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SUSTAINABLE RUBBER BIO-COMPOSITE FOAMS WITH SILANE MODIFIED WOOD FIBER FOR ENHANCED THERMAL AND MECHANICAL PROPERTIES

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ABSTRACT

Ethylene propylene diene monomer (EPDM) rubber-based bio-composites, filled with silane-modified wood fiber (SiWF), underwent chemical foaming to produce crosslinked foams with enhanced properties. The incorporation of SiWF with peroxides played pivotal roles in reducing water absorption and improving thermomechanical performance. These innovative bio-composite foams demonstrated impressive enhancements in tensile strength and modulus, up to 90% and 420%, respectively, compared to the pure foam. Compressive strength and modulus also experienced notable increases, reaching up to 170% and 190%, respectively. Moreover, the foams exhibited lower apparent thermal conductivity than unfilled pure EPDM foam across the heating temperature range, suggesting their potential application as effective insulation materials. The fabrication process involved batch mixing and compression molding of EPDM bio-composites with Si-WF. Investigation into fiber loading, silane modification, and in situ cross-linking revealed Si-WF's reduced surface energy, resulting in substantially lower water absorption and heightened thermal stability compared to EPDM with unmodified wood fibers. The enhanced dispersion of Si-WF in the elastomer matrix, observed through fractography studies, played a crucial role in the observed improvements in tensile strength and modulus of the EPDM bio-composites. This multifaceted approach demonstrates the potential of these bio-composite foams for diverse applications, particularly as advanced insulation materials with superior mechanical and thermal properties.

1 INTRODUCTION

EPDM rubber, prized for its industrial versatility, faces environmental challenges in curing processes involving toxic sulfur, additives, and catalysts. Growing global concerns around climate change and petrochemical related pollution are steering the rubber industry toward eco-friendly solutions [1]. Sulfur-free crosslinking methods, like reactive silane grafting, are gaining traction for EPDM [2]. Simultaneously, the incorporation of bio-based fillers, especially wood fibers (WF), into EPDM composites is explored for sustainability. WF's inherent polarity is mitigated via silane modification that led to enhanced compatibility and participation in EPDM cross-linking, as well as improving thermal and mechanical properties [3].

For EPDM foam, both physical and chemical foaming methods are employed, with chemical foaming being cost-effective and well-established [4]. The commonly used chemical foaming agents include sodium bicarbonate, 4,4'oxybis(benzenesulfonylhydrazide) (OBSH), and azodicarbonamide (ADC). However, the lower decomposition temperatures of the former two are insufficient for optimal mixing when high filler loadings, like WF, are involved. High shear mixing leads to undesired high temperatures (up to 180 °C) causing premature foaming. On the contrary, ADC foaming requires higher temperatures (> 200 °C), leading to thermal degradation of WF. Achieving optimal foaming with ADC at lower temperatures necessitates a decomposition accelerator, enabling effective mixing while preventing thermal degradation of thermolabile bio-based fillers. This multifaceted approach aligns with the industry's shift towards environmentally sustainable EPDM processing.

This study focuses on the development of functional and high-performance EPDM bio-composite foams. Silane-modified wood fibers (SiWF) serve as simultaneous reinforcing and crosslinking agents for these foams. The investigation emphasizes the impact of factors, such as fiber loading, silane modification, and cross-linking on the physical and mechanical properties of the prepared EPDM bio-composite foams. The comparison includes water absorption, mechanical properties, thermomechanical properties, thermal conductivity and inner morphology. The findings of this research contribute to advancing high-performance EPDM composite foams and expanding the applications of rubber-based bio-composites.

2 MATERIALS AND METHODS

2.1 Materials

EPDM: SABIC, Saudi Arabia. Dicumyl peroxide (DCP), azodicarbonamide (ADC) and zinc oxide (ZnO, the foaming accelerator): Sigma Aldrich. Wood fiber (WF): Ontario Sawdust Supplies, Canada. Vinyltriethoxysilane: Evonik, Germany.

2.2 Methods

The silane modifications of WF and the batch mixing were following a previous study [3]. The compound sheets were foamed at 185 °C for 20 min. The sample code and compositions are displayed in **Table 1**. Some real life foam samples are shown in **Fig. 1**.

Table 1. Sample code and compositions

Sample code	EPDM (wt.%)	DCP (phr.)	ADC (phr.)	ZnO (phr.)	WF (wt.%)	SiWF (wt.%)
Pure foam	100	0	8	0.1	0	0
10WF	90	0	8	0.1	10	0
20WF	80	0	8	0.1	20	0
10SiWF	90	0	8	0.1	0	10
20SiWF	80	0	8	0.1	0	20
10SiWF-DCP	90	0.1	8	0.1	0	10
20SiWF-DCP	80	0.1	8	0.1	0	20

The water uptake was recorded periodically and the absorption percentage was calculated based on the weight increase after soaking in distill water. The tensile tests were following the ASTM D412. The compressive test was performed at a compression speed of 5 mm/min. Compressive strength was determined at 80% deflection, while compressive modulus was calculated at 5% compression of the original thickness. The thermal conductivity was tested according to ASTM E2548. The internal structure of the EPDM bio-composite foams was analyzed using environmental scanning electron microscopy (ESEM, FEI Quanta FEG 250). The observations were conducted at a voltage of 20 kV under low vacuum conditions. The thermomechanical properties were measured via a dynamical mechanical analyzer (DMA, Q800, TA Instrument).

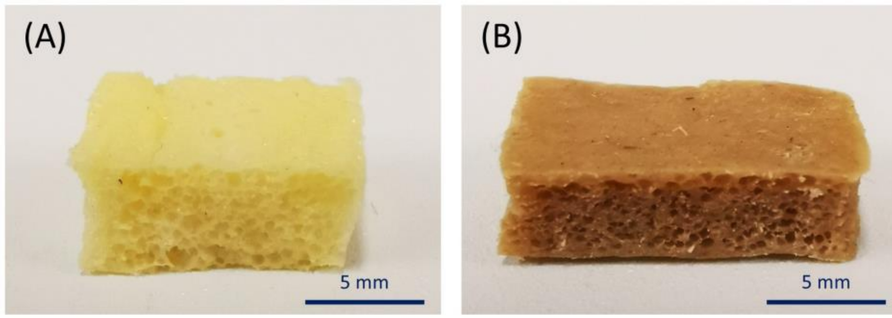

Figure 1. Real life EPDM foams. (A) Pure foam; (B) 10SiWF-DCP

3 RERSULTS AND DISCUSSION

3.1 Water absorption

The water absorption of EPDM foam is shown in **Table 2**. As soaking days increased from 4 to 32 days, water absorption generally rises across all samples. The EPDM foams with pristine WF exhibit the highest water absorption percentages at each soaking duration, while the samples containing SiWF and SiWF-DCP show the lowest absorption rates, even lower than the unfilled pure foam. Additionally, the incorporation of DCP further reduces water absorption compared to SiWF alone. These findings suggest that both silane modification and DCP induced crosslinking contributed to enhancing the water resistance of EPDM bio-composite foams.

Table 2. Water absorption percentage over soaking days

Sample code	4 days (%)	8 days (%)	16 days (%)	24 days (%)	32 days (%)
Pure foam	11.7 ± 0.2	13.4 ± 0.6	15.6 ± 0.5	23.2 ± 2.1	24.1 ± 2.8
10WF	10.2 ± 0.5	12.7 ± 0.6	17.0 ± 0.8	31.4 ± 2.7	32.2 ± 1.6
20WF	12.3 ± 0.3	18.6 ± 1.9	24.6 ± 0.6	30.9 ± 1.3	31.8 ± 1.0
10SiWF	6.4 ± 0.8	6.4 ± 0.5	11.5 ± 1.8	19.2 ± 1.8	20.5 ± 0.5
20SiWF	7.1 ± 0.1	10.6 ± 0.8	14.1 ± 0.2	24.7 ± 1.3	25.9 ± 0.4
10SiWF-DCP	5.7 ± 0.2	5.7 ± 0.2	8.1 ± 0.4	15.2 ± 1.1	16.2 ± 0.7
20SiWF-DCP	6.7 ± 0.1	9.6 ± 0.6	13.5 ± 0.2	19.1 ± 1.3	20.2 ± 0.3

3.2 Thermomechanical properties

The thermomechanical properties of EPDM foam is displayed in **Table 3**. The table provides data on the storage modulus (G') and glass transition temperature (T_g) of various EPDM bio-composite foam samples at different temperatures. At -70°C, the storage modulus ranges from 249.4 MPa for pure foam to 880.1 MPa for 10SiWF-DCP foam, indicating increased stiffness with the incorporation of wood fibers and further enhancement with silane modification and DCP induced crosslinking. At -40°C and 20°C, similar trends in G' are observed, with higher values associated with foam samples filler with WF and further improved once cross-linked. The T_g tends to increase with the addition of wood fibers and the silane modification, suggesting the prohibition of the fillers on the chain mobility. It is further increased when DCP was added, showing the chain mobility being constrained by the formed crosslinking. These results highlight the effectiveness of incorporating silane-modified wood fibers, particularly when treated with DCP, in enhancing the thermomechanical properties of EPDM bio-composite foams across a range of temperatures.

Table 3. Thermomechanical properties of EPDM bio-composite foams

Sample code	G' (MPa)			T_g (°C)
	-70 °C	-40 °C	20 °C	
Pure foam	249.4	12.3	0.9	-43.3
10WF	432.3	40.8	2.8	-41.0
10SiWF	544.7	39.2	2.3	-40.5
10SiWF-DCP	880.1	75.9	4.2	-39.7

3.3 Mechanical properties

3.3.1 Tensile properties

The tensile properties are shown in **Table 4**. The table outlines the tensile strength and tensile modulus of various EPDM bio-composite foam samples. Tensile strength measures the maximum stress a material can withstand before breaking under tension. 10SiWF-DCP exhibits the highest tensile strength at 2.51 MPa that shows 90% improvement than the pure foam, which has the lowest tensile strength at 1.32 MPa. Tensile modulus represents a material's stiffness or resistance to deformation under tension. 20SiWF-DCP shows the highest tensile modulus at 3.07 GPa, indicating its superior stiffness compared to other samples. It is 420% higher than the pure foam, which shows the lowest tensile modulus at 0.59 GPa.

Table 4. Mechanical properties of EPDM bio-composite foams

Sample code	Tensile strength (MPa)	Tensile modulus (MPa)	Compressive strength (MPa)	Compressive modulus (MPa)
Pure foam	1.32 ± 0.09	0.59 ± 0.05	5.48 ± 0.38	0.82 ± 0.07
10WF	1.56 ± 0.20	1.57 ± 0.11	9.05 ± 0.26	1.34 ± 0.11
20WF	1.76 ± 0.08	2.73 ± 0.20	10.45 ± 1.18	1.96 ± 0.06
10SiWF	2.12 ± 0.11	2.1 ± 0.11	11.19 ± 0.11	2.09 ± 0.16
20SiWF	2.09 ± 0.20	2.63 ± 0.15	11.37 ± 0.20	2.65 ± 0.22
10SiWF-DCP	2.51 ± 0.18	2.63 ± 0.15	10.57 ± 0.18	1.99 ± 0.15
20SiWF-DCP	1.90 ± 0.08	3.07 ± 0.12	14.95 ± 0.08	2.35 ± 0.07

3.3.2 Compressive properties

The compressive properties are shown in **Table 4**. The table summarizes the compressive strength and tensile modulus of the prepared EPDM bio-composite foams. Compressive strength refers to the maximum stress a material can withstand before deforming or collapsing under compression. 20SiWF-DCP demonstrates the highest compressive strength at 14.95 MPa, which is 170% increased than the pure foam (5.48 MPa). Compressive modulus measures a material's resistance to deformation under compressive loads. Once again, 20SiWF-DCP displays the highest compressive modulus at 2.35 GPa, while pure foam shows the lowest at 0.82 GPa. The former shows an improvement of 190%.

Overall, the incorporation of wood fibers, especially silane-modified ones, enhances the mechanical properties of EPDM bio-composite foams. Silane modification improves interfacial adhesion between fibers and the EPDM matrix, resulting in increased strength and stiffness. Additionally, the application of DCP further enhances mechanical properties by forming crosslinking within the composite foams.

3.4 Thermal insulation

The apparent thermal conductivity (λ) values are summarized in **Table 5**. The table presents the apparent thermal conductivity values (in W/(m·K)) of various EPDM bio-composite foam samples at different temperatures (310 K, 320 K, and 330 K). The results indicated that the λ of all samples increased with temperature, which is likely due to the increased molecular chain mobility. At each temperature, apparent thermal conductivity values decrease as the percentage of wood fibers increases in the foam composition. For instance, at 310 K, pure foam exhibits the highest apparent thermal conductivity of 0.047 W/(m·K), while 10SiWF-DCP demonstrates the lowest at 0.026 W/(m·K). This trend continues across all tested temperatures. Furthermore, the incorporation of DCP alongside silane-modified wood fibers results in varied thermal conductivity values compared to their counterparts without DCP treatment. Notably, 10SiWF-DCP and 20SiWF-DCP show fluctuating thermal conductivity values across different temperatures, suggesting a complex interplay between DCP induced crosslinking and thermal conductivity. Overall, the findings highlight the benefit of WF as fillers on the thermal conductivity of EPDM bio-composite foams, with potential implications for applications requiring thermal insulation and heat management.

Table 5. Apparent thermal conductivity (λ) of EPDM bio-composite foams

Sample code	**λ (W/(m·K)) at varied temperatures (K)**		
	310	**320**	**330**
Pure foam	0.05	0.08	0.13
10WF	0.03	0.05	0.07
20WF	0.04	0.05	0.11
10SiWF	0.04	0.06	0.09
20SiWF	0.04	0.05	0.10
10SiWF-DCP	0.03	0.05	0.11
20SiWF-DCP	0.04	0.07	0.12

3.5 Cell and fiber morphology

The foam cell and fiber morphology of the selected samples are shown in **Fig. 2**. For the 10WF sample (Fig. 2A), it displays mixed open and close-cell structures. The WF can be seen dispersed within the EPDM matrix. As shown in Fig. 2A and Fig. 2D, it is observed that there is interfacial detachment between the WF and rubber matrix, due to the incompatibility. For the foam with silane modified WF (10SiWF, shown in Fig. 2B), it shows a close-cell structure basically, and the modified fiber has improved dispersion and compatibility with the rubber, as shown in the magnified figure (Fig. 2E). The morphology of cells and fibers correlate well with the water absorption results. Once the foam was cross-linked, it shows a close-cell morphology, the fibers show compact interface and bonding with the rubber matrix. The enhanced dispersion of Si-WF in the elastomer matrix, observed through morphology studies, played a crucial role in the observed improvements in tensile strength and modulus of the EPDM bio-composites. Furthermore, the figures show consistent outcome with the water absorption and thermomechanical properties.

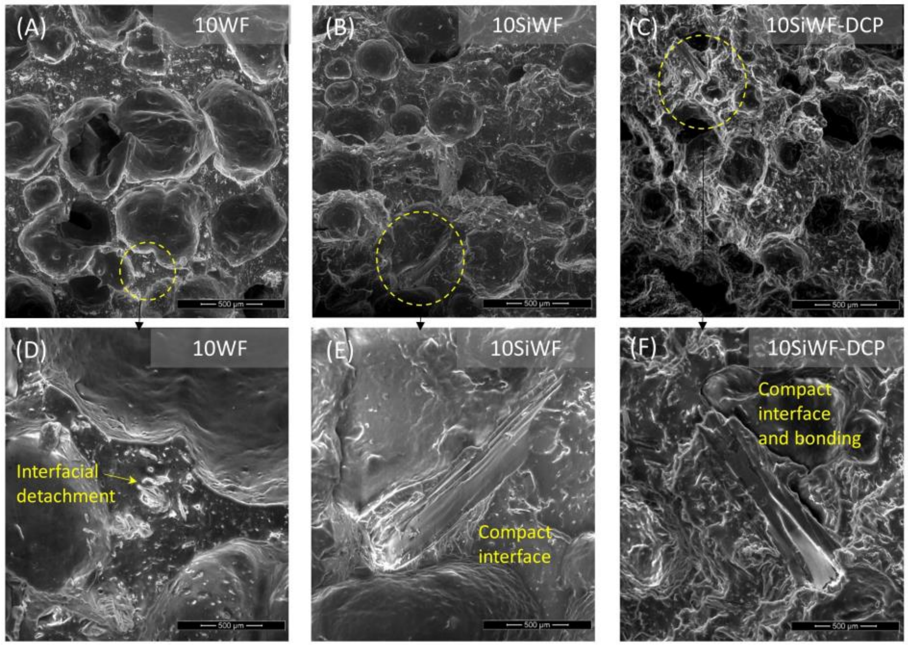

Figure 2. Cell and fiber morphology of the EPDM foam filled with wood fiber.
(A, D) 10WF; (B, E) 10SiWF; (C, F) 10SiWF-DCP

4 CONCLUSIONS

EPDM-based bio-composite foams, with silane-modified wood fibers (SiWF) and dicumyl peroxide (DCP), showed significant enhancements in properties. Tensile strength and modulus improved up to 90% and 420%, while compressive strength and modulus increased by up to 170% and 190%, respectively, compared to pure foam. Lower water absorption and improved thermal conductivity were observed. SiWF's enhanced dispersion in the elastomer matrix and the DCP induced crosslinking contributed to these enhancements. These bio-composite foams exhibit potential for various applications, particularly as advanced insulation materials with superior mechanical and thermal properties.

5 REFERENCES

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