Journal of Fibers and Polymer Composites 1 (1): 43-51 (2022)

Journal of Fibers and Polymer Composites

https://journals.gesociety.org/index.php/jfpc/index

INFLUENCE OF NANOPARTICLE $CaCO_3$ ADDITION TO THE PHYSICAL AND MECHANICAL PROPERTIES OF POLYPROPYLENE-$CaCO_3$ COMPOSITE

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Abstract. *Influence of Nanopaticle $CaCO_3$ Addition to the Physical and Mechanical Properties of Polypropylene-$CaCO_3$ Composite. This research was carried out to study the effect of adding $CaCO_3$ nanoparticle on the physical and mechanical properties of polypropylene-$CaCO_3$ composites. It was characterized by several parameters such as tensile strength, hardness, and thermal analysis including both melting point and heat of fusion using Differential Scanning Calorimetry (DSC). Based on XRD results, the particle size of $CaCO_3$ after 24 hours of milling was 39 nm. There are various compositions of polypropylene-CaCO3 composites (PP MF35: nano-$CaCO_3$) made in this study, namely 40%:60%, 35%:65%, 30%:70%, and 25%:75%. The results showed that the tensile strength of the PP MF35-$CaCO_3$ composites decreased with increasing nano-$CaCO_3$ content. Meanwhile, the hardness of the nanocomposites increased with increasing nano-$CaCO_3$ content, but decreased the melting point and heat of fusions (ΔH_m) of the nanocomposites. The infrared spectrum showed that the interaction between PP MF35 and nano-$CaCO_3$ was only physical interaction and there was no chemical reaction.*

Keywords: *polypropylene; nano-$CaCO_3$;tensile strength; composite.*

1. Introduction

An increasing population is always followed by an increase in the necessities of life. This is what underlies the increasing need for plastic as a packaging of food, beverage and other necessities. By 2050, it is estimated that the world's population will reach 9 billion and the level of plastic production will exceed 1 billion tons.

Plastic as a packaging has several advantages such as strong, light, transparent, stainless, easy to shape and to color and also has a low price. Plastics can be applied in various human life sector like household, automotive, agriculture and health [1]. Market demand for good quality goods at competitive prices and the increasingly rapid development of polymer technology have prompted scientists to make polymer-based plastics by mixing polymers with nano-sized fillers. In this research, a polymer composite was made by mixing polypropylene as a matrix and $CaCO_3$ as a filler.

Received February 7, 2022; Accepted March 10, 2022; Published March 30, 2022
https://doi.org/10.55043/jfpc.v1i1.34

Polypropylene (PP) is a type of thermoplastic polymer, which is a linear hydrocarbon polymer formed by propylene monomers. In this study, polypropylene was used because it is widely used as a raw material of packaging for food, beverages and other applications [2]. One of the fillers that can be applied is $CaCO_3$. It is used because the presence of $CaCO_3$ in nature is abundant, cheap, inert and it has high melting point. The economic price of the filler causes the final product price to be lower, so that economically, it will benefit producers and consumers [3]. $CaCO_3$ as a filler is made in nanometer size. Because the smaller the size of filler particle, it is expected that the more filler can interact with the matrix, so that the less polymer matrix is applied. Moreover, it caused changes in the physical and mechanical properties of polypropylene. It can improve the physical and mechanical properties of polypropylene [3]. Based on previous research, the addition of micro-sized $CaCO_3$ reduces the mechanical properties of PP-$CaCO_3$ composites. Meanwhile, both tensile strength and flexural strength of Polyethylene-terephthalate (PET)/Polypropylene (PP)/$CaCO_3$ are increased after the addition of specific composition of $CaCO_3$. [5]. It also improved the melting point of polypropylene [6]. Therefore, the effect of nano-sized $CaCO_3$ on properties of PP MF35-$CaCO_3$ nanocomposites was investigated in this study [4–6].

2. Experimental Methods

2.1. Materials

The polypropylene with melt flow of 35g/10 min is a product of PT TRI POLYTA INDONESIA, Tbk, Cilegon – Banten. Calcium carbonate (pro analyzed) used the (MERCK catalog) as a filler, Yasicha brand mica plastic and nitrogen liquid.

2.2. Experimental Procedure

2.2.1. Manufacture of Nano-sized CaCO3

High Energy Mill (HEM, brand SPEX Centripep 8000-series Mixer/Mills) is used to manufacture nano-sized $CaCO_3$. First of all, $CaCO_3$ and sphere go tri with weight ratio of 1:2 was put into vial and then milled with HEM to obtain a nanometer size. After that, the milling process was carried out with different time variations such as 0, 6, 12, 18 and 24 hours on different samples.

2.2.2. Synthesis of PP MF35-CaCO3 Composite

First of all, laboplastomill (Toyoseiki brand, Japan) is cleaned with acetone to avoid impurities during material synthesis. Then, mix the melted polypropylene 35 with nano-sized $CaCO_3$ in laboplastomill at a temperature of 1800^oC for 10 minutes with a rotating speed of 40 rpm. The variations of $CaCO_3$ are 60, 65, 70, and 75wt% and the propylene of 25, 30, 35, and 40wt%. After mixing homogeneously, then the mixture was made a film using Hydraulic Hot Press at a temperature of 1800^oC for 5 minutes and a pressure of $150 kg/cm^2$. Then the film molding tool is put into the cold pressing machine (a/s 16 Tons Hydraulic Press).

2.2.3. Characterization.

The manufacture of nano-sized $CaCO_3$ is carried out using High Energy Mill (HEM) for 24 hours to minimize the particle size of material. The particle size of $CaCO_3$ after milling for 24 hours were measured using X-Ray Diffraction (XRD-PAN Analytical 610) with Cu–Kα source at wavelength (λ) = 0.154 nm). Infra-red (IR) spectrum for identification of functional groups and metal oxide bonds was measured by means of Fourier Transformation Infra-Red (FTIR) type Tensor 27 Bruker. Samples in powder form as much as 5 mg were mixed with KBr then crushed and homogenized and then pressed to form pellets. Samples were irradiated with IR in the wave number range of 500 cm^{-1} to 3000 cm^{-1}.

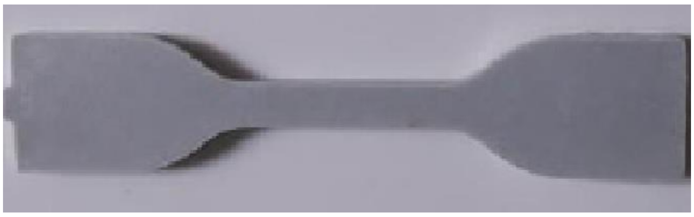


Figure 1. Specimen of the tensile test.

Tensile strength specimens were produced by using the TKC series-vertical injection mold machine, following the ASTM D638 standard. The tensile specimen size was 19 mm wide, 113 mm length, and thickness 4 mm (Fig. 1). Five samples were tested for each composition. The experiment was carried out on Strograph R1, Toyoseiki (Japan) with longitudinal extension, a high resolution (1.8 µm). Some basic specifications are described as follows: The maximum test power was 20 kN, in range of speed 0.001-1600 mm/min, speed accuracy ± 0.1 % test speed, the operating temperature at 5-50°C, data acquisition speed 1000 Hz. SEM characterization was carried out to determine the morphology, microstructure and particle size distribution of the $CaCO_3$, the test was carried out with a magnification of 5000 times using a SEM- JEOL 6510 LA.

3. Result and Discussion

3.1. Manufacture of Nano-sized $CaCO_3$

The manufacture of nano-sized $CaCO_3$ is carried out using High Energy Mill (HEM). In HEM, there is a process of $CaCO_3$ attrition. The attrition method is a method in which micrometer-sized material is hammered into a particular ball milling in order to minimize the particle size of material [7]. So that finally we get a material with a smaller particle size (in nanometers).

The results of the measurement of the x-ray diffraction pattern from the mechanical milling process which are expected to form $CaCO_3$ nanoparticles are shown in Figure 2. Figure 2 shows the x-ray diffraction pattern with milling time variations of 0, 6, 12, 18, and 24 hours. Phase identification shows that the sample after milling has an unchanged phase, in other words, that milling does not find any foreign phase. In this research, particle size analysis used X-ray diffraction using the Scherer method in which the crystalline scale is determined based on the reaming of the X-ray diffraction peaks that appear. Based on this method, the more small-scale crystals, the wider the diffraction peaks will be. The relationship between scale crystals and X-ray peak diffraction width can be seen with the Scherer equation [8]:

$$D \approx K \frac{\lambda}{B \cos \theta_B} \quad \text{...(1)}$$

Where D is crystallite size in nano-meter; κ a constant whose value depends on particle shape; *B* is FWHM (Full Width at Half Maximum); λ is the wavelength of incident beams in nm and θ is Bragg's angle. Based on result of gauging at milling 24 hours, we obtained that the average D value of $CaCO_3$ after milling for 24 hours was about 39 nm.

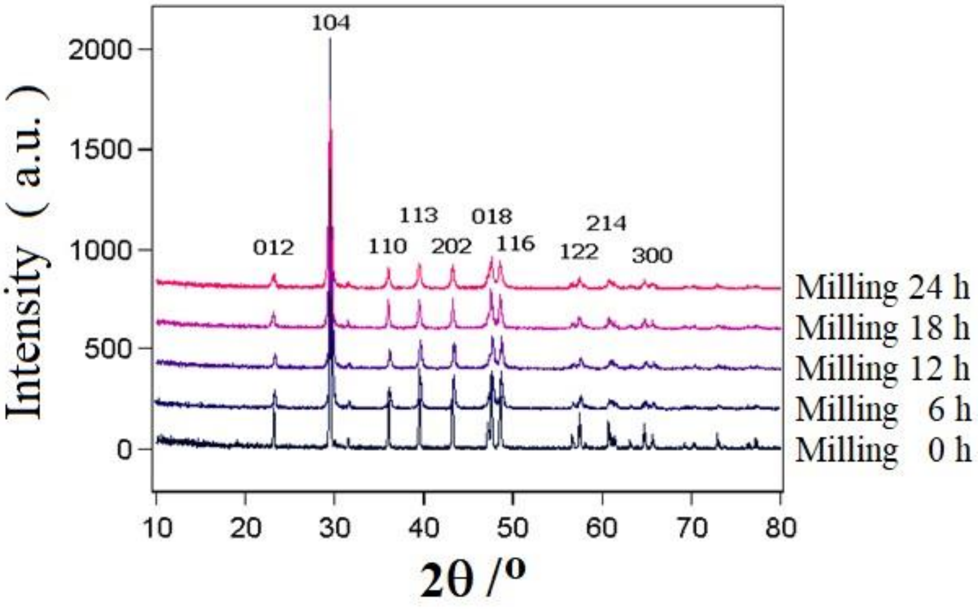


Figure 2. X-ray diffraction pattern of $CaCO_3$ milling time variation.

3.2. Analysis of Mechanical Properties (Tensile Strength)

The tensile was the tensile properties that were determined using five samples for each composition to study the effect of $CaCO_3$ on tensile properties. Tensile strength specimens were produced by using the TKC series-vertical injection mold machine, following the ASTM D638 standard. Tensile strength can be determined by applying force to the test material until it breaks. Tensile strength, which is a measure of the ability of a polymer to withstand pulling stresses is usually measured by pulling a dumbbell specimen [9,10].

Table 1. Tensile Strength of PPMF35+$CaCO_3$

No.	Samples	Heat of Fusions (J/g)
1.	PP MF35	283
2.	PPMF35-40% + 60% $CaCO_3$	181
3.	PP MF35-35% + 65% $CaCO_3$	148
4.	PP MF35-30% + 70% $CaCO_3$	125
5.	PP MF35-25% + 75% $CaCO_3$	87

Based on the results above, it is known that the tensile strength decreased with the increasing of nano-sized $CaCO_3$ filler content. Meanwhile, it decreased due to uneven distribution of nano-sized $CaCO_3$. This is because nano-sized $CaCO_3$ filler has very small particles, so that the nano-sized $CaCO_3$ tends to clump and form a larger drain structure or known as agglomeration which has an impact on the decreasing of tensile strength [9,11]. The tendency to form very large agglomerates is due to electrostatic forces between $CaCO_3$ particles. Particles with a diameter of less than 1 µm have a relatively high tendency for agglomeration to occur.

Polypropylene MF35/nano-$CaCO_3$ composite have tensile strength with higher level if compared to PP MF35-$CaCO_3$ composite at the same concentration. PP MF35-$CaCO_3$ composite at concentration of $CaCO_3$ equal to 60% have the tensile strength at about 148kg/cm^2. Meanwhile, tensile strength of PP MF35/nano-$CaCO_3$ composite at concentration of $CaCO_3$ 60% is about 181kg/cm^2. The increase of tensile strength is equal to 18%. This caused by filler nanometer $CaCO_3$ which has big equi-amplitude surface district so that it will give more contact between filler and matrix resulting mechanical properties of polymers composite to increase [12].

3.3. Analysis of Physical Properties

3.3.1. Hardness

Hardness is the resistance to local deformation that is often measured as the ease or difficulty for a material to be scratched, indented, marred, cut, drilled, or abraded. In this research, hardness was measured by Shore A.

Tabel 2. Hardness of PPMF35/$CaCO_3$

No.	Samples	Heat of Fusions (J/g)
1.	PP MF35	91
2.	PP MF35 40% + 60% nano-$CaCO_3$	92
3.	PP MF35 35% + 65% nano-$CaCO_3$	93
4.	PP MF35 30% + 70% nano-$CaCO_3$	94
5.	PP MF35 25% + 75% nano-$CaCO_3$	95

Based on the table, the hardness of the composites increased with the increasing of nano-$CaCO_3$ composition because the addition of $CaCO_3$ can increase the molecular weight of the polymer so that it can also increase the solidity of polymer. Consequently, it increased the crystallinity of polymer [13].

3.3.2. Analysis of Thermal

The analysis of thermal properties includes melting point (Tm) and heat fusion (ΔHm) using Differential Scanning Calorimetry (DSC, Perkin Elmer Brand) method. Melting point describes the phase transformation from solid to liquid without undergoing a transformation of the composition. Melting is basically the separation of polymer chains in a crystalline region which allows the polymer to flow.

Table 3. Melting Point of PP MF35/Nano-$CaCO_3$

No.	Sample	Heat of Fusions (J/g)
1.	PP MF35 40% + 60% nano-$CaCO_3$	160
2.	PP MF35 35% + 65% nano-$CaCO_3$	158
3.	PP MF35 30%+ 70% nano-$CaCO_3$	159
4.	PP MF35 25%+ 75% nano-$CaCO_3$	156

Tabel 4. Heat of fusion of composite PP MF35/nano-$CaCO_3$

No.	Sample	Heat of Fusions (J/g)
1.	PP MF35 + 60% nano-$CaCO_3$	25
2.	PP MF35 + 65% nano-$CaCO_3$	22
3.	PP MF35 + 70% nano-$CaCO_3$	20
4.	PP MF35 + 75% nano-$CaCO_3$	14

Based on the Table 4, the melting point of nanocomposites decreased with the increasing of nano-$CaCO_3$ filler content. This is because the polymer chain was physically degraded and was released to the wall together with the filler, causing the breakdown of the polymer molecular chain bonds. The addition of filler to polymer matrix shows that the interaction of filler with the amorphous part of PP MF35 was also increasing, so that it reduced the crystallinity of PP MF35 and its melting point [14].

The reduction of heat fusion occurred due to the higher concentration of nano-$CaCO_3$ in the composites. As a result, the concentration of PP MF35 in the composite reduced, then it also reduced the required energy to break polymer chains of PP MF35 when it changed from a solid to liquid state.

3.3.3. Analysis of Functional Groups with Fourier Transform Infra-Red (FT-IR)

FT-IR analysis is applied to identify organ compounds based on readings of the functional groups of the compounds in the form of spectrum read on the graph. Polypropylene, $CaCO_3$, and PP/nano-$CaCO_3$ composites were identified for functional groups using FT-IR.

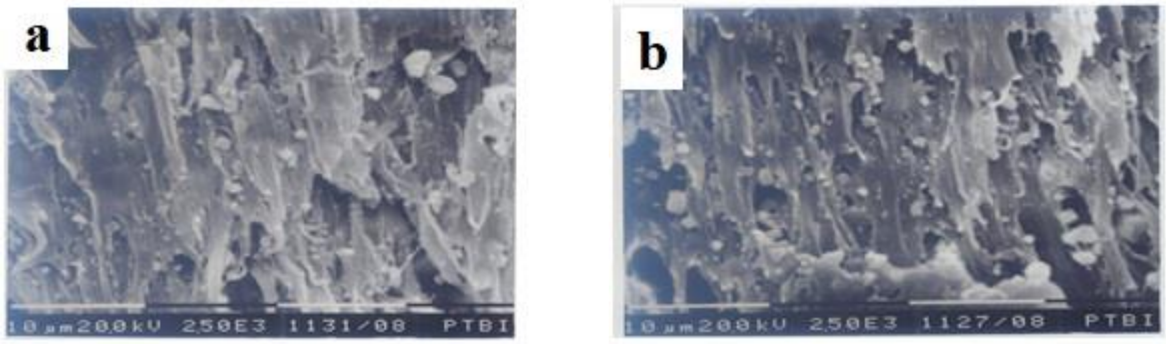
Based on spectral data, we see the absorption peak at wave number around 3382cm^{-1} which is a stretching vibration absorption of primary NH_2, NH stretching vibration absorption at wave numbers around 1570cm^{-1}, and aliphatic CH vibration absorption at wave numbers around 2800 - 3000cm^{-1}. Si-OC vibrations identified in the wave numbers 1100 and 1085 cm^{-1}. O-CH_3 vibrations identified in the wave numbers 1450 and 1434 cm^{-1}. CH_2 bending vibrations identified in the wave numbers around 1485 and 1150-1162cm^{-1} while the C-CH_3 bending identified in the wave numbers 1382, 1337 and 958cm^{-1}.

Table 5. Infrared spectrum of PP MF35/nano-$CaCO_3$ composite

No.	Group	Wavenumber (cm^{-1})
1.	C-H streching	2800-3000
2.	CH_2 bending	1162
3.	CH_3 bending	1382, 1337 and 958

3.3.4. Distribution Nano-$CaCO_3$ in Polymers Composite

Figure 1 showed the morphology of $CaCO_3$ which was observed using Scanning Electron Microscopy (SEM). $CaCO_3$ undergoes agglomeration due to its small scale. Based on figure 1, the cupola of volume diffraction composition of PP MF-35/nano-CaCO3 (40wt%/ 60wt%) looks a bit slippery, rather flat, rather dense and looks rather compact when compared to the addition of volume diffraction greater than 60wt%. With the addition of the diffraction percentage of the $CaCO_3$ filler composition into the nanocomposite, the real composition will be greater and larger chambers. Meanwhile, its distribution is more coarse, uneven, and not compact. This is due to the influence of nano-$CaCO_3$ which tends to agglomerate [15].



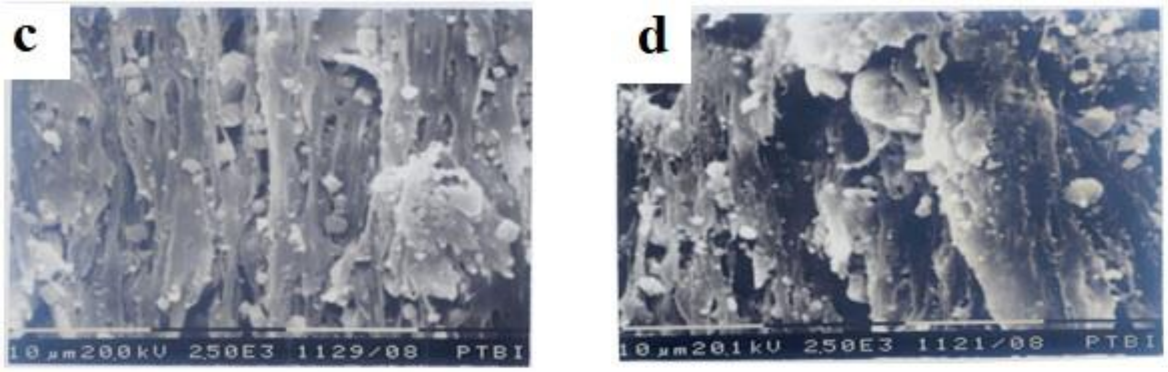


Figure 1. SEM image of nano-$CaCO_3$ distribution in polypropylene-$CaCO_3$ composite. (a) in composition PP MF35 60%-40% $CaCO_3$ (b) in composition PP MF35 65%-35% $CaCO_3$ (c) in composition PP MF35 70%-30% $CaCO_3$and (d) in compositionPPMF35 75%-25%$CaCO_3$.

3. Conclusion

Based on XRD results, the particle size of $CaCO_3$ after 24 hours of milling was 39 nm. The tensile strength of the PP MF35-$CaCO_3$ composites decreased with the increasing of nano-sized $CaCO_3$ filler content. Meanwhile, the hardness of the nanocomposites increased with the increasing of nano-sized $CaCO_3$ filler content, but both the melting point and the heat of fusions (ΔH_m) the nanocomposites decreased. The infrared spectrum showed that the interaction between PP MF35 and nano-$CaCO_3$ was only physical interaction and there was no chemical reaction occurred.

4. References

[1] A. Pratap and D. A. Sarjubala, “Microplastics and single use plastics: A curse of over consumerism,” *Int. J. Adv. Sci. Res. Manag.*, vol. 4, no. 4, pp. 384–388, 2019, [Online]. Available: www.ijasrm.com.

[2] G. W. Curtzwiler, M. Schweitzer, Y. Li, S. Jiang, and K. L. Vorst, “Mixed post-consumer recycled polyolefins as a property tuning material for virgin polypropylene,” *J. Clean. Prod.*, vol. 239, p. 117978, 2019, doi: https://doi.org/10.1016/j.jclepro.2019.117978.

[3] H. P. S. Abdul Khalil *et al.*, “Microbial-induced CaCO3 filled seaweed-based film for green plasticulture application,” *J. Clean. Prod.*, vol. 199, pp. 150–163, 2018, doi: https://doi.org/10.1016/j.jclepro.2018.07.111.

[4] H. Mao, B. He, W. Guo, L. Hua, and Q. Yang, “Effects of Nano-CaCO3 content on the crystallization, mechanical properties, and cell structure of PP nanocomposites in microcellular injection molding,” *Polymers (Basel).*, vol. 10, no. 10, 2018, doi: https://doi.org/10.3390/polym10101160.

[5] H. N. T. Pham and V. T. Nguyen, “Effect of calcium carbonate on the mechanical properties of polyethylene terephthalate/polypropylene blends with styrene-ethylene/butylene-styrene,” *J. Mech. Sci. Technol.*, vol. 34, no. 10, pp. 3925–3930, 2020, doi: https://doi.org/10.1007/s12206-020-2201-1.

[6] X. Jing, W. Gong, Z. Feng, M. Zhang, X. Meng, and B. Zheng, “Novel Comb-Like

Copolymer Dispersant for Polypropylene/CaCO3 Composites and Its Influence on Dispersion, Crystallization, Mechanical, and Thermal Properties," *Polym. - Plast. Technol. Eng.*, vol. 57, no. 10, pp. 986–996, 2018, doi: https://doi.org/10.1080/03602559.2017.1370105.

[7] A. P. Nugroho, Masruroh, and S. P. Sakti, "The design and optimization process of ball mill to reduce particle size of calcium carbonate materials," *AIP Conf. Proc.*, vol. 2296, no. November 2020, pp. 5–10, 2020, doi: https://doi.org/10.1063/5.0030531.

[8] S. J. Tracy, S. J. Turneaure, and T. S. Duffy, "In situ X-Ray Diffraction of Shock-Compressed Fused Silica," *Phys. Rev. Lett.*, vol. 120, no. 13, p. 135702, 2018, doi: https://doi.org/10.1103/PhysRevLett.120.135702.

[9] S. Samal, "Effect of shape and size of filler particle on the aggregation and sedimentation behavior of the polymer composite," *Powder Technol.*, vol. 366, pp. 43–51, 2020, doi: https://doi.org/10.1016/j.powtec.2020.02.054.

[10] J. Yu and C. K. Y. Leung, "Using Limestone Calcined Clay to Improve Tensile Performance and Greenness of High-Tensile Strength Strain-Hardening Cementitious Composites (SHCC)," *Calcined Clays Sustain. Concr.*, p. 2020, 2020.

[11] Y. Kezuka and M. Tajika, "Fracture strength evaluation of agglomerates of fatty acid-coated caco3 nanoparticles by nano-indentation," *ChemEngineering*, vol. 3, no. 3, pp. 1–9, 2019, doi: https://doi.org/10.3390/chemengineering3030073.

[12] C. Budiyantoro, H. Sosiati, B. P. Kamiel, and M. L. S. Fikri, "The effect of CaCO3 filler component on mechanical properties of polypropylene," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 432, no. 1, 2018, doi: https://doi.org/10.1088/1757-899X/432/1/012043.

[13] M. Barczewski *et al.*, "Thermo-mechanical and mechanical behavior of hybrid isotactic polypropylene glass fiber reinforced composites (GFRC) modified with calcium carbonate (CaCO3)," *Polym. Eng. Sci.*, vol. 60, no. 7, pp. 1588–1603, 2020, doi: https://doi.org/10.1002/pen.25404.

[14] E. A. Bilalova, E. V. Prut, and O. P. Kuznetsova, "Polypropylene composite material and its rheological and mechanical properties depending on the size of the filler CaCO3," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 525, no. 1, 2019, doi: https://doi.org/10.1088/1757-899X/525/1/012006.

[15] O. Ersoy and H. Köse, "Comparison of the effect of reactive and nonreactive treatments on the dispersion characteristics of a calcium carbonate (calcite) filler in a polypropylene matrix composite," *Polym. Compos.*, vol. 41, no. 9, pp. 3483–3490, 2020, doi: https://doi.org/10.1002/pc.25634.