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Research Article

Usability of Pine Sawdust and Calcite Together as Filler in Polyester Composites

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Abstract:

Two different types of fillers are used in composites, natural and synthetic. Natural fillers are gaining popularity as an alternative to synthetic fillers due to low production cost, lightweight, and abundance of renewable resources. Although thermoplastics are widely used as matrix material in natural fillers-filled composite materials, there are thermoset polymers such as epoxy and polyester. The most known and used natural-organic fillers are wood sawdust and fibres. Wood sawdust can be obtained easily and cheaply as waste in furniture production and is generally used after appropriate sieving. In this study, general-purpose polyester resin was preferred as matrix material. Calcite and pine wood sawdust are used as fillers. Calcite is used as a synthetic filler and pine wood sawdust is a natural filler and can be found easily. Thus, the usability of natural and synthetic fillers together was investigated. Composite samples were prepared by pouring the mixture into an open Teflon mold. The physical properties of the samples such as tensile, impact, density, and hardness were investigated. Images of broken surfaces were analysed by SEM. As a result of the study, it was evaluated that pine sawdust and calcite can be used together in polyester-based composite applications.

1. Introduction

Natural fibres have been used in composites for over 3000 years as both filler and reinforcement. Recently, the use of natural fibre-filled composites is very common. As natural fibres, many types of natural fibres such as flax, hemp, jute, straw, wood fibre, rice husk, wheat, barley, oats, rye, cane (sugar and bamboo), grass canes, kenaf, ramie, oil have been investigated for use in plastics. Natural fibres have the advantage of being renewable resources and having marketing appeal. Natural fibres have been used in world markets for many years. Natural fibres are increasingly used in automotive and packaging materials. Agricultural wastes include wheat husk, rice husk, and their straw, hemp fibre, and peels of various dried fruits. These agricultural wastes are preferred to prepare fibre-reinforced polymer composites for commercial use [1-7].
Due to the global energy crisis and the pursuit of sustainability, natural fibre reinforced polymer composites attract more attention than synthetic fibre reinforced polymer composites with their superior properties such as non-toxicity, non-irritation to the skin, eyes, and respiratory tract, and non-corrosive [8].
Recently, natural fibres have been preferred as reinforcing fillers in polymer matrices. Composite materials prepared with natural fibres have replaced traditional materials in automotive parts, wood substitutes and various technical applications due to some reasons such as being easy to process and light [9].
Natural fibre composites are lightweight, environmentally friendly, renewable, biodegradable, accessible, and sustainable. Natural fibres outperform man-made or synthetic fibres in terms of performance. However, the morphology and chemical composition of natural fibres cannot be completely controlled compared to synthetic fibres [10].
Natural fibres have certain advantages over synthetic fibres. The main advantages of lignocellulose fibre reinforced polymer composite materials are that they are biodegradable, easy to find, and easily degradable [11].
Natural fibre-based fibres are also commonly used with both thermoset and thermoplastic-based matrix

materials [12]. The polymers used in natural fibre composites are mostly polyolefins. This allows the processing temperature to be below 200 °C. Above this temperature, degradation of the fibres was observed [9,13,14]. However, it can also be used in thermosets. In this study, unsaturated polyester resin was preferred as the matrix material of the composite due to its widespread use.

Unsaturated polyester resin is a thermoset polymer with good properties such as high economic potential and easy application in industry. It forms about -three-quarters of the thermosets used in the polyester composite industry, which is used extensively in coatings and as a matrix material. It is very useful as it can be chemically modified with crosslinkers. Unsaturated polyester resins are intertwined with almost all areas of the composite industry such as adhesives, coatings, sealants, and laminates. The important advantages of unsaturated polyester resins come from their good mechanical properties, dimensional stability, resistance to chemicals, electricity, air, ability to be processed by conventional methods, and low cost [15-20]. Unsaturated polyester resins have a wide application area and these areas are expanding with market demands they are materials that are developing to produce more environmentally friendly products [21-25]. Particle use in composites has both filler and reinforcing uses. Particles such as graphene oxide and magnesium hydroxide in micron or nano sizes are used as reinforcing for polymer matrix composites. The particles are collected under 3 main groups natural, synthetic, and organic. The vast majority of fillers such as talc, mica, and calcium carbonate are available industrially and are used in different fields [26]. Among them, calcium carbonate is mainly used because of its low cost and commercial abundance. With the addition of optimum calcium carbonate concentration, the thermal, mechanical, and optical characteristics of the polymers are significantly expanded [27]. Calcium carbonate ($CaCO_3$) is widely used as a filler in the plastics industry. It is used not only in thermoplastics such as Polyvinylchloride (PVC) but also in thermosets such as polyester. Calcium carbonate is abundant in nature as limestone and marble, and $CaCO_3$ filler can be produced from these minerals at a very low cost. Its natural color is white and can be easily colored. Chemically stable up to 800 °C [28]. Inorganic fillers such as calcium carbonate, metal particles, and mica provide sufficient thermal stability to the polymer, as well as provide higher wear resistance, toughness, and hardness when used in composite materials compared to pure polymer [29].

In this study, the use of pine sawdust, which is produced as a large amount of waste in the furniture industry, and calcite, which is heavily preferred in the industry, as a filler were examined. Pine trees are known as coniferous (coniferous) tree species and their wood is hard, durable, resinous, and of good quality. It is used as a building material because it has good nail and screw-holding resistance and is easy to process. Due to its easy processing, it is used in the building materials, furniture, and packaging industries, and waste sawdust is obtained intensively [30].

2. Material and Methods

2.1. Materials

Calcite and pine sawdust were used together as a filler in the composite material. Pine sawdust was obtained as waste from local companies manufacturing furniture. Pine sawdust was sieved and used in sizes of 0-250 µm. Calcite (Nidaşcarb 3), which is used extensively industrially, was obtained from Nidaş Madencilik A.Ş. Physical and chemical properties of calcium carbonate are shown in Table 1. Polyester was chosen because of its widespread use in the industry as a thermoset resin. Methyl ethyl ketone peroxide (Erco Boya, Istanbul) was used as a reaction initiator. Cobalt naphthalate, which is used as an accelerator, was not used separately because it was included in the resin. Teflon mold was used to prepare test samples.

Table 1. *Properties of Calcium Carbonate*

Physical Properties		**Chemical Properties**	
Density (g/cm^3)	2,7	$CaCO_3$	>99,6%
Hardness (Mohs)	3	MgO	<0,20%
Refractive index	1,59	FeO_2	<0,01%
		SiO_2	<0,01%
		Al_2O_3	<0,02%

2.2. Sample preparation

Pine wood sawdust was kept in an oven at 40 °C for 2 hours to dry before they were used in the experiment. The sawdusts were sieved (250 µm size).

For the resin, 1.5% MEK-P was used as a hardener. The mixture was poured into a Teflon mold on a flat surface. It waited for 12 hours at room temperature for the samples to cure, then they were removed from the mold. Composite samples prepared with different weight ratios of sawdust and calcite are shown in Table 2.

2.3. Tests and Analysis

The tensile test of the samples prepared according to the ISO 527 standard was carried out in the Zwick

Table 2. *Contents of samples (by weight, %)*

Samples	Pine Sawdust	Calcium Carbonate	Polyester
Neat Polyester	**0**	**0**	**100**
5PS15CC	**5**	**15**	**80**
10PS10CC	**10**	**10**	**80**
15PS5CC	**15**	**5**	**80**
20PS	**20**	**0**	**80**
20CC	**0**	**20**	**80**

Abbreviations: PS, pine sawdust; CC, calcium carbonate.

Z010 universal tensile device with a tensile speed of 5 mm/min. The impact strength of the unnotched samples prepared according to the ISO 180 standard was tested using a 5.4 J Izod hammer in the Zwick B5113.30 impact device. Hardness measurements were made in Zwick Shore D device, 15 sec. made with a waiting period. For SEM analysis, the samples were coated with a 10 Å thick gold/palladium alloy. The SEM test was performed with the Polaron SC branded device located in the Marmara University Faculty of Technology Laboratory.

3. Results and Discussions

The tensile properties of natural fiber-reinforced polymers for both thermoplastics and thermosets are affected by the interfacial adhesion between the matrix and the fibers (Fig.1). Various chemical modifications are used to improve the interfacial matrix-fiber bond, resulting in increased tensile properties of composites. Factors such as the filler ratio and size used in the composite, and the bond strength of the matrix layer between the filler also affect the strength.

In general, the tensile strength of natural fiber-reinforced polymer composites increases with fiber content up to an optimum value, then decreases. However, Young's modulus of natural fiber-reinforced polymer composites can increase with increasing fiber content. The tensile strength values of the samples are shown in Table 3 and Fig.2.

Table 3. *Elastic modulus, tensile strength, and strain values of composite materials*

Samples	Elastic Modulus (MPa)	Tensile Strength (MPa)	Strain (%)
Neat Polyester	2035	25	1,2
5PS15CC	2330	18,1	0,81
10PS10CC	2220	16,5	0,66
15PS5CC	2130	16,1	0,59
20PS	1920	15,2	0,78
20CC	2660	22,8	0,79

According to the tensile test results, it was observed that the highest tensile strength was in neat polyester. The tensile strength of the neat polyester sample was determined as 25 MPa. A decrease in tensile strength was observed with the addition of pine sawdust filler. The lowest tensile strength value was found in the 20% sawdust-filled composite sample and it was determined as 15 MPa. The tensile strength of the 20% Calcite filled sample was found to be 22.8 MPa. The tensile strength of the sawdust filled samples decreased as expected. The weak interfacial bond between the polymer matrix and the filler content reduces the tensile strength of the composite. It has been reported in different studies that agglomeration tendency with increasing filler amount or insufficient hydrogen bonding between sawdust particles and matrix causes a decrease in tensile strength [31,32].

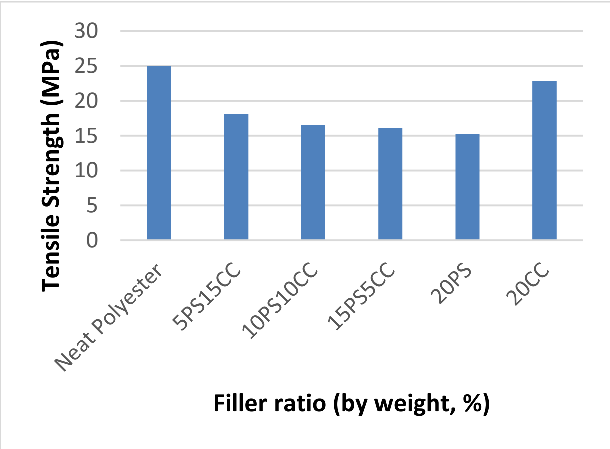


Figure 1. *Tensile strength properties of composites materials*

While filler can increase the tensile strength to the ideal ratio and then cause a decrease, on the contrary, the modulus value can increase as the amount of filler increases. The highest E modulus value of the composite samples was reached with 20% calcite filler (2660 MPa). Although the modulus value increased slightly with the addition of sawdust, this value decreased below the neat polyester with the addition of 20% only sawdust. Except for the 20% sawdust filled sample, the modulus value of all samples is higher than that of neat polyester. In Figure 3, the variation of Izod impact strength according to the filler ratio is given. It has been reported in the literature that the impact strength decreases with the increase of the sawdust ratio, and the toughness partially increases with the use of calcite [4,29,33]. The impact strength of polyester decreased with the addition of sawdust. The highest impact strength was achieved with the

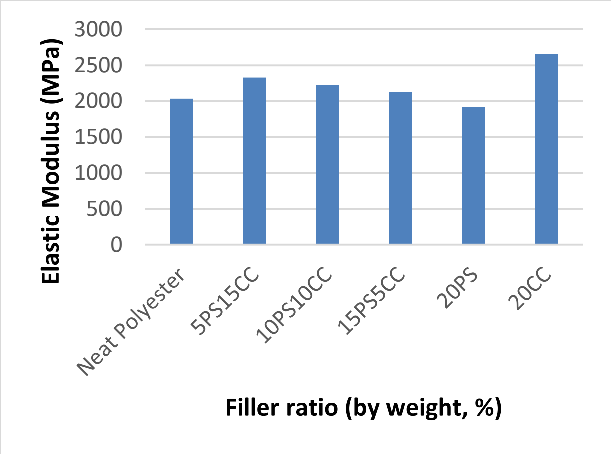


Figure 2. *Elastic modulus properties of composites materials*

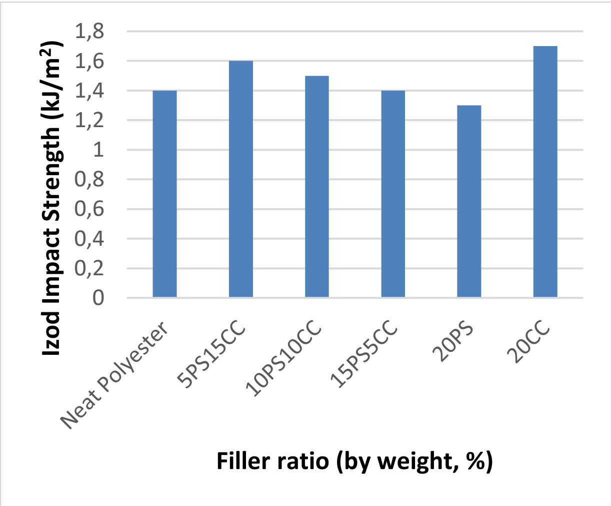


Figure 3. *Izod impact strength properties of composite samples*

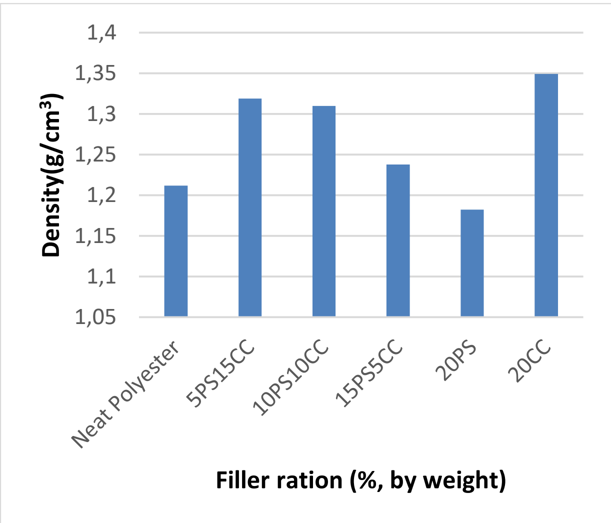


Figure 4. *Density values of composite samples*

20% calcite-filled sample. It is seen that the impact strength value when used together with calcite and sawdust is partially above that of neat polyester. In Figure 4, the density values of composite samples are given. Compared to neat polyester, the density of sawdust in cellulosic structure is low, and the density of calcite in inorganic structure is high. As expected, the density is low in the samples with sawdust content, and the density increases in the samples containing calcite. The Shore D hardness value of the samples is given in Figure 5. The lowest hardness value was determined in neat polyester. The hardness values also changed with the change and increase in the filler ratio, and the highest hardness value was observed in the 20% calcite-filled sample. Although the hardness value of the sawdust increased a bit, the hardness value increased more with the increase of the calcite ratio.

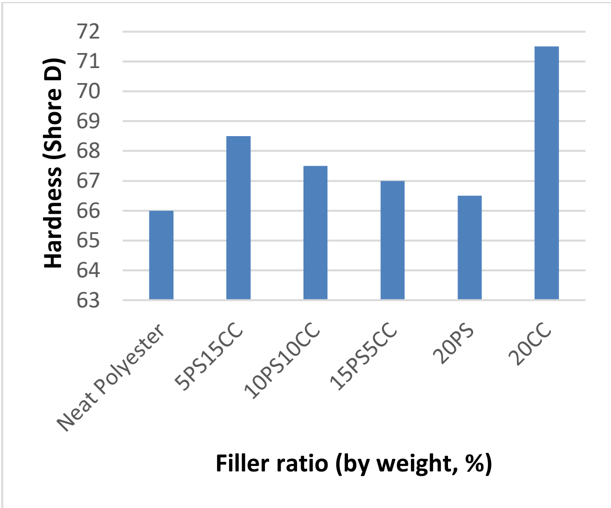
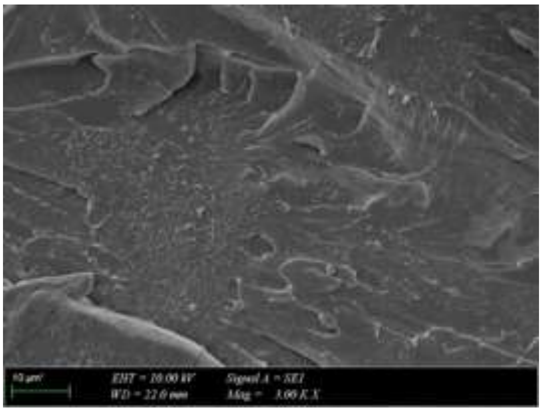
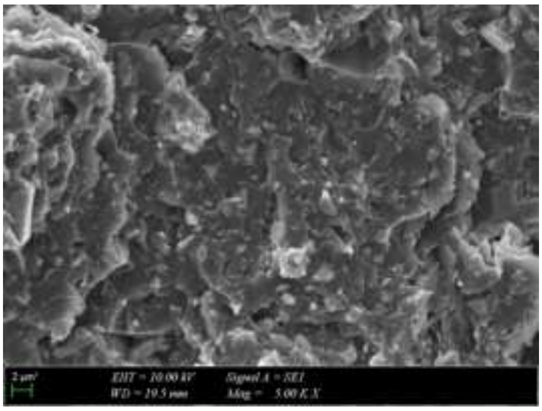


Figure 5. *Hardness properties of composite samples*

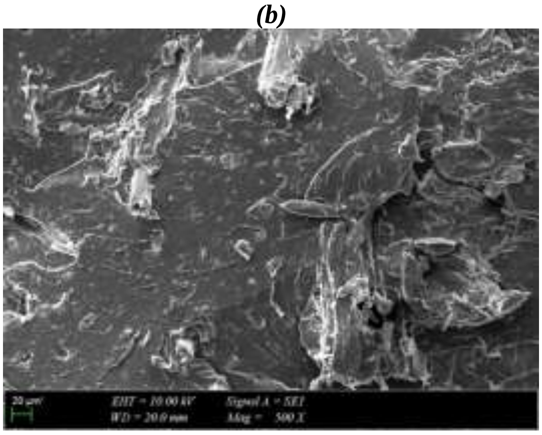
SEM images of the samples are given in Figure 6. Figure 6(a) (neat polyester resin) shows that the rupture surface is plane. This characteristic is associated with the brittle rupture observed in most neat polyester materials. The other SEM image, figure 6(b), contains 20% calcite. It is clear that calcite adheres very well to polyester. As can be seen from the image, it is confirmed to be 3 microns in size. Figure 6(c) is the fracture surface images of the sample with 5% calcite-15% sawdust, and 6(d) is the sample with 20% sawdust. In different studies, 20% sawdust filler was determined as the upper limit. In this study, the filler ratio was kept at 20%. Agglomeration was observed in samples containing 20% and above filler, especially in samples with sawdust particles. This is thought to cause the formation of bubbles and pores that may interfere with the mechanical properties of the composites. Observations in this analysis have been similarly reported in other studies [4-5].



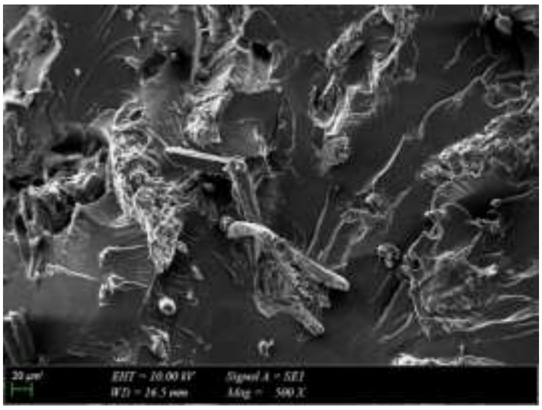
(a)



(b)



(c)



(d)

Figure 6. *SEM images of samples a)neat polyester b)20CC c)5CC15PS d)20PS*

4. Conclusions

Natural filler/fiber-containing polymeric composites are of great interest to both engineers and researchers due to their many advantages. For this reason, these lightweight composites replace traditional structural materials in many applications. Natural fibers compete with synthetic fillers when used as fillers. Natural fiber composites are already applied in the automobile and furniture industries.

In this study, the use of pine wood sawdust and calcite as a filler in polyester-based composite material was investigated.

According to the tensile test data, a partial decrease was observed as the sawdust filler increased, while this decrease was less in the addition of calcite. There was no obvious change in the impact properties. In the density values, only the sawdust-filled sample remained below the neat polyester, while the density of the other samples increased. The hardness results increased with the addition of both sawdust and calcite. It was understood from the SEM images that the fillers were homogeneously mixed in the structure. At the end of this study, when the data of all samples were examined, it was determined that sawdust filler and calcite could be used together as filler in polyester, which would reduce the amount of polyester used and reduce the cost. It is also clear that the use of natural fillers instead of synthetic fillers will contribute to the solution of environmental problems.

As a result, it was concluded that the use of pine sawdust together with calcite as a filler in polyester matrix composite material applications may be a suitable decision.

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

References

[1] Demirer, H., Kartal, İ., Yıldırım, A., & Büyükkaya, K. (2018). The Utilisability of Ground Hazelnut Shell as Filler in Polypropylene Composites. *Acta Physica Polonica A*, 134: 254-256. https://doi.org/10.12693/APhysPolA.134.254

[2] Kartal, İ. (2020). Effect of Hornbeam Sawdust Size on the Mechanical Properties of Polyethylene Composites. *Emerging Materials Research*, 9(3):979-984. https://doi.org/10.1680/jemmr.20.00164

[3] Kartal, İ., Naycı, G., & Demirer, H. (2019a). Cam ve Bambu Lifleriyle Takviyelendirilmiş Vinilester Kompozitlerinin Mekanik Özelliklerinin İncelenmesi. *International Journal of Multidisciplinary Studies and Innovative Technologies*, 3(1):34-37.

[4] Kartal, İ., Naycı, G., & Demirer, H. (2019b). Kestane/Gürgen Talaşı Dolgulu Vinilester Kompozitlerin Mekanik Özelliklerinin İncelenmesi. *European Journal of Science and Technology*, 16:723-728. https://doi.org/10.31590/ejosat.566756

[5] Kartal, İ., Naycı, G., & Demirer, H. (2020). The Effect of Chestnut Wood Flour Size on the Mechanical Properties of Chestnut Wood Flour Filled Vinylester Composites. *Emerging Materials Research*, 9:1-6. https://doi.org/10.1680/jemmr.19.00179

[6] Kushwanth Theja, K., Bharathiraja, G., Sakthi Murugan, V., & Muniappan, A. (2023). Evaluation of mechanical properties of tea dust filler reinforced polymer composite. *Materials Today: Proceedings*, 80: 3208-3211. https://doi.org/10.1016/j.matpr.2021.07.213

[7] Şengör, İ., Cesur, S., Kartal, İ., Oktar, F. N., Ekren, N., İnan, A. T., & Gündüz, O. (2018). *Fabrication and Characterization of Hazelnut ShellPowder with Reinforced Polymer Composite Nanofibers*. ICNMA: 2018 20th International Conference on Nanostructured Materials and Applications, Zurich, Switzerland.

[8] Kumar, R., Ul Haq, M. I., Raina, A., & Anand, A. (2019). Industrial Applications of Natural Fibre-reinforced Polymer Composites – Challenges and Opportunities. *International Journal of Sustainable Engineering*, 12(3): 212-220. https://doi.org/10.1080/19397038.2018.1538267

[9] Albinante, S. R., Platenik, G., & Batista, L. N. (2017). Composites of Olefin Polymer/Natural Fibers: The Surface Modifications on Natural Fibers. In *Handbook of Composites from Renewable Materials* https://doi.org/10.1002/9781119441632.ch79

[10] Singh, P., Singari, R. M., Mishra, R. S., & Bajwa, G. S. (2022). A review on recent development on polymeric hybrid composite and analysis of their enhanced mechanical performance. *Materials Today: Proceedings*, 56: 3692-3701. https://doi.org/10.1016/j.matpr.2021.12.443

[11] Devaraju, S., & Alagar, M. (2019). Chapter 2 - Unsaturated Polyester—Macrocomposites. *Unsaturated Polyester Resins*. Elsevier. https://doi.org/10.1016/B978-0-12-816129-6.00002-8

[12] Netravali, A. N., & Chabba, S. (2003). Composites get greener. *Materials Today*, *6*(4): 22-29. https://doi.org/10.1016/S1369-7021(03)00427-9

[13] Ichazo, M. N., Albano, C., González, J., Perera, R., & Candal, M. V. (2001). Polypropylene/wood flour composites: treatments and properties. *Composite Structures*, 54(2): 207-214. https://doi.org/10.1016/S0263-8223(01)00089-7

[14] Joseph, K., Thomas, S., & Pavithran, C. (1996). Effect of chemical treatment on the tensile properties of short sisal fibre-reinforced polyethylene composites. *Polymer*, 37(23): 5139-5149. https://doi.org/10.1016/0032-3861(96)00144-9

[15] Oleksy, M., & Galina, H. (2013). Unsaturated Polyester Resin Composites Containing Bentonites Modified with Silsesquioxanes. *Industrial & Engineering Chemistry Research*, *52*(20): 6713-6721. https://doi.org/10.1021/ie303433v

[16] Mohammed, M. H., & Dauda, B. M. (2014). Unsaturated Polyester Resin Reinforced With Chemically Modified Natural Fibre, *Journal of Polymer and Textile Engineering*, 1(4):31-38.

[17] Paauw, M., & Pizzi, A. (1993). Some filler effects on cross-linking of unsaturated polyesters. *Journal of Applied Polymer Science*, *50*(7): 1287-1293. https://doi.org/10.1002/app.1993.070500720

[18] K. Dinakaran, S. Devaraju, M. Alagar (2013) *Thermoset nanocomposites Unsaturated Polyester Resin Clay Hybrid Nanocomposites*, Wiley-VCH.

[19] Kanimozhi, K., Prabunathan, P., Selvaraj, V., & Alagar, M. (2014). Vinyl silane-functionalized rice husk ash-reinforced unsaturated polyester nanocomposites. *RSC Advances*, *4*(35): 18157-18163. https://doi.org/10.1039/C4RA01125B

[20] Dinakaran, K., & Alagar, M. (2003). Development And Characterization Of Vinyl Ester Oligomer (Veo) Modified Unsaturated Polyester Intercrosslinked Matrices And Composites. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 52(11-12): 957-966. https://doi.org/10.1080/714975880

[21] Anand Prabu, A., & Alagar, M. (2004). Mechanical and thermal studies of intercross-linked networks based on siliconized polyurethane-epoxy/unsaturated polyester coatings. *Progress in Organic Coatings*, 49(3): 236-243. https://doi.org/10.1016/j.porgcoat.2003.09.018

[22] Chozhan, C. K., Alagar, M., Sharmila, R. J., & Gnanasundaram, P. (2007). Thermo mechanical behaviour of unsaturated polyester toughened epoxy–clay hybrid nanocomposites. *Journal of Polymer Research*, 14(4): 319-328. https://doi.org/10.1007/s10965-007-9114-x

[23] Mandhakini, M., Devaraju, S., Venkatesan, M. R., & Alagar, M. (2012). Linseed vinyl ester fatty amide toughened unsaturated polyester-bismaleimide composites. *High Performance Polymers*, 24(3): 237-244. https://doi.org/10.1177/0954008311436263

[24] Mohammed, M. H., & Dauda, B. M. (2014). Unsaturated Polyester Resin Reinforced With Chemically Modified Natural Fibre.

[25] Sharmila, R. J., Premkumar, S., & Alagar, M. (2010). Preparation and Characterization of Organoclay-Filled, Vinyl Ester-Modified Unsaturated Polyester Nanocomposites. *High Performance Polymers*, *22*(1), 16-27. https://doi.org/10.1177/0954008308099491

[26] Kandemir, B., Karagöz, İ., & Sepetçioğlu, H. (2023). Experimental Investigation of Effects of the Nucleating Agent on Mechanical and Crystallization Behavior of Injection-Molded Isotactic Polypropylene. *El-Cezerî Journal of Science and Engineering*, 10(1):109-120. https://doi.org/10.31202/ecjse.1165527

[27] Baştürk, B. (2022). An Investigation on the Flexural and Thermo-mechanical Properties of CaCO3/Epoxy Composites [Articles]. *Celal Bayar University Journal of Science*, *18*(2), 161-167. https://doi.org/10.18466/cbayarfbe.1015351

[28] Mallick, P. K. (2000). Particulate and Short Fiber Reinforced Polymer Composites. In A. Kelly & C. Zweben (Eds.), Comprehensive Composite Materials (pp. 291-331). Pergamon. https://doi.org/10.1016/B0-08-042993-9/00085-1

[29] Croitoru, C., Spirchez, C., Cristea, D., Lunguleasa, A., Pop, M. A., Bedo, T., Roata, I. C., & Luca, M. A. (2018). Calcium carbonate and wood reinforced hybrid PVC composites. *Journal of Applied Polymer Science*, *135*(22), 46317. https://doi.org/10.1002/app.46317

[30] Orman Genel Müdürlüğü (2023). *Asli Ağaç Türleri* https://www.ogm.gov.tr/tr/e-kutuphane-sitesi/Yayinlar/Asli%20A%C4%9Fa%C3%A7%20T%C3%BCrleri.pdf

[31] Hornsby, P.R., Hinrichsen, E. and Tarverdi, K. (1997) Preparation and Properties of Polypropylene Composites Reinforced with Wheat and Flax Straw Fibres: Part II Analysis of Composite Microstructure and Mechanical Properties. *Journal of Materials Science*, 32: 1009-1015. https://doi.org/10.1023/A:1018578322498

[32] Panthapulakkal, S., Zereshkian, A., & Sain, M. (2006). Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites. *Bioresource Technology*, 97(2): 265-272. https://doi.org/10.1016/j.biortech.2005.02.043

[33] Kompozit Pazarı (2023), *Kalsit 5 Mikron Ürünü,* https://www.kompozitpazari.com/urun/kalsit-5-mikron