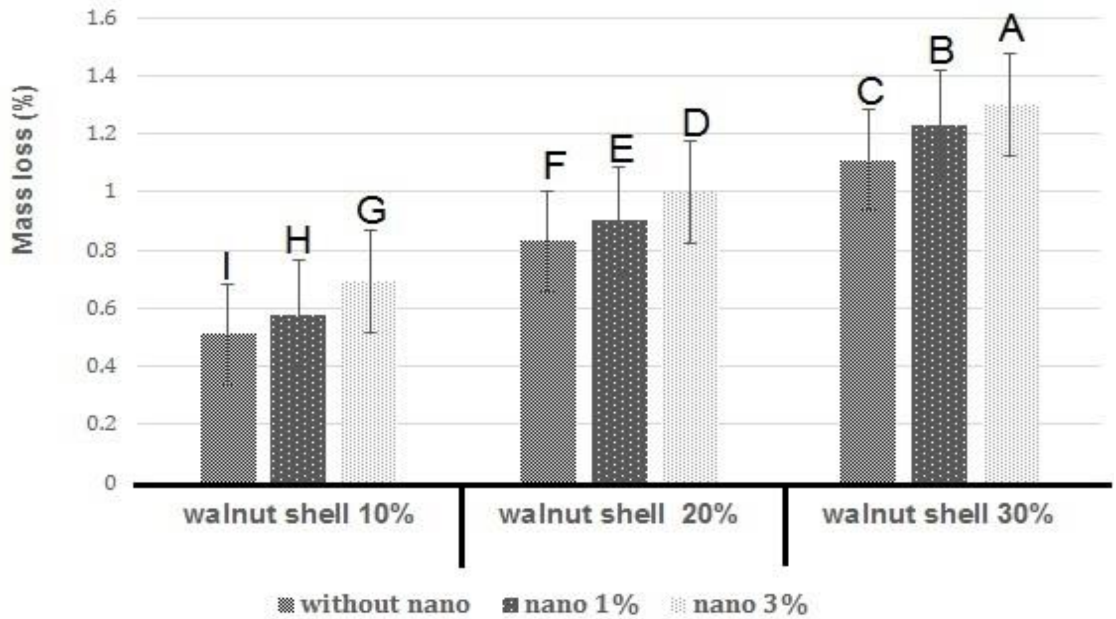

Fig. 8. Interaction of walnut shell mix ratio, cement and cellulose nano gel on mass loss of composites with Duncan's grouping

Nanocellulose likewise reduced the fire resistance of boards because of its minimal heat transfer and organic nature. Cellulose nano gel has more surface energy and because of the increase in the contact surface between cement and walnut-shell, it strengthens the common surface and fills possible voids inside the board, and as a result, it has increased the density of the board. This issue is evident in the microscopic photography (Fig. 9-A). The results obtained in this research are consistent with the results of Hassanpoor Tichi *et al*. (2019).

Microscopic Scanning

Microscopic photography (SEM) was used to examine the broken surface of the boards. In Fig. 9, different amounts of nanocellulose can be seen in the boards. As depicted in Fig. 9A, increasing nanocellulose content from 0% to 3% improved the connectivity and compatibility between walnut-shell and cement, which can lead to higher mechanical and physical strengths of boards. Furthermore, higher percentages of nanocellulose in the boards and reaction of this material with calcium sulfate resulted in high production of hydrated calcium silicate gel (Fig. 9A). This gel prevents the penetration of chlorine ions, sulfates, and destructive chemicals into the boards. It reduces permeability, durability, and self-healing between cement and walnut-shell. Further, these pictures show that nanocellulose contributed to cohesion, with a firmer and stronger connection between walnut-shell and cement. Thus, it filled the voids inside the board and increasing the dimensional stability and density of the boards. However, in Fig. 9-C, it is observed that the absence of nanocellulose in the boards led to the creation of large holes and caused a weak connection between walnut-shell and cement.

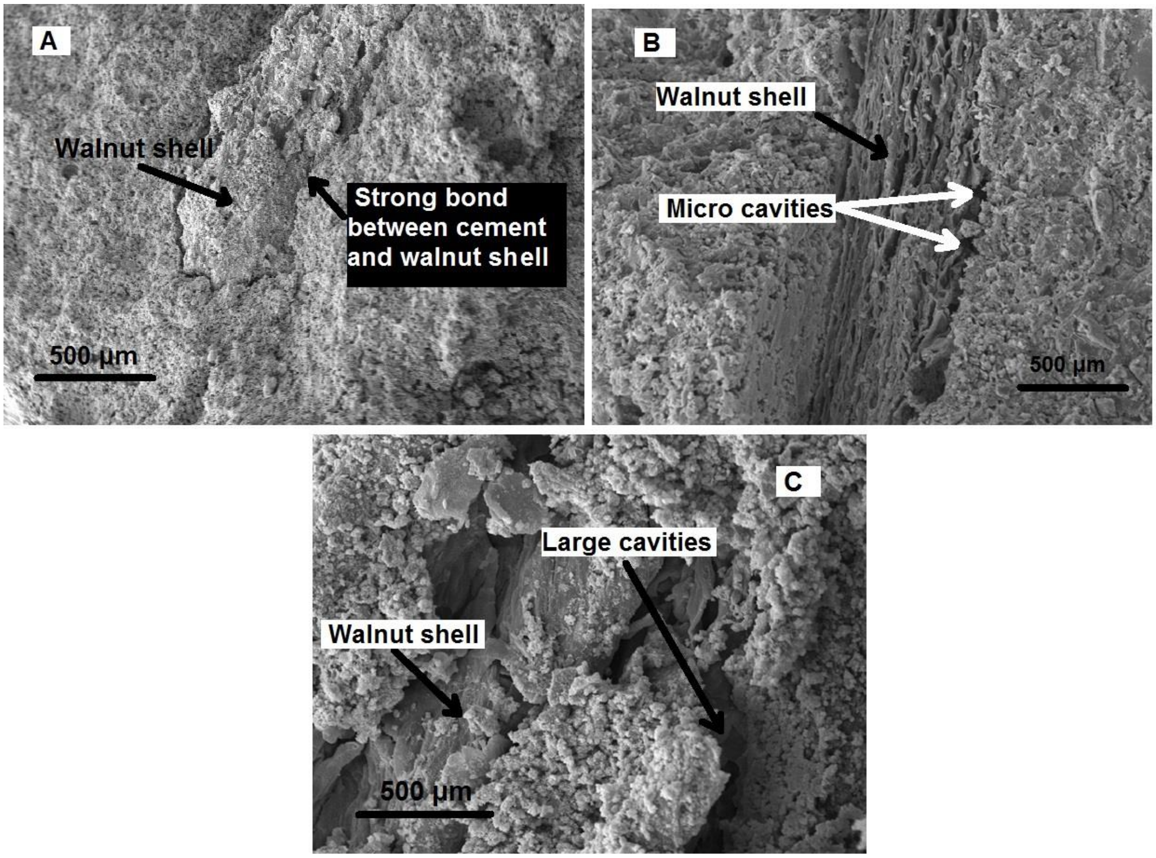

Fig. 9. Microscopic images of refractive surfaces, A: Boards containing 3% nanocellulose, B: Boards containing 1% nanocellulose, C: Boards without- nanocellulose

CONCLUSIONS

1. Modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond strength (IB) increased with addition of nanocellulose content. This is because of better compaction and distribution of particles and higher hydration temperature of boards.
2. The thickness swelling (TS) of the cement boards decreased with the addition of nanocellulose content (1% and 3%). This could have been related to the density of nanocellulose. The intrinsic density of nanocellulose density is greater than that of cement; thus, by increasing percentage, the board density increases.
3. Nanocellulose significantly decreased fire-retardant properties in the board. The low thermal conductivity of nanocellulose decreased heat transfer, which decreased the fire resistance of the composite boards. Also use of nanocellulose is not flame resistant due to its organic nature.
4. Compared to other wood products such as particle boards, medium density fiberboard (MDF) and oriented strandboard (OSB), this composite can be a suitable option for construction purposes due to its high fire resistance and less water absorption.

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