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Ecofriendly modification of both rice husk and recycled HDPE by coupling agent producing excellent wood plastic composite

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Abstract

Excellent wood plastic composite produced by reaction of rice husk, recycled high-density polyethylene (RH/HDPE) and polyethylene grafted maleic anhydride (PEGMA). The impact of varying concentrations of polyethylene grafted maleic anhydride (PEGMA) as a coupling agent in rice husk and recycled high-density polyethylene composites (RH/HDPE) on their mechanical and physical properties was examined. Analysis using scanning electron microscopy (SEM) revealed improved homogeneity of RH fibers within the HDPE matrix due to the presence of PEGMA. FT-IR findings indicated the formation of a new chemical bond at 1734 cm^{-1} between RH fibers and HDPE chains. Thermal gravimetric analysis (TGA) demonstrated enhanced thermal stability with higher PEGMA concentrations. The results revealed that the modulus of elasticity, maximum stress, maximum strain, and Shore D hardness of the samples increased with increasing PEGMA concentration, reaching a peak and then decreasing after reaching 2% wt. Abrasion resistance improved with higher PEGMA concentrations. Furthermore, swelling parameters in distilled water exhibited significant enhancement with increasing PEGMA concentration. The study will help in efficient utilizing rice husk and recycled HDPE as an alternate resource for the industrial manufacture of particleboards.

Keywords: Wood-plastic Composites (WPC), high-density polyethylene (HDPE), coupling agent (C.A), polyethylene grafted maleic anhydride (PEGMA), and Rice husk (RH)

1. Introduction

Wood polymer composites (WPCs) are becoming increasingly favored over natural wood in various applications such as automotive and construction. [1–4] . WPCs, or wood polymer composites, are composite materials crafted from a blend of natural fibers and polymer resins. These resins are often sourced from recycled plastics like polyvinyl chloride (PVC), polypropylene (PP), or polyethylene (PE).[1,2]. WPCs present numerous advantages as a construction material compared to natural wood. Their improved durability, resistance to moisture, dimensional stability, low maintenance needs, sustainability, and flexibility in design render them a viable option across various construction applications. The reinforcing fibers serve as the primary load-bearing component in composites. When subjected to stress, these fibers provide exceptional strength, stiffness, and resistance to bending and breaking. Effective bonding at the interface between the fillers and the matrix is crucial for transferring stress from the matrix to the fillers. Coupling agents play a key role in enhancing the adhesion between the polymer matrix and the wood fillers at this interface.

In wood polymer composites (WPCs), coupling agents are frequently employed to augment the adhesion and compatibility between natural fibers and the polymer matrix. Serving as a bridge, these agents bolster the bond between the two components, thus enhancing the overall performance of the composite material. [1,3]. The coupling agent aids in surmounting the inherent polarity and chemical distinctions between natural fibers and polymers. Natural fibers tend to be polar (hydrophilic), whereas PE is non-polar (hydrophobic). [4–6]. Such incompatibility may lead to inadequate adhesion between the polymer and wood fibers in wood-plastic composites (WPCs).[7]. Several coupling agents are commonly employed for WPCs, with maleic anhydride (MA) being one of the most prevalent. MA can react with the hydroxyl groups found in natural fibers, thus forming covalent bonds with the polymer matrix. [7–10]. Incorporating MA can improve the interfacial adhesion, mechanical properties, and water resistance of WPCs. [11]. Other coupling agents like Toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), and organofunctional silanes are frequently utilized in WPCs. These agents can interact with the hydroxyl groups present in wood fibers and the polymer matrix, resulting in the formation of urethane linkages. [12–14].

The choice of coupling agent is influenced by various factors, such as the particular polymer matrix, types of natural fibers utilized, desired properties, and processing parameters. Both the concentration and method of incorporating the coupling agent are significant in determining its efficacy. Optimizing the formulation of the coupling agent and adjusting processing parameters are crucial steps in achieving the desired performance of WPCs. Polyethylene grafted maleic anhydride (PEGMA) is frequently utilized in PE/wood composites to enhance wood dispersion and improve the compatibility between PE and wood fibers. [15–17]

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Rice Husk (RH), an agricultural lignocellulosic fiber that can be readily crushed into chips or small particles, has been selected as a substitute for wood-based raw materials. [18,19]. The utilization of RH can help conserve virgin forests, particularly in regions where wood resources are limited. Additionally, in response to environmental considerations, the burning of straw has been prohibited, as no practical applications for these waste materials have been identified, despite their widespread availability.

The objective of this study is to examine the impact of a coupling agent (PEGMA) on the mechanical properties of rice husk/high-density polyethylene (RH/HDPE) composites, as well as key mechanical parameters including stress, strain, density, water absorption, and hardness. This research is a component of an ongoing exploration into the recyclability of plastic and agricultural wastes, and their potential utilization in the manufacturing of wood polymer composites (WPCs)..

1. Experimental

The raw rice husk (RH) materials were procured from a local Egyptian company, ground, and then sieved to achieve a particle size of 140 µm. Subsequently, the RH was dried for 24 hours at 40°C to eliminate any moisture content. Recycled high-density polyethylene (HDPE) served as the plastic matrix in the RH/HDPE composite. The recycled HDPE pellets were obtained from an Egyptian company. Grafted polyethylene maleic anhydride (PEGMA) was utilized as a coupling agent, sourced from ALDRICH (456624). The chemical structure of PEGMA is depicted in Figure 1, while the working mechanism of the coupling agent is illustrated in Figure 2.

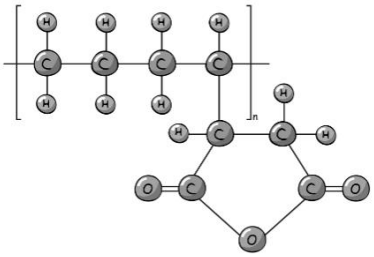

Fig.1 Chemical structure of the PEGMA

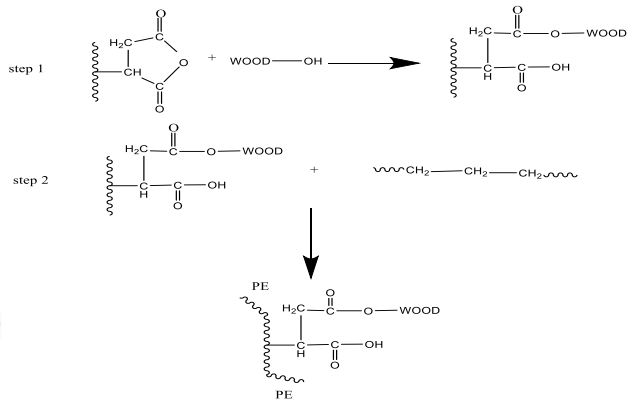

Fig. 2 The PEGMA work mechanism

Table 1 presents the constituents of the WPC composites employed in this investigation, featuring varying concentrations of PEGMA (0, 1%, 2%, 3%, and 5% wt.). Uncoated calcium carbonate was procured from the Egyptian Carbonate Co. for Mining. Stearic acid (SA) $C_{18}H_{36}O_2$, with a molecular weight of 284.49, was sourced from SRLCHEM and utilized as a lubricant. All materials were thoroughly mixed using a laboratory mixer for 5 minutes to ensure a homogeneous blend. Subsequently, the mixture underwent extrusion via a co-rotating twin-screw extruder (length/diameter = 13 and diameter = 29 mm). The barrel temperatures of the four zones ranged from 130 to 160°C from the feeding to the die zones. The screw speed was set at 80 rpm.

The extruded composite was crushed into small pieces and grinded to prepare it for molding by hot pressing. A mold measuring 200 x 200 x 10 mm was utilized for the hot pressing process. The hot press conditions were set at 150°C and 150 bar for a duration of 10 minutes. Subsequently, the mold was cooled down to room temperature using an air compressor. The resulting samples were then cut according to ASTM standards for subsequent mechanical and physical measurements.

Table 1. Study-developed formulas (in gram).

	NF0	NF1	NF2	NF3	NF5
RH	**60**	**60**	**60**	**60**	**60**
HDPE	**30**	**30**	**30**	**30**	**30**
$CaCo_3$	**10**	**10**	**10**	**10**	**10**
SA	**1**	**1**	**1**	**1**	**1**
PEGMA	**0**	**1**	**2**	**3**	**5**

Measurements

To investigate changes in chemical bonds, FT-IR analysis was conducted using a Bruker Alpha FTIR spectrometer. The transmittance range of the scan spanned from 4000 cm^{-1} to 400 cm^{-1}. Morphological analysis of the prepared composites was performed using scanning electron microscopy (SEM) with a Superscan S-550 instrument, operating at an accelerating voltage of 15 kV. Thermal stability assessments were carried out via thermogravimetric analysis (TGA) using a TGA-50 Shimadzu instrument. The TGA analysis was conducted under a nitrogen atmosphere with a flow rate of 30 ml/min, over a temperature range from room temperature to 900 ºC. Mechanical properties were evaluated using a Shimadzu AGX-100kNV2 100 kN

tensile machine, following ASTM D7031 standards. Abrasion resistance testing was performed according to ASTM D7031-11(2019) Section 5.17 and ASTM D4060-19, utilizing a homemade abrasion tester (refer to Fig. 3). The abrasion loss percentage (A_b) was calculated using the following formula:

$$A_b\% = \frac{(m_0 - m)}{m_0}\, x\, 100\ \%$$

where (m_0), and (m) represent the sample weight before and following abrasion, respectively.

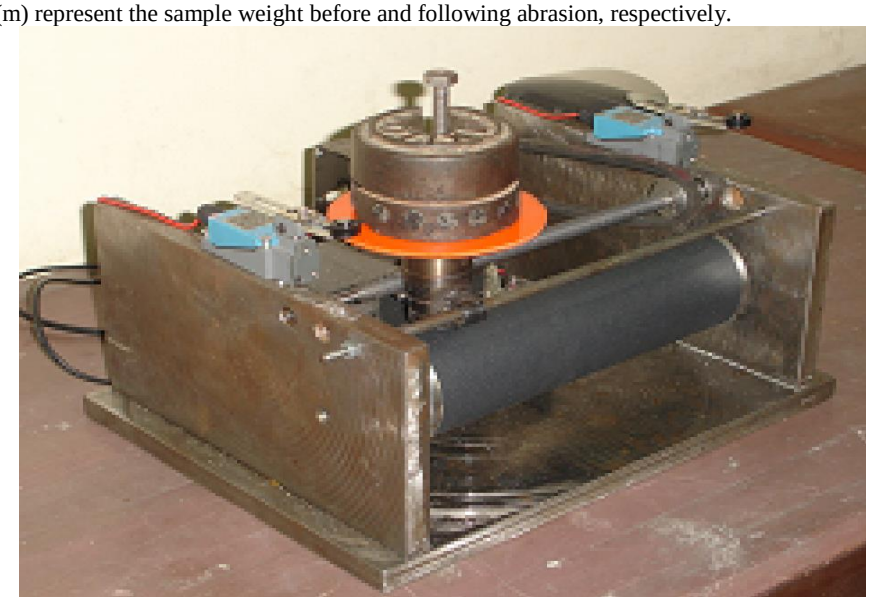

Fig. 3 handmade abrasion tester

The hardness of the prepared composites has been measured by using a durometer PCE-DD-D Shore D. Swelling was measured using ASTM-D-570-95 standard test techniques for the WPC property influence of water. Three cubic-shaped test pieces with dimensions of 10 x 10 x 10 mm^3 were employed. Weighed in a weighing bottle and immersed in 100 cm^3 distilled water at room temperature for 24 days. To remove excess water from the sample's surface, the samples were removed from the water and wiped using filter paper. The samples' swelling percentage (ΔM%) was estimated as follows:

$$\Delta M\% = \frac{(m_s - m_d)}{m_d}\, x\, 100\ \%$$

where (m_s) and (m_d) are the weights of the samples after swelling and free of water (dry sample), respectively. The following equation is used to compute the volume swelling in percentage (swelling index):

$$q - 1 = \frac{[\left(\frac{w_2}{w_1}\right) - 1]\rho_c}{\rho_s}$$

where (q) represents the ratio of a sample's swelled volume to its initial un-swollen volume, (q - 1) represents the swelling index, (w_1) represents the sample's dry weight, (w_2) represents the sample's weight after swelling, and (ρ_c) and (ρ_s) represent the densities of the specimen and the test solvent respectively [20].

3. Results and Discussion

Fig. 4 shows the morphology of the surfaces of the RH/HDPE composites at 0, 1, 2, and 3 wt. % of PEGMA. Fig. 4a shows numerous cavities for the micrograph of 0 wt. % PEGMA surface. The presence of these cavities and pulled-out fibers confirms that the adhesion and interfacial bonding between the wood and the matrix polymer was poor and weak which means the poor of the mechanical properties of the composites. However, by increasing the coupling agent contents to the composites, the cavities and cracks in the composite noticeably decreased, which means that the bonding and adhesion between the RH and the HDPE matrix increased and the composite got harder, as it can be shown in Fig. (4b, 4c and 4d) [7, 21].

3.2 FT-IR analysis

A new peak appeared in Fig. 5 (b) at 1739 cm^{-1} which confirmed the creation of ester bonds (-COO) between the RH fibers and PEGMA, as the reaction shown in Scheme 1 [22]. The interface between RH fiber and HDPE matrix appears to be better when PEGMA has been used at concentrations 2 wt. % and slightly better at 3% and 5% as shown in Fig. 5 (c and d). The backbone molecule of polyethylene had a strong peak of (-CH) at about 2915 cm^{-1} and 2847 cm^{-1}, where -CH2 bonds in HDPE were observed at 719 $cm^{-1.}$

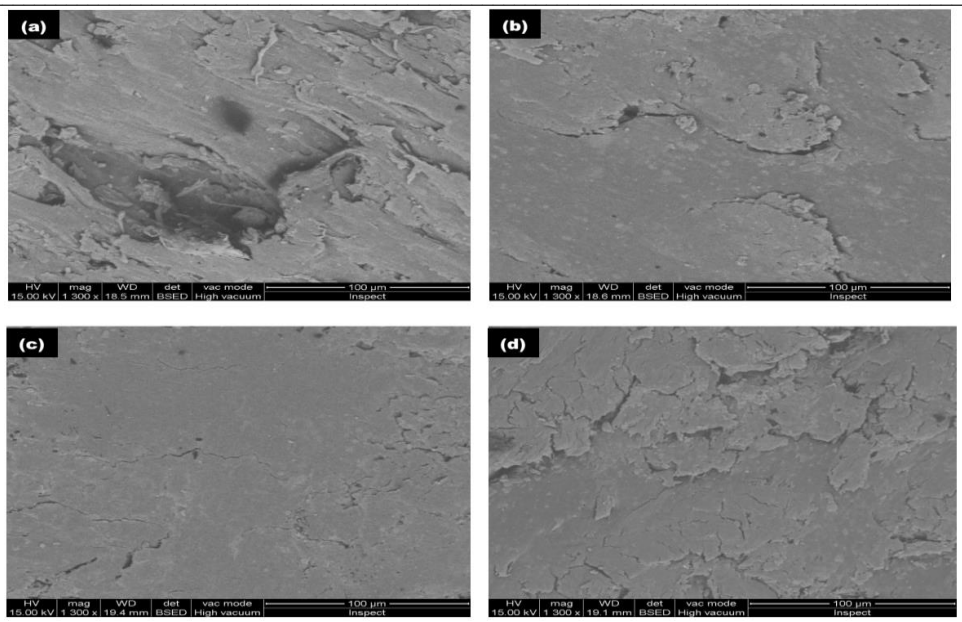

Fig. 4 (a) SEM of the composites without PEGMA, (b) treated with 1% of PEGMA, (c) treated with 2% of PEGMA and (d) treated with 3% of PEGMA.

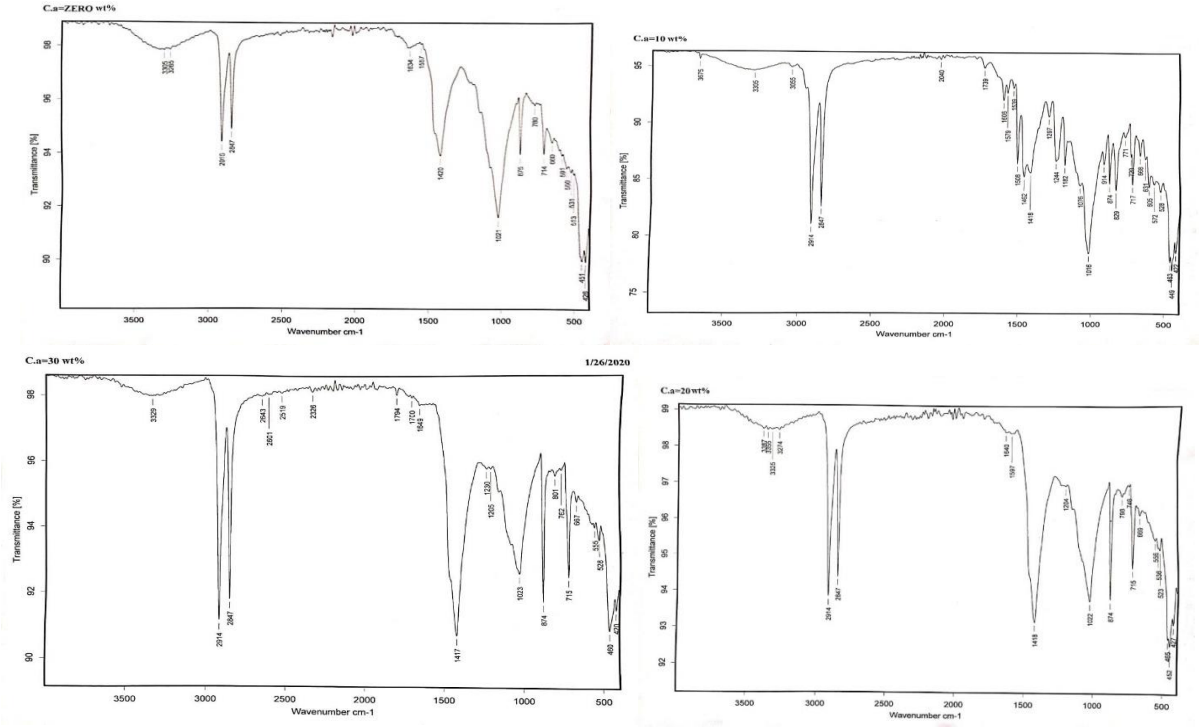

Fig. 5 FT-IR spectrum for RH/HDPE with (a) 0 wt. %, (b) 2 wt. %, (c) 3 wt. %, and (d) 5 wt. % of PEGMA

3.3 Thermogravimetric analysis (TGA)

TGA has been used to measure the thermal stability of WPCs prepared samples and illustrated in Fig. 6. One can see that, there are many steps of decomposition. First, some decrease in the weight started from the room temperature to 100 ° C which can be attributed to the dehydration process. The second stage in the mass loss is due to the decomposition of the RH fibers which starts at 200 ° C. In this stage, one can see the zero and 2 wt. % of coupling agent samples decompose faster than the other samples with a higher concentration of PEGMA. This behavior can be attributed to the created strong chemical bond between the PE chains and the RH fiber because the PEGMA has a positive significant effect on the thermal stability of the prepared WPCs samples. On the other hand, HDPE starts to decompose around 400 ° C (see the inset in Fig. 6) and finishes at around 500 ° C (23,24). After the full decomposition of HDPE and the RH fiber, the residual material is carbon and the inorganic materials e.g. $CaCO_3$. The final stage is the decomposition of $CaCO_3$. Upon heating past 600 °C the $CaCO_3$ begins the thermal decomposition whereby

$$CaCO_3 \rightarrow CaO + CO_2.$$

After the entire sample has experienced the breakdown reaction, or when the temperature has risen to about 850 o C, the solid phase CaO is still present on the scale [25].

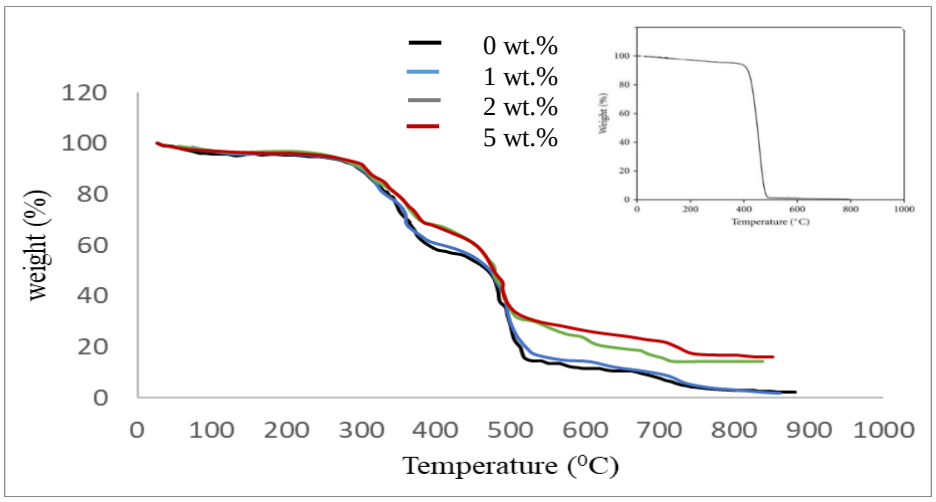

Fig. 6 TGA of RH/HDPE with different PEGMA content specimens.

3.4 Mechanical Properties measurements

Fig. 7 illustrates the stress-strain curves of the prepared composites. One can see that, the addition of PEGMA improved the tensile strength and by increasing the PEGMA percentage, the mechanical properties improved. Meanwhile, we found that the best improvement in the mechanical properties was achieved for 2 wt. % of PEGMA. This conclusion can be confirmed by Fig. 8, which shows the elastic modulus versus the PEGMA content. Furthermore, Fig. 9 and 10 show improvement of the PEGMA on the tensile strength of RH/HDPE composites.

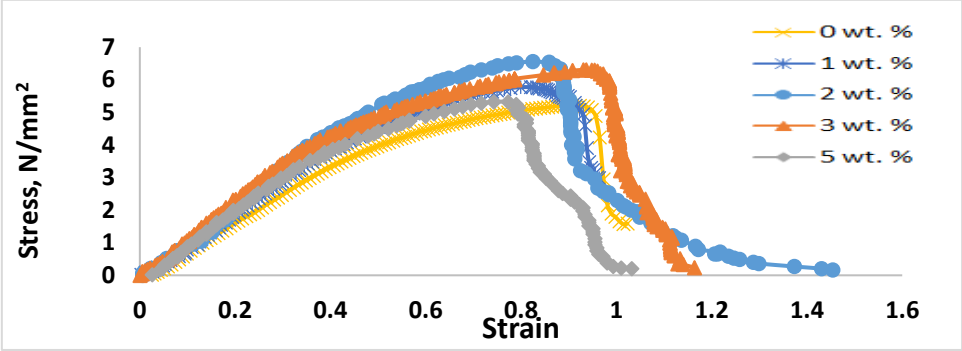

Fig. 7 Effect of PEGMA concentration on the stress-strain of WPC.

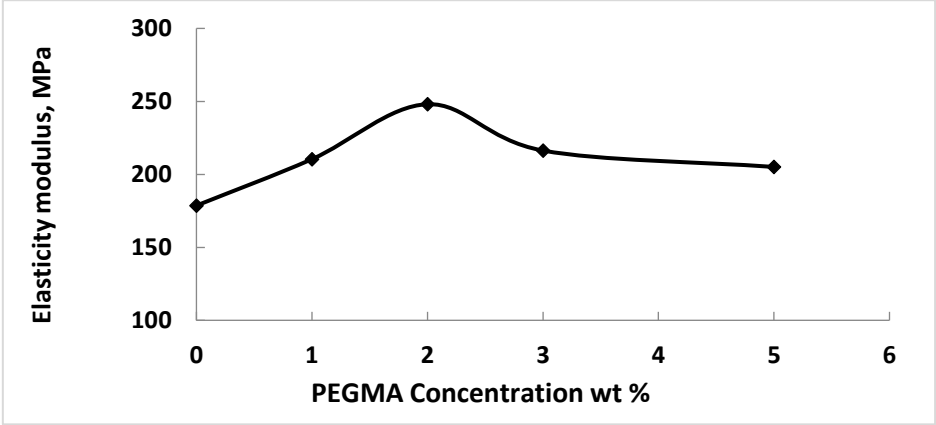

Fig. 8 Effect of PEGMA contents on modulus of elasticity of WPC.

Shore D of the WPCs prepared samples has been measured to study the effect of the concentration of PEGMA on the hardness of the samples, and illustrated in Fig. 11. It's clear from Fig. 11 that, by increasing the concentration of the PEGMA, the hardness increases and then saturates slightly after 2 wt. % of the coupling agent. This can be attributed to the creation of new chemical bonds. By increasing the bonds between the RH and the polymer chains, the composite becomes more rigid. As the concentration of PEGMA is increased, the percentage of abrasion is gradually reduced as shown in Fig. 12. This results in a stronger bond between the two materials, which makes the WPC more resistant to abrasion.

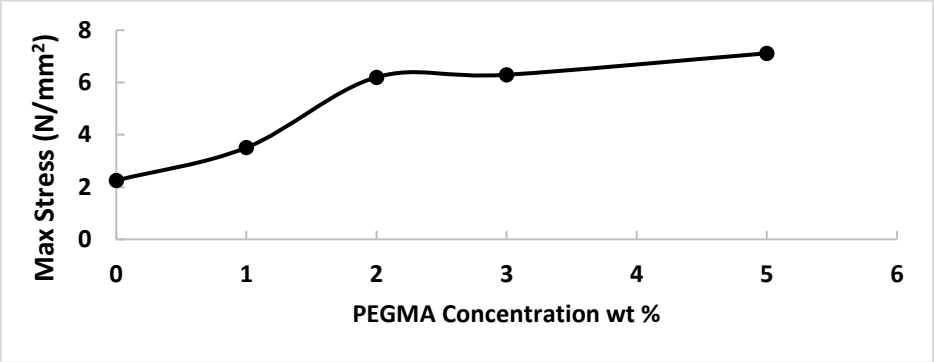

Fig. 9 Effect of PEGMA with various filler contents on max. Stress of WPC.

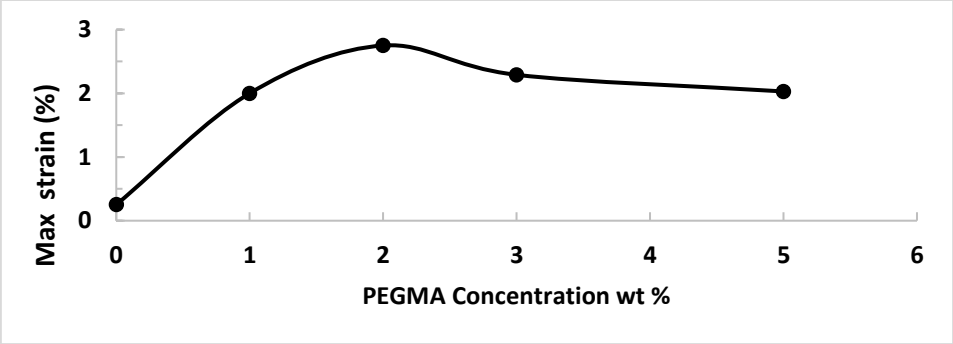

Fig.10 Effect of PEGMA with various filler contents on max. Strain of WPC.

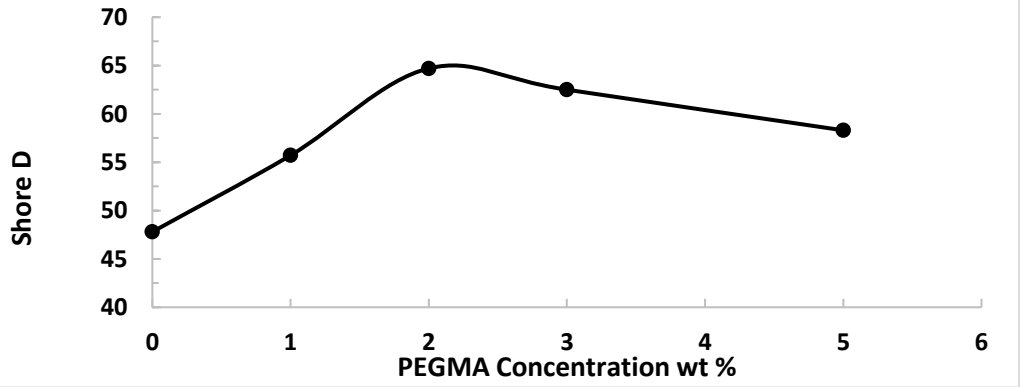

Fig. 11 Shore D vs the PEGMA concentration of RH/HDPE samples

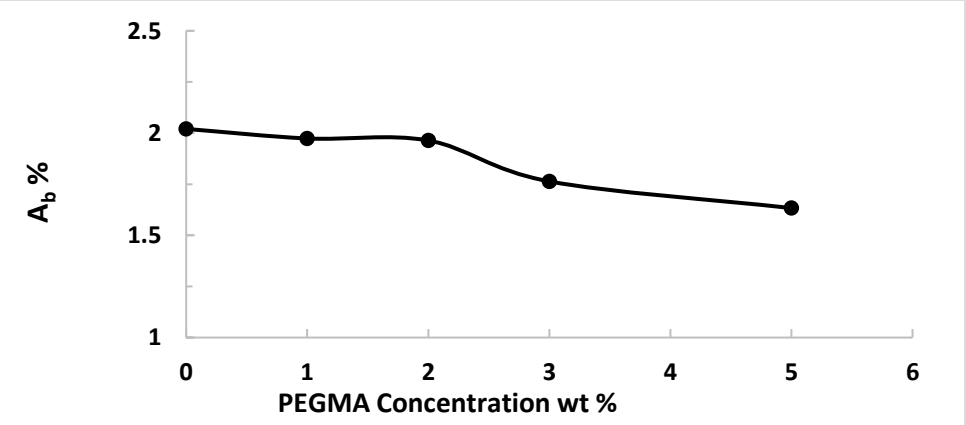

Fig. 12 Abrasion loss versus PEGMA content for RH/HDPE samples

Fig. 13 shows that the water absorption percent decreases while the PEGMA ratio increases, this may be attributed to the higher crosslinking density of the HDPE with RH fibers. In contrast, the swelling ratio is a direct indicator of the degree of crosslinking. The density of such cross-linking is estimated using the Flory-Rehner ratio and the average molecular weight of the polymer between cross-links (M_c) using equilibrium swelling measurements [15].

The graph of M_s/M_d vs $t^{1/2}$ for WPC filled with different ratios of PEGMA is shown in Fig. 14. All sorption processes are observed to be similar in nature and to have sigmoidal-shaped profiles. The effect of increasing the PEGMA content on the diffusion coefficient of water in the WPC matrix is shown in Fig. 15. By increasing the PEGMA loading, the diffusion coefficient drops until it reaches a minimum of 5 % wt. PEGMA content. The swelling index and crosslink density values for each of the suggested WPC specimens used in this study at varied PEGMA loadings are shown in Fig. 16. The swelling index reduces as PEGMA content increases, yet the degree of crosslink density rises, as seen in the figure. It is clear that the sample of the PEGMA with a swelling index of 5 % wt. has the maximum crosslink density and the lowest swelling index, making it the concentration that is regarded to be best based on swelling measurement [26].

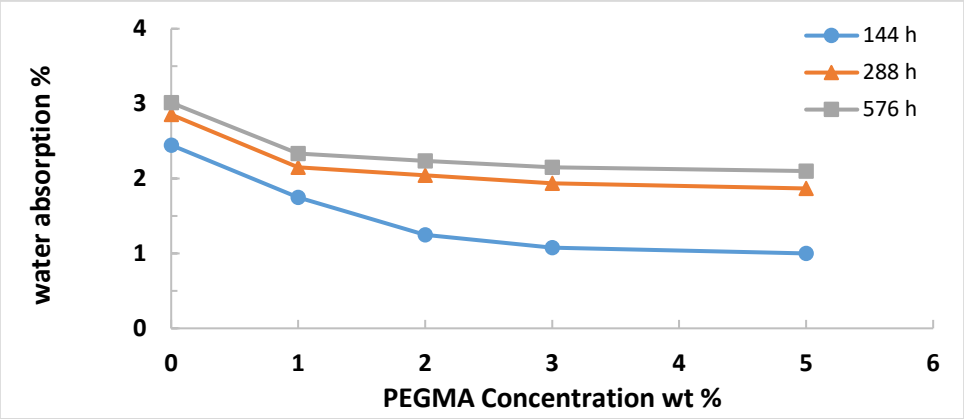

Fig. 13 Water absorption vs. PEGMA Conce. of RH/HDPE samples for 144, 288 and 576 h.

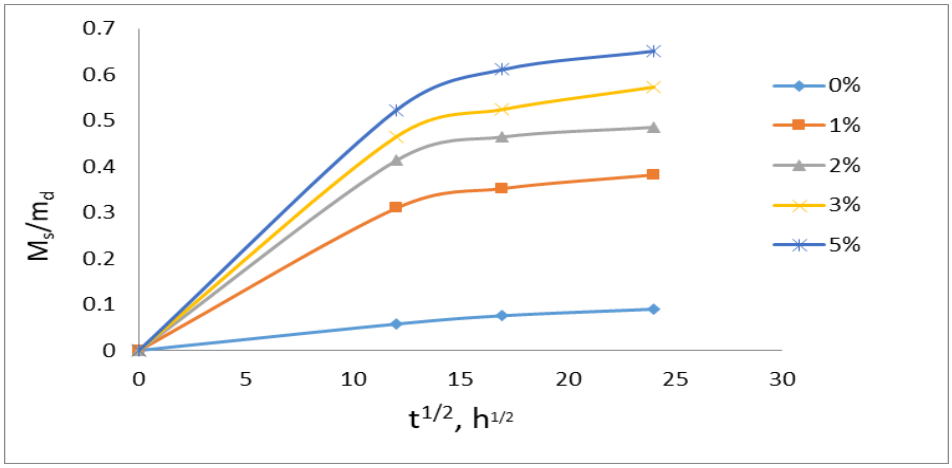

Fig.14 Variation of Ms/Md vs. $t^{1/2}$ for RH/HDPE composites at different PEGMA concentrations.

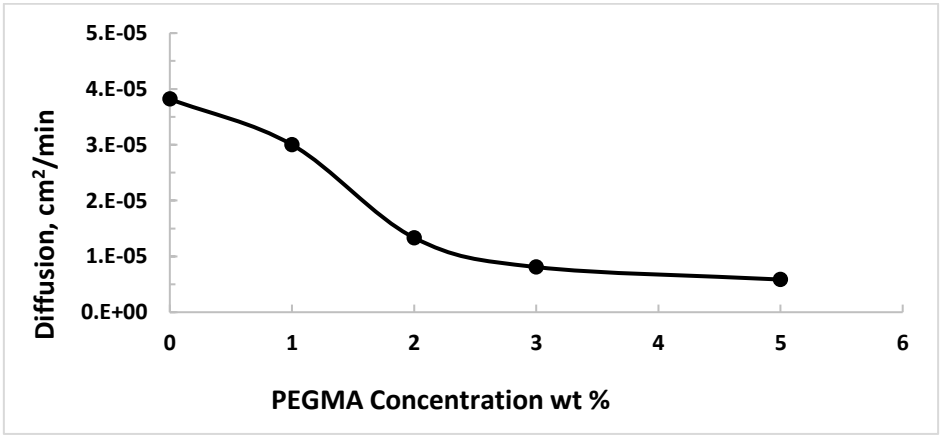

Fig. 15 Variation of the swelling index, crosslink density vs. PEGMA concentration.

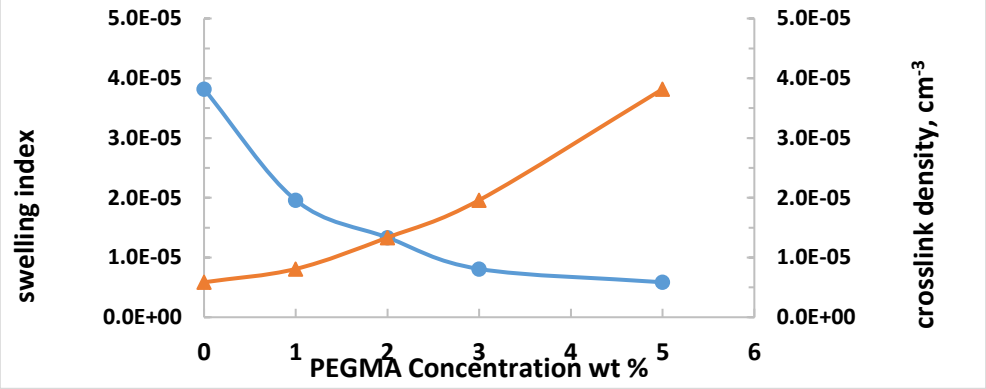

Fig. 16 Variation of diffusion coefficient vs. of PEGMA concentration.

Conclusion

This study demonstrates that the different concentrations of polyethylene grafted maleic anhydride (PEGMA) play a critical role in enhancing the physical and mechanical properties of RH/HDPE composites. An optimal PEGMA ratio enhances interfacial adhesion, resulting in improved water absorption resistance, and mechanical performance. However, excessive coupling agent content can lead to diminishing returns or even detrimental effects. These findings provide valuable insights for designing and optimizing wood-plastic composites with superior properties and performance.

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Data availability: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Supplementary information: Not Applicable

Compliance with Ethical Standards

- **Competing Interests:** The authors declare no competing interests.
- **Ethical Approval:** This research, focusing on materials science, does not involve experiments with human or animal tissues.

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Non-financial interests: none.

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