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RESEARCH ARTICLE

Polymer COMPOSITES WILEY

Effect of waste toner powder on the performance of microcrystalline cellulose-talc reinforced polypropylene hybrid composites

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Abstract

This study examines reducing the environmental hazards of toner waste and producing low-cost: high-performance value-added hybrid polypropylene-PP-composites. The incorporation of microcrystalline cellulose (MCC) and inorganic filler(s) into a polymer matrix leads to superior performance and environmental advantage compared to inorganic-filled polymer composites. Waste toner (WT) was used up to 2% by weight with increments of 0.5 and the other fillers: MCC/talc/polypropylene carbonate loading ratios were kept constant as 5/10/3 wt% in this study. The production process of hybrid PP composites was carried out with single-screw extrusion and molding. Chemical and thermal characterization of the filler and the hybrid PP composites were performed by FTIR and it was revealed that the main resin of WT consists of polystyrene co-acrylate. In DSC analysis, the highest crystallinity value was calculated as 52.36% in the composite containing 1.5% waste toner. SEM micrographs proved the PPC prompts the dispersion quality of MCC and talc in the PP matrix. Mechanical, water absorption and surface properties of the hybrid composites were enhanced by adding WT at 1 and 1.5 wt%. Above this ratio, all properties of the hybrid composites moderately decreased. In light of the results, the WT could be utilized as a filler up to 1.5% in the PP-matrix.

Highlights

- TS of the composites increased by increasing the waste toner content to 1.5%.
- PP-based hybrid composites had higher flexural properties than unfilled PP.
- The crystallinity increased up to the addition of 1.5% wt.
- PPC-coupling agent promoted the interaction between talc/MCC and PP matrix.

KEYWORDS

hybrid PP composites, MCC, talc, waste toner

1 | INTRODUCTION

The composite industry, like other industries, has to keep up with the green transformation in today's century. Due to the fact that raw material supply and natural resources required for composite production have come to the point of consumption throughout the world. Recently researchers have intense studies on inorganic fillers such as glass fiber, talc, halloysite hollow glass microspheres, etc., and natural fiber(s) hybridization effect for the properties of the hybrid composites.[1–4] It was concluded that the hybrid composites were higher than those of neat polymer and composites with a single reinforcer/filler by the researchers. Considering environmental factors, sustainability and increasing demand for multifunctional materials, "hybrid composites" with multicomponent additives/reinforcers are becoming more promising solutions instead of single matrix and single reinforcement.[5]

Glass and carbon fibers have traditionally been the most widely used reinforcement materials in lightweight composites due to their high mechanical strength and stiffness. As the importance of environmental factors in the commercialization of products increases, renewable source natural fibers have been used more intensively in lightening applications than traditional fiber supplements by reason of factors such as low density, low cost, acceptable strength, recyclability, improved energy recovery, safe use of fibers.[6–8] A significant amount of research has been reported aimed at improving the performance of natural fiber-reinforced composites. However, more research in this field needs to be addressed.[6,7,9]

Cellulose nano-fibrils such as microcrystalline cellulose (MCC), CNF, and bacterial cellulose obtained from renewable biomass are widely used for micro-addition to composite materials.[10] MCC is also naturally occurring crystalline cellulose derived from high-quality wood pulp. MCC has a high specific surface area compared to other conventional cellulose fibers.[11] The use of cellulose as a mechanical additive in the polymer matrix has stood out with other positive properties including having a reactive surface, low density, renewable, low price, and no abrasion in the material process.[12–16]

The inorganic fillers are most often utilized additives in thermoplastic polymer for reducing the cost of plastic products and enhancing their properties such as hardness, impact strength, hardness, wear resistance, and toughness. These final properties may vary depending on the degree of dispersion of the filler on the polymer matrix.[17–27] Talc, one of the inorganic fillers, is a traditional filler used to reinforce polyolefin due to its low cost and high aspect ratio.[28,29] Moreover, talc is in great demand for the synthesis of polymeric composites due to its excellent blending nature, thermal resistance, superior electrical resistance and chemical inertness,[30] therefore, it improves both thermal and mechanical properties.[31–33] Talc-reinforced composites have been used in automotive applications for many years. On the other hand, the automotive industry has focused on the search for both environmentally friendly alternatives and low-cost waste raw materials to solve the matter of resource depletion.

Toners are principally composed of polystyrene, polyacrylate, Fe_3O_4, and SiO_2.[34,35] Waste toner powders in expired toner cartridges are part of the e-waste that is landfilled or disposed of throughout the world, and their quantity has increased following the increasing demand for printers and replicators. It is estimated that 1.1 billion cartridges are sold annually worldwide, of which more than 500 million are wasted. An end-of-life toner cartridge may contain up to 8% by weight of residual toner powder. Given the number of cartridges thrown away each year, this means a significant amount of toner powder is disposed of in an unsafe and environmentally harmful way like the incineration process. This causes great harm to the environment due to the low decomposition rate of plastic in the toner and the leaching of toxic chemicals, especially from residual toner dust into the soil and the groundwater layer, besides, the occurrence of furan and dioxin gases during its incineration process, which are responsible for global warming, and the loss of valuable substances.[35] Also, the remaining toner dust is flammable and has a very fine particle size, increasing the risk of dust explosion if airborne. This situation further increases the impact of the dangers mentioned.[36] Therefore, recycling of waste toner cartridges is crucial not only for waste management but also for environmental protection. Considering these situations, the upcycling of waste toners in the hybrid thermoplastic composite as an additive can be promising to overcome substantial waste disposal. It is thought that the polymeric content in the toner waste helps to act as a compatibilizer. On the other hand, the automobile and construction industries are perpetually in search of low-density and inexpensive additives/raw materials to enhance the performance of their products. They also care about recycling waste in terms of the circular economy and circular materials. In the literature, a few research studies have claimed that could be an alternative additives for polymer compounding industries. For instance, Hammani et al.[37] studied the assessment of waste toner in an LDPE/HIPS polymer blend and Daniel-Mkpume et al.[38] investigated the utilization of it for the polyester-based composites as a potential filler. Even if the waste toner's effect on the properties of single-filler-based polymer composites has been investigated; more intensive studies are still needed on the suitability of waste toners especially for hybrid composites.

This study aims to evaluate waste toner in the hybrid composite with a single polypropylene matrix and multiple fillers. The hybrid PP composites were processed with two main hybridization fillers MCC and talc. The effect of waste toner on the physical, mechanical, thermal, and surface properties of the hybrid composite was examined in detail. FTIR-ATR characterization of waste toner, MCC, and hybrid composites was also carried out.

2 | EXPERIMENTAL

2.1 | Materials

Polypropylene (PP) homopolymer and polypropylene carbonate (PPC) were purchased from Petkim Petrochemical Company in Izmir, Turkey. MCC as lignocellulosic material addition was obtained by Merck. Talc (CAS Number 14807-96-6) was supplied from Isik Maden Company in Turkey. The waste toner powders were obtained from printer toners that had reached the end of their useful life. The composition of waste toner powder consists of carbon (90.57%), oxygen (8.50%), and silica (0.65%).

2.2 | Manufacture of the hybrid PP composite

The experimental design for the hybrid PP composites is given in Table 1. The moistures of MCC, talc, and toner were removed by drying at low temperature (~50°C for 2 h) before extrusion.

The filler(s) and polymer were mixed using a laboratory mixer for 5 min. The mixture was fed into a single-screw laboratory extruder (Rondol, UK). The extruder was set to a screw speed of 100 rpm and temperatures of 170°C, 175°C, 180°C, and 185°C. The extrudates were cooled using a water cooling system and grinding. The oven-dried pellets were molded in the hot press for 5 min at a pressure of 10 MPa and a temperature of 180°C. The hybrid PP composites were conditioned in the climate room overnight at 20°C and 65% relative humidity, and they were cut to the related standards for each test.

2.3 | Mechanical properties of the hybrid PP composites

The mechanical properties of the hybrid PP composites including tensile, flexural and impact tests were determined according to ASTM D 638,[39] ASTM D 790[40] and ASTM D 256.[41] The tensile and flexural tests were carried out on a Zwick/Roell brand Z010 model and 50kN load Universal Test Machine. Before the impact test, all samples were notched with a Ray-Ran test Equipment Ltd. (Polytest, UK), and then performed on the Zwick impact testing machine (HIT5.5P, Germany). Ten samples were used for each group of the hybrid PP samples in the mechanical tests.

2.4 | FTIR-ATR analysis and electrical conductivity

Characterization of Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) for MCC, waste toner, and the hybrid composite sample surfaces was accomplished with a Shimadzu brand IR Prestige-21/Pike Miracle ATR equipment. The spectra of the pellets produced from each oven-dried samples, collected at the wavenumber range 600–4000 cm^{-1} and 24 scans at 16 cm^{-1}, were investigated.

The electrical conductivity of the hybrid PP composites filled with waste toner was applied using a four-point probe instrument an Ossila brand T2001A3 model which measures the sheet resistance/conductivity of a sample. Unexpectedly, any electrical conductivity has not been detected for all hybrid PP composite samples with/without the presence of toner. Two possible reasons may explain this situation. First, the toner contains a high amount of non-conductive polystyrene co-acrylate, and second, low the amount of carbon in the toner does not occur a sufficient conductive pathway. Therefore, this parameter is not placed in the results and discussion section.

TABLE 1 The experimental design for the hybrid PP composites.

Samples	PP (%)	PPC (%)	Talc (%)	MCC (%)	Toner (%)
PP	100	–	–	–	–
MCC/T	85	–	10	5	–
MCC/T/PPC	82	3	10	5	–
0.5 T	81.5	3	10	5	0.5
1.0 T	81	3	10	5	1
1.5 T	80.5	3	10	5	1.5
2.0 T	80	3	10	5	2

Note: Values are percentage by weight (wt%).
Abbreviations: MCC, microcrystalline cellulose; PP, polypropylene; PPC, polypropylene carbonate.

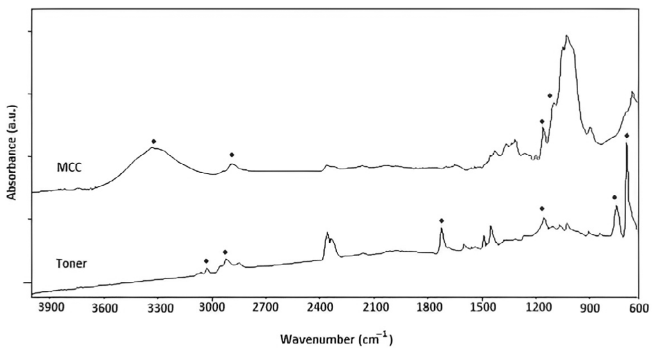

FIGURE 1 FTIR-ATR spectra of toner and microcrystalline cellulose.

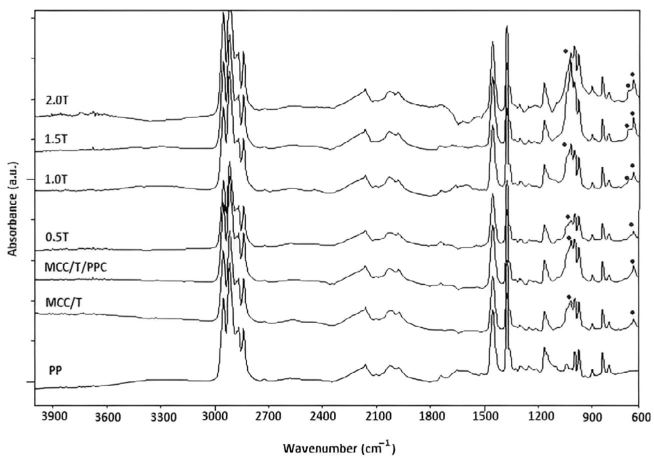

FIGURE 2 FTIR-ATR spectra of PP–hybrid composites.

2.5 | Differential scanning calorimetry analysis

Differential scanning calorimetry analysis (DSC) was accomplished on a Perkin Elmer (Model DSC 8000) under nitrogen atmosphere. Roughly 5–7 mg of oven-dried samples were put in aluminum pans and heated from room temperature to 250°C at a scanning rate of 10°C/min and then cooled with 20 mL/min of nitrogen flow rate. After cooling the sample was reheated to 250°C. It was measured in three steps under nitrogen atmosphere heating, cooling, and reheating. The polymer's degree of crystallinity (Xc) was calculated based on the Wunderlich equation.[42]

$$X_c(\%) = \left(\frac{\Delta H_m}{\Delta H_0 x W}\right) x100 \tag{1}$$

where ΔH_m and ΔH_0 indicate the heat fusion of composite and 100% crystalline polypropylene, respectively, and W refers to the plastic ratio. ΔH_0 value was used as 207 J/g for PP.

2.6 | Water absorption of the hybrid PP composites

The ASTM D 1037[43] standard was used to calculate the water absorption rate of hybrid composites. For each hybrid composite group, eight samples of 50 × 50 × 5 composite thickness (mm) were weighed with an accuracy of 0.01 g. The hybrid composites were then immersed in water at 20 ± 2°C. The measurements were taken in the first 24 h, and then every week for 2 months. Before their weight was taken, the excess water on their surface was removed with a towel. The measured values were calculated by proportioning to the initial weights.

2.7 | Surface roughness of the hybrid PP composites

The surface roughness of hybrid composites was measured using a surface profilometer (Mitutoyo SJ-210). The stylus has a radius of 5 and a contact angle of 90°, and it runs at a speed of 0.5 mm/s. From the surface, 25 random measurements with a span of 15 mm were taken. The four measurements of the surface parameters (R_a, R_q, and R_z) were performed at cross directions for each sample. The arithmetic averages of these values were given.

2.8 | Scanning electron microscope analysis

The surface morphology of the fractured samples was examined under vacuum using (ZEISS EVO LS 10, Carl Zeiss NTS GmbH, Germany) with an acceleration voltage of 10 kV. Prior to the analyses, the samples were coated with gold using a sputtering system. The SEM images were taken at a magnification of 500×.

2.9 | Statistical analyses

The statistical evaluation of this study's results was carried out using the statistical package software SPSS 21.0. The analysis of variance (one-way ANOVA) was applied for the mechanical tests' results of the composite samples and their homogeneity groups were determined with the Duncan multiple range test. The water absorption results of the samples were analyzed based on repeated measures ANOVA.

3 | RESULTS AND DISCUSSION

3.1 | FTIR-ATR characterization

The FTIR-ATR spectra of MCC and waste toner are presented in Figure 1. In the spectrum of MCC, peaks indicating the O—H stretching vibration in the hydroxyl groups of cellulose at the 3440 cm^{-1} band and, the C—H stretching vibrations in the —CH_2— groups at the 2910 cm^{-1} band are seen. The peak at 1437 cm^{-1} indicates the presence of CH_2 of MCC and the band at 1366 cm^{-1} means the C—O stretching vibration of CH_2—OH groups of MCC. In addition, peaks related to the C—O stretching vibration of cellulose in the 1044 cm^{-1} band and the C—O—C symmetrical tension of cellulose in the 1120 cm^{-1} band are seen in the spectrum of MCC.[44]

Regarding the spectrum of waste toner, the 3000 cm^{-1} band of waste toner illustrates C—H stretching, while the peaks in the 700 and 760 cm^{-1} bands refer to out-of-plane deformation substitutions of polystyrene. The presence of ester carbonyl and the C—O—C stretch are referred to as the peaks in the 1730 band and 1130 cm^{-1} band, respectively.[45] According to these results, it can be said that the major resin of toner waste consists of polystyrene co-acrylate. This is also in line with the results of Yordanova et al.[34]

Figure 2 shows the FTIR-ATR spectra of PP and hybrid composites. In PP composites containing 5% MCC (MCC/T, MCC/TPPC, 0.5 T, 1.0 T, 1.5 T, and 2.0 T) as filler, cellulose origin peak formations were observed at 1044 and 1120 cm^{-1} band. Also due to Si—O—Mg bond, talc origin peak observed at 677 cm^{-1} band.[46] With the addition of 1%, 1.5%, and 2% toner waste to the composite composition, an increase in the peak intensity was observed in the 700 cm^{-1} band, and peak formation was observed at 760 cm^{-1} band due to

TABLE 2 Mechanical properties of talc/MCC/waste toner hybrid composites.

ID	TS**	TM***	FS***	FM***	IS*
PP	19.34 (b) *4.92*	3657.4 (cd) *400.9*	47.76 (d) *1.32*	1864 (d) *62.29*	2.97 (ab) *0.37*
MCC/T	25.58 (a) *1.99*	4542 (a) *387.52*	50.86 (cd) *3.90*	2418 (bc) *165.44*	3.20 (a) *0.48*
MCC/T/PPC	26.16 (a) *1.46*	4662 (a) *400.46*	52.40 (bc) *0.72*	2492 (b) *87.86*	3.10 (ab) *0.22*
0.5 T	24.98 (a) *2.05*	4020 (bc) *260.48*	50.92 (cd) *2.12*	2474 (b) *138.13*	2.70 (bc) *0.27*
1.0 T	25.28 (a) *2.37*	4346 (ab) *355.43*	55.78 (a) *2.31*	2766 (a) *248.15*	2.53 (c) *0.18*
1.5 T	25.40 (a) *1.68*	3692 (cd) *133.30*	55.36 (ab) *1.30*	2628 (ab) *182.54*	2.84 (abc) *0.13*
2.0 T	20.42 (b) *2.24*	3528 (d) *328.51*	46.34 (d) *3.21*	2238 (c) *135.35*	2.87 (abc) *0.27*

Note: Letters indicate statistically significant differences between the groups.
Abbreviations: FM, flexural modulus of elasticity; FS, flexural strength (MPa); IS, impact resistance (J/m); MCC, microcrystalline cellulose; PP, polypropylene; PPC, polypropylene carbonate; TM, tensile modulus of elasticity (MPa); TS, tensile strength (MPa).
$^{*}p < 0.05$; $^{**}0.0001 < p < 0.001$; $^{***}p < 0.0001$.

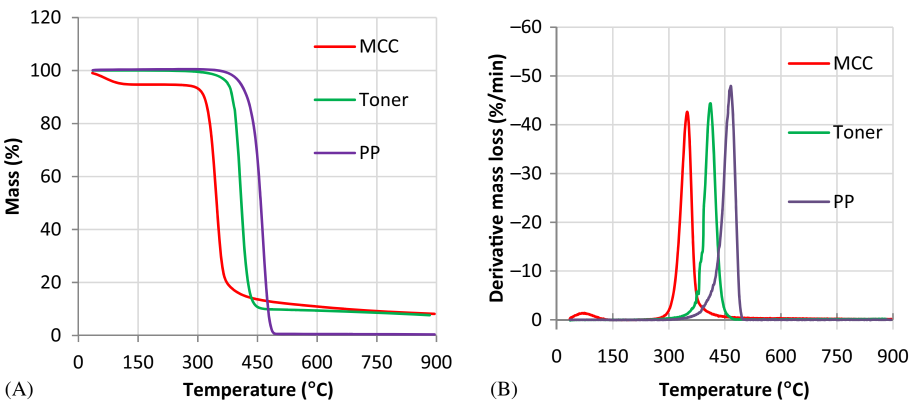

FIGURE 3 TGA (A) and DTGA (B) curves of the components of the hybrid composites.

TABLE 3 Thermal properties of filler, additives, and hybrid composites.

	First degradation step				Second degradation step				
	Onset temperature (°C)	Inflection Point temperature (°C)	Endset temperature (°C)	ΔY (%)	Onset temperature (°C)	Inflection point temperature (°C)	Endset temperature (°C)	ΔY (%)	Residual at 895°C (%)
MCC	320.60	349.67	366.20	79.94	–	–	–	–	8.16
Toner	392.51	410.61	427.56	88.01	–	–	–	–	7.68
PP	–	–	–	–	439.89	465.44	478.60	99.38	0.40
MCC/T	303.18	304.28	316.84	6.10	445.12	466.34	484.06	72.77	5.49
MCC/T/PPC	336.62	350.89	362.21	12.93	451.49	471.07	486.24	64.18	8.50
0.5 T	332.02	349.97	358.52	8.59	443.64	467.23	483.64	74.32	4.90
1.0 T	334.80	339.28	342.49	6.51	440.09	466.53	481.01	79.07	2.75
1.5 T	329.83	347.83	356.08	6.40	438.78	466.20	480.38	79.58	4.33
2.0 T	337.10	351.74	360.08	6.36	441.31	463.11	480.39	81.20	4.62

the out-of-plane deformation substitutions of polystyrene.[44]

3.2 | Mechanical properties of the hybrid PP composites

The mechanical properties of the effect of different percentages of waste toner powder into PP polymer matrix incorporation with talc and MCC are shown in Table 2. All the hybrid PP composites had superior mechanical properties over un-filled PP due to the hybridization effect. This phenomenon is supported by some investigations.[47–49] Reale Batista et al.[49] studied on comparison of cellulose/inorganic-hybrid PP composites to neat polymer and inorganic reinforced composites in terms of performance. They stated that the hybrid composites had the highest mechanical properties among both neat PP and inorganic PP composites. In another previous study,[50] the recycled talc-based polypropylene composites were reinforced with bamboo fibers and this caused a significant increase in the mechanical properties. The effect of coupling agent was examined, and maleic anhydride grafted PP enhanced the interaction between natural fiber and talc-based polymer matrix.

The tensile strength (TS) values of hybrid composites varied from 20.42 to 25.58 MPa. Compared to TS of unfilled PP composites, the improvement with the hybridization was observed between ~6% (2.0 T) and 35% (MCC/T/PPC). The PPC addition promoted the tensile/flexural strengths and modulus values of the hybrid PP composites by 2.5%–3% increments. The tensile strength values of the hybrid composites increased by increasing the waste toner content to 1.5% by weight and then decreased by adding 2% by weight. The highest tensile modulus (4346 MPa) was obtained from the 1.0 T composite.

PP-based hybrid composites had higher flexural properties than un-filled PP samples owing to the hybridization effect. As expected, PPC acted as a coupling agent to enhance the interaction at the matrix/reinforce(s) interphase and led to improvement in the flexural properties of the hybrid composites. The hybrid composite with 1% waste toner exhibited higher flexural strength of 55.78 MPa and flexural modulus of 2766 MPa in comparison with 26.16 and 2492 MPa of MCC/T/PPC composite. On the other hand, the addition of 1–1.5% of waste toner into the MCC/T/PCC promoted the flexural strength and modulus of composites by amounts of 11% and 6%, respectively. Waste toner increased the strength of the hybrid composite due to carbon content in waste toner. It is known that carbon when used in appropriate amounts, positively affects thermal and mechanical properties including the crystallinity of the polymer composites.[51] The crystallinity of the toner may be responsible for this. Since DSC analysis revealed that crystallinity values of the hybrid composites with waste toner were higher than that of neat PP. Generally, the mechanical behavior of hybrid composite materials depends on crystallinity, fiber aspect ratio morphology, interface properties, modulus, and volume fraction of each filler and matrix.[52] However, using more than 1.5% of waste toner reduced the tendency to improve the mechanical properties of PP hybrid composites.

The impact strength values of the hybrid composites varied from 3.20 to 2.53 J/m. As waste toner content increased, the impact strength values of all composites generally increased. The impact strength value for MCC/T composite without waste toner and PPC was higher than all other composites. Merrill et al.'s[45] assertion is that polystyrene co-acrylate constitutes the major component of toner resin. The presence of PS in the waste toner may moderately increase the viscoelasticity of the samples containing waste toner, and hence impact strength may increase.

3.3 | Thermal properties of the hybrid PP composites

Figure 3 shows the TGA and DTGA diagrams of the filler and PP used in the composite composition. The inflection point temperature of MCC was determined as 349.67°C, the inflection point temperature of polystyrene-*co*-acrylate due to toner waste was determined as 410.61°C and the inflection point temperature of PP was determined as 465.44°C. As can be seen from Figure 3, the degradation temperature of the waste toner was located between PP and MCC.

Table 3 summarizes the thermal properties of MCC, toner waste, PP, and the hybrid composites. TGA and DTGA diagrams of the hybrid composites are also shown in Figure 4A,B, respectively. As can be seen from Figure 4 and Table 3, two degradation steps occurred in the composites due to the fillers and PP content. It is thought that the first step (Figure 4C) is MCC and the second step (Figure 4D) is predominantly PP-based. Waste toner continued to degrade in both steps. As a result of the addition of PPC as a compatibilizer to the MCC/Talc/PP composite, the inflection point temperature increased from 304.28°C to 350.89°C in the first degradation step. This improvement can be explained by the compatibilizer providing greater fusion of the talc and fibers to the plastic and slowing the thermal degradation. Waste toner addition to the composite composition partially reduced the first degradation step by 1% and 1.5%. In the second decomposition step, with the addition of MCC and Talc to PP, the inflection point temperature increased from 465.44°C to 466.34°C. The use of PPC as a compatibilizer increased the inflection point temperature to 471.07°C. However, with the addition of waste toner to the composite content, the inflection point temperature

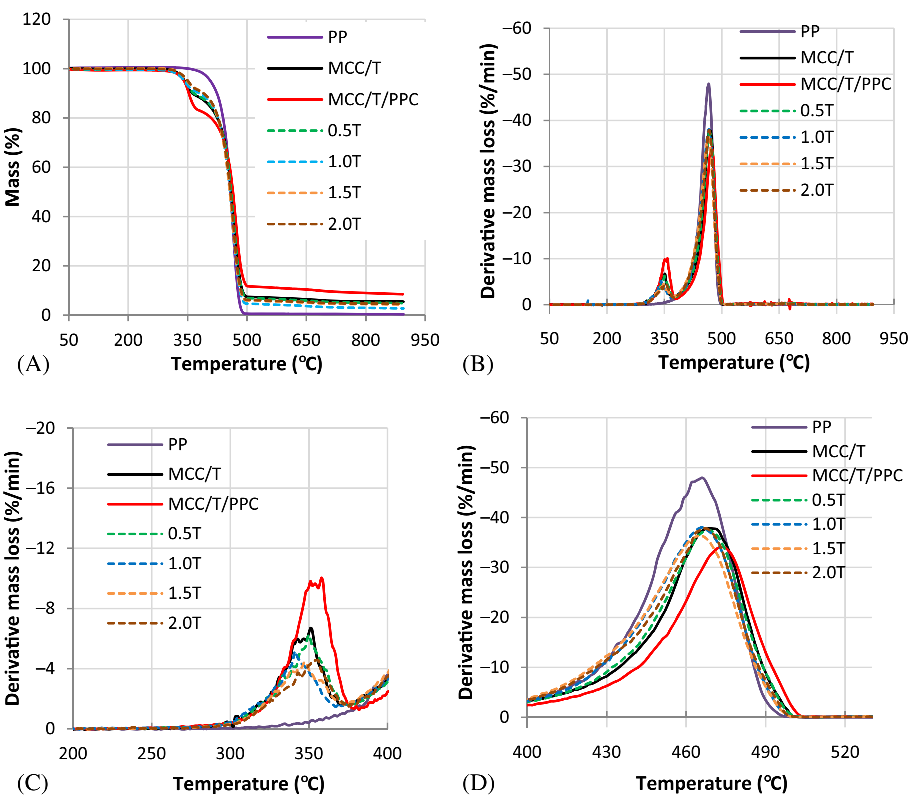

FIGURE 4 (A) TGA, (B) DTGA curves of the hybrid PP composites, (C) The first step of decomposition (200–400°C), and (D) the second step of decomposition (400–520°C).

TABLE 4 DSC results of the hybrid PP composites.

	T_{cold} (°C)	Peak $height_{cold}$ (mW)	ΔH_{cold} (J/g)	T_{melt} (°C)	Peak height melt (mW)	ΔH_{melt} (J/g)	$X_{corr.}$ (%)
PP	106.91	−27.6691	−86.1589	162.62	14.4578	86.5639	41.82
PPC	89.67	−20.4009	−66.3287	133.32	5.0305	58.6547	28.83
MCC/T	120.02	−24.6595	−84.7739	164.11	15.2167	83.2744	47.33
MCC/T/PPC	119.30	−14.0839	−54.4651	162.22	8.5651	49.9066	29.40
0.5 T	119.13	−16.1952	−63.9081	162.28	10.6851	60.8665	36.08
1.0 T	118.08	−18.1371	−75.3697	162.90	12.2809	74.2481	44.28
1.5 T	119.32	−26.9094	−87.9839	163.10	15.7038	87.2543	52.36
2.0 T	118.98	−21.6004	−76.5918	162.54	13.0136	75.0450	45.32

decreased to 467.23°C at a rate of 0.5% and to 463.11°C at a rate of 2%. The reason for the decrease in the inflection point temperature of the second degradation step with the increased amount of toner waste is that the inflection point temperature of polystyrene-*co*-acrylate (410.61°C), the main resin of the toner, is lower than the inflection point temperature of PP (465.44°C).

Table 4 shows the DSC results of the composites. The crystallinity of PP was calculated as 41.82%. However, the crystallinity of the PPC used as compatibilizer was calculated as 28.83%. This explains why the crystallinity increased to 47.33% with the addition of MCC and talc to the PP composition, but decreased to 29.40% with the addition of 3% PPC. If the MCC/T/PPC composite is considered as the control group, it was determined that the crystallinity increased up to the addition of 1.5% waste toner. The highest crystallinity value was calculated as 52.36% in the composite containing 1.5% waste toner. A similar increase was obtained in the study of Pesman and Güleç[53] by adding toner-printed office paper fiber. After 1.5% waste toner ratio, the crystallinity started to decrease. The reason for the decrease due to excessive use may be that waste toner acts as a heterogeneous nucleator due to its structure.[37]

3.4 | Water absorption of the hybrid PP composites

The hybrid PP composites' rates of water absorption (WA) after 1 day, 1, 2, 3, 4, 5, 6, 7, and 8 weeks and their Duncan's homogeneous groups were given in Figure 5. The WA values from the lowest (0.06%) to the highest (0.48%) were ranging as PP < MCC/T/PPC≤1.0 T ≤ 1.5 T < MCC/T < 0.5 T < 2.0 T in the hybrid composite groups.

The WA values of the hybrid PP composites were periodically increased. This increase was remarkably indicated for the samples including two percentages of

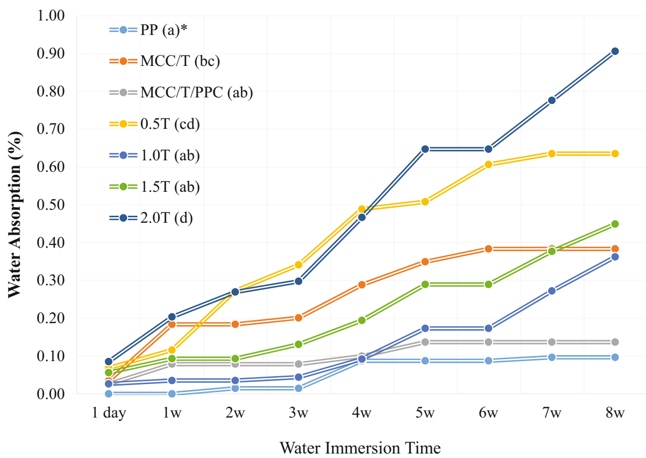

FIGURE 5 The water absorption of the hybrid PP composites during 2 months of water immersed. *: the letter(s) refer to homogeneous subsets for the hybrid composite groups based on variance analysis ($p < 0.0001$).

waste toner powder (2.0 T). On the contrary, the 1.0 T groups of samples had a lower water absorption rate compared to those of other waste toner loading rates. This is compatible with mechanical test results and surface roughness parameters of the hybrid composites. Besides the filler being hydrophobic or hydrophilic in nature, the dispersion and compatibility are also key factors for the physical properties. Heterogeneity or ununiform dispersion of the filler into the polymer matrix caused gaps/voids or agglomerates to increase the water absorption of the hybrid composites.[16]

As shown also in Figure 5, the MCC/T/PPC composite's water absorption rates had better results than the MCC/T composite. It was observed that the PPC enhanced the interface between the fillers and the polymer matrix.[54,55]

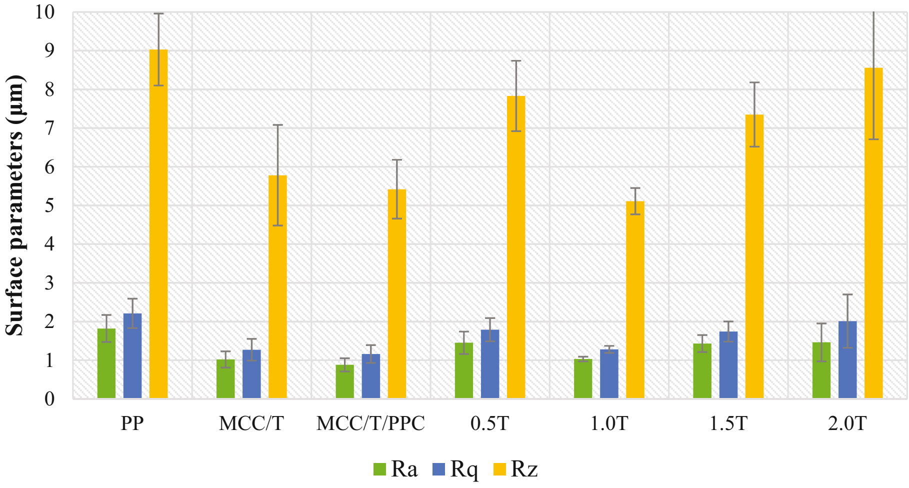

FIGURE 6 The surface parameters of the hybrid PP composites.

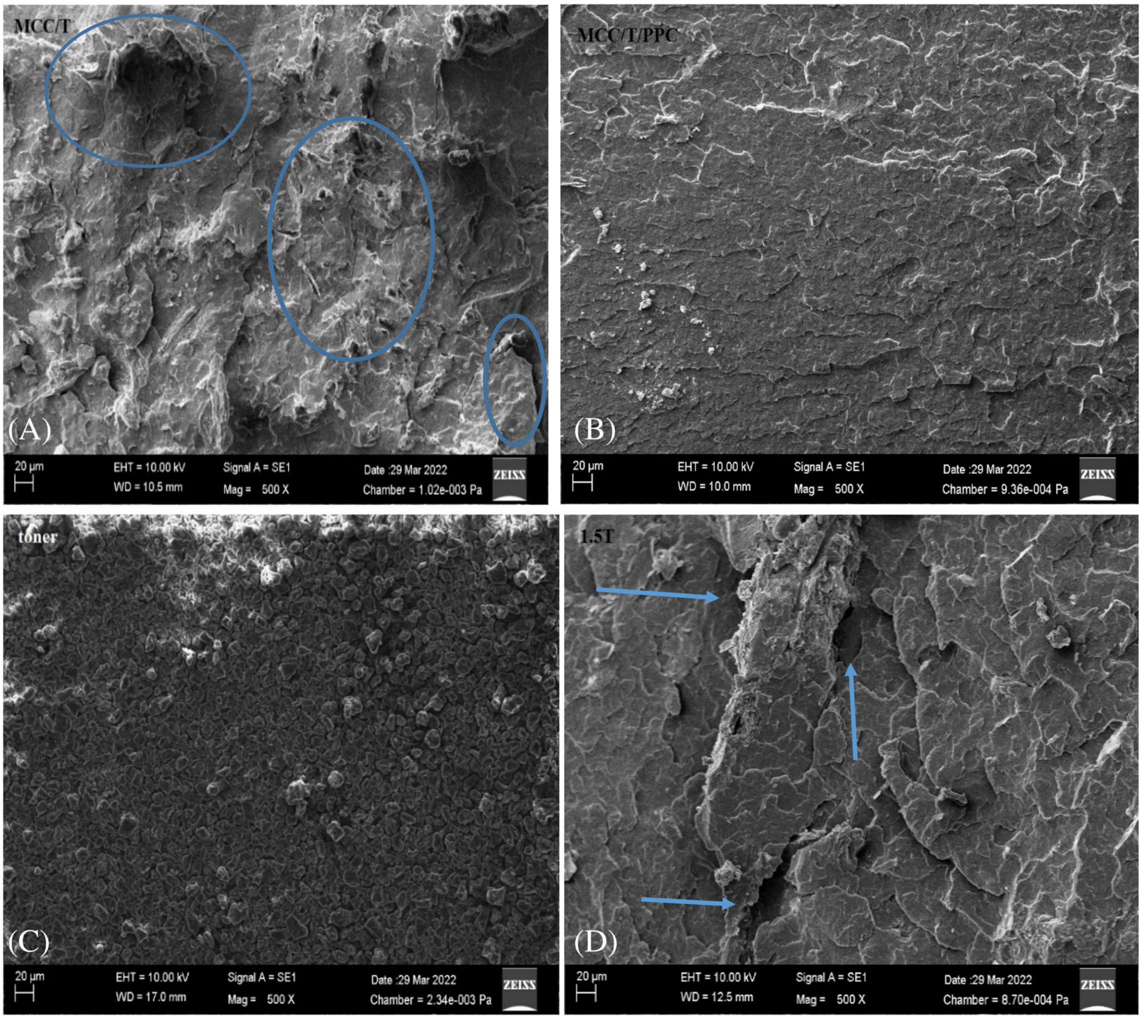

FIGURE 7 SEM photographs of the fractured surfaces of MCC/T (A), MCC/T/PPC (B), and toner powder (C), and the composite of 1.5 T(D) at 500× magnification.

3.5 | Surface properties of the hybrid PP composites

The measured surface roughness parameters (R_a: roughness average, R_q: Root mean square roughness; and R_z: average max. height of the profile) of the hybrid PP composite samples are shown in Figure 6.

The highest values were observed for PP samples without filler. The incorporation of the fillers MCC, talc, coupling agent, and waste toner at 1 wt% resulted in a quiet similar effect on the surface roughness parameters. The use of waste toner at high loading affected adversely the smoothness of the surface of the hybrid composites. This supported the mechanical test results. When a high amount of the waste toner increased the tendency of agglomerate formation in the PP matrix this led to incompatibility and reduced all properties of the hybrid composite. Kuroda et al.[55] studied talc size effect on the surface roughness PP composites. They reported if particle size of filler (talc) increases the self-formed skewness and fine irregularities occur due to PP shrinkage in the non-transferred region. It is known that to get the smoother surface of the reinforced composites is needed a sufficient dispersion or well transfer of the microstructure fillers into the polymer matrix.[56,57] Varying filler sizes and loading levels in the hybrid composite manufacturing process are the points to be emphasized.[5,58] The waste toner has nanosize particles[37] and is in need of good dispersion/blending before extrusion or injection process. If nanofiller is not dispersed uniformly, it prevents enhancement of the properties including surface characteristics of the hybrid composite even reducing them. In addition, the Teflon plate that was used for compounding might not properly separate from some of the hybrid composites and caused different surface roughness profiles. Kaneda et al.[59] supported this hypothesis, they reported also the processing method also changed the surface quality and stated that the composites produced by injection molding had smoother surfaces than those of press molding.

3.6 | Morphological properties of the hybrid PP composites

Figure 7 shows the SEM micrographs of the fractured surface of the hybrid PP composites and waste toner powder. Figure 7A observed that MCC and talc were not dispersed uniformly in the polymer matrix, gaps and roughness were seen in the micrographs of MCC/T–hybrid PP composites. As can be shown the Figure 7B, the use of a PPC coupling agent promoted the interaction between talc and polypropylene matrix at the interface, resulting in no void in the matrix and a smooth surface. SEM observation of toner waste and the fracture surface of the hybrid composite with 1.5 wt% are illustrated in Figure 6C,D. It seemed that the spherical shape of toner powder shifted flat and larger particles due to the polymerization of toner when used in the matrix by extrusion and compress molding processes. Trumic and Antonijevic[60] stated that toner shapes changed with thermal treatment. In Figure 7D, the flat shape of toner powders dispersed homogenously in the PP matrix was observed.

4 | CONCLUSIONS

Hybrid composite produced by the hybridization of different natural fibers and/or mineral additives has become widespread comparing single-additive composite. In this study, the use of toner waste placed the "e-Waste" group was investigated in the field of polymer composites. MCC and talc based hybrid composites enhanced their physical, mechanical and surface properties with presence of PPC and waste toner. Based on the FTIR–ATR and TGA result of the toner, its major resin was detected as polystyrene co-acrylate which was lower than the inflection point temperature of PP (465.44°C). The SEM graphs shows that the spherical shape of the toner shifted flat and larger particles in the hybrid PP composites. Water absorption values for the 1.0 T and 1.5 T groups of samples were lower than those of waste toner added hybrid composites. Addition of waste toner up to 1.5% increased crystallinity of the hybrid PP composites. The highest crystallinity value was 52.36%. But higher 1.5% of the toner caused deterioration of all hybrid composites. Based on the findings of this experimental results, it was stated that the optimum usage range was between 1% and 1.5%. Toner waste without being released into nature upcycling as a filler, would be an alternative solution in terms of minimizing environmental effects and circular economy. Supported by further studies, it could be a promising filler in polymer composites for automotive under-the-hood applications due to its high carbon content.

AUTHOR CONTRIBUTIONS

Ayfer Donmez Cavdar: conceptualization, investigation, methodology, writing – reviewing, and editing. Emrah Peşman: methodology, writing- reviewing, validation, editing. Sevda Boran Torun: methodology, reviewing and editing, supervision.

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DATA AVAILABILITY STATEMENT

All data, materials, and resources will be made available upon reasonable request.

CONSENT FOR PUBLICATION

We affirm that the work described has not been previously published, is not currently under consideration for publication elsewhere, and has the full approval of all the authors. Furthermore, if accepted, it will not be published in the same form, whether in English or any other language, including electronically, without obtaining written consent from the copyright holder.

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REFERENCES

1. Kumar N, Mireja S, Khandelwal V, Arun B, Manik G. Lightweight high-strength hollow glass microspheres and bamboo fiber based hybrid polypropylene composite: a strength analysis and morphological study. *Compos B: Eng*. 2017;109:277-285.
2. Gogoi R, Kumar N, Mireja S, Sethi SK, Manik G. Twenty-Second International Conference on Composite Materials (ICCM22), Melbourne, Australia. 2019.
3. Gogoi R, Kumar N, Mireja S, Ravindranath SS, Manik G, Sinha S. Effect of hollow glass microspheres on the morphology, rheology and crystallinity of short bamboo fiber-reinforced hybrid polypropylene composite. *JOM*. 2019;71:548-558.
4. Ertas M, Altuntas E, Donmez Cavdar A. Effects of halloysite nanotube on the performance of natural fiber filled poly(lactic acid) composites. *Polym Compos*. 2019;40(11):4238-4247.
5. Çavdar AD, Torun SB, Peşman E, Angin N, Ertaş M, Mengeloğlu F. In: Rakesh PK, Davim JP, eds. *Cellulose Composites: Processing and Characterization*. De Gruyter; 2023.
6. Faruk O, Błędzki AK, Fink HP, Sain MM. Progress report on natural fiber reinforced composites. *Macromol Mater Eng*. 2014;299:9-26.
7. Ahmad F, Choi HS, Park MK. A review: natural fiber composites selection in view of mechanical, light weight, and economic properties. *Macromol Mater Eng*. 2015;300:10-24.
8. Pervaiz M, Panthapulakkal S, Sain M, Tjong J. Emerging trends in automotive Lightweighting through novel composite materials. *Mater Sci Appl*. 2016;7(1):26-38.
9. Pickering KL, Sawpan MA, Jayaraman J, Fernyhough A. Influence of loading rate, alkali fibre treatment and crystallinity on fracture toughness of random short hemp fibre reinforced polylactide bio-composites. *Compos Part A Appl Sci Manuf*. 2011;42:1148-1156.
10. Jonoobi M, Harun J, Mathew AP, Oksman K. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Compos Sci Technol*. 2010;70(12):1742-1747.
11. Mathew AP, Oksman K, Sain M. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). *J Appl Polym Sci*. 2005;97(5):2014-2025.
12. Xu X. Ph.D Thesis, Georgia Institute of Technology. 2008.
13. Seydibeyoğlu MÖ, Oksman K. Novel nanocomposites based on polyurethane and micro fibrillated cellulose. *Compos Sci Technol*. 2008;68(3–4):908-914.
14. Kiziltas A, Gardner DJ, Han Y, Yang HS. Determining the mechanical properties of microcrystalline cellulose (MCC)-filled PET-PTT blend composites. *Wood Fiber Sci*. 2010;2:165-176.
15. Boran S, Kiziltas A, Kiziltas E, Gardner DJ. Characterization of ultrafine cellulose-filled high-density polyethylene composites prepared using different compounding methods. *BioResources*. 2016;11(4):8178.
16. Cavdar AD, Torun SB, Ertas M, Mengeloglu F. Ammonium zeolite and ammonium phosphate applied as fire retardants for microcrystalline cellulose filled thermoplastic composites. *Fire Saf J*. 2019;107:202-209.
17. Móczó J, Pukanszky B. Polymer micro and nanocomposites: structure, interactions, properties. *J Ind Eng Chem*. 2008;14(5):535-563.
18. DeArmitt C, Rothon R. In: Kutz M, ed. *Applied Plastics Engineering Handbook*. 2nd ed. William Andrew Publishing; 2017.
19. Liang JZ. Reinforcement and quantitative description of inorganic particulate-filled polymer composites. *Compos Part B Eng*. 2013;51:224-232.
20. Pérez E, Alvarez V, Pérez CJ, Bernal C. A comparative study of the effect of different rigid fillers on the fracture and failure behavior of polypropylene based composites. *Compos B: Eng*. 2013;52:72-83.
21. Duleba B, Spišák E, Greškovič F. Mechanical properties of PA6/MMT polymer nanocomposites and prediction based on content of Nanofiller. *Procedia Eng*. 2014;96:75-80.
22. Kluenker E, Faymonville K, Peter M, Moeller M, Hopmann C. Reactive extrusion processing of polypropylene/SiO2 nanocomposites by in situ synthesis of the nanofillers: experiments and properties. *Polymer*. 2014;55(21):5370-5380.
23. Zaman HU, Beg MDH. Effect of CaCO3 contents on the properties of polyethylene nanocomposites sheets. *Fibers Polym*. 2014;15:839-846.
24. Qiu F, Hao Y, Li X, Wang B, Wang M. Functionalized graphene sheets filled isotactic polypropylene nanocomposites. *Compos Part B Eng*. 2015;71:175-183.
25. do Nascimento EM, Eiras D, Pessan LA. Composites Part B. *Engineering*. 2016;91:228-234.
26. Zare Y. Modeling the strength and thickness of the interphase in polymer nanocomposite reinforced with spherical nanoparticles by a coupling methodology. *J Colloid Interface Sci*. 2016;465:342-346.
27. Rueda MM, Auscher MC, Fulchiron R, et al. Rheology and applications of highly filled polymers: a review of current understanding. *Prog Polym Sci*. 2017;66:22-53.
28. Qiu F, Wang M, Hao Y, Guo S. The effect of talc orientation and transcrystallization on mechanical properties and thermal stability of the polypropylene/talc composites. *Compos Part A Appl Sci Manuf*. 2014;58:7-15.
29. Lapcik L Jr, Jindrova P, Lapcikova B, Tamblyn R, Greenwood R, Rowson N. Effect of the talc filler content on the mechanical properties of polypropylene composites. *J Appl Polym Sci*. 2008;110(5):2742-2747.
30. Parvin N, Ullah MS, Mina MF, Gafur MA. Structures and mechanical properties of talc and carbon black reinforced high density polyethylene composites: effects of organic and inorganic fillers. *J Bangladesh Acad Sci*. 2013;37(1):11-20.
31. Racca LM, Pacheco EBAV, Bertolino LC, et al. Composites based on polypropylene and talc: processing procedure and

prediction behavior by using mathematical models. *Adv Condens Matter Phys*. 2018;8:2018.
32. Wang K, Bahlouli N, Addiego F, et al. Effect of talc content on the degradation of re-extruded polypropylene/talc composites. *Polym Degrad Stab*. 2013a;98(7):1275-1286.
33. Fiorentino B, Fulchiron R, Bounor-Legaré V, Majesté JC, Leblond JC, Duchet-Rumeau J. Chemical modification routes of synthetic talc: influence on its nucleating power and on its dispersion state. *Appl Clay Sci*. 2015;109:107-118.
34. Yordanova D, Angelova S, Dombalov I. On fatigue behaviour of two spring steels. Part II: mathematical models. *J Environ Sci*. 2014;3:140-1466.
35. Ruan J, Li J, Xu Z. An environmental friendly recovery production line of waste toner cartridges. *J Hazard Mater*. 2011;185(2–3):696-702.
36. Gaikwad V, Kumar U, Pahlevani F, Piadasa A, Sahajwalla V. Thermal transformation of waste toner powder into a value-added ferrous resource. *ACS Sustain Chem Eng*. 2017;5(12):11543.
37. Hammani S, Barhoum A, Nagarajan S, Bechelany M. Toner waste powder (TWP) as a filler for polymer blends (LDPE/HIPS) for enhanced electrical conductivity. *Materials*. 2019;12(19):3062.
38. Daniel-Mkpume CC, Ahaiwe RC, Ifenatuorah CL, Ike-Eze ICE. Potential end of life application of African star apple shell and waste toner powder as composite filler materials. *J Mater Cycles Waste Manag*. 2022;24(2):680-691.
39. ASTM D 638. *Standard Test Method for Tensile Properties of Plastics*. ASTM International; 1994.
40. ASTM D 790. *Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*. ASTM International, West Conshohocken; 2004.
41. ASTM D 256. *Determining the Izod Pendulum Impact Resistance of Plastics*. ASTM International; 2022.
42. Wunderlich B. The basis of thermal analysis. *Thermal Analysis*. Academic Press; 1990 **THE BASIS OF THERMAL ANALYSIS**.
43. ASTM D 1037. *Evaluating Properties of Wood-Based Fiber and Particle Panel Materials*. ASTM International; 1996.
44. Liang CY, Marchessault RH. Infrared spectra of crystalline polysaccharides. II. Native celluloses in the region from 640 to 1700 cm.1. *J Polym Sci*. 1959;39:269-278.
45. Merrill RA, Bartick EG, Taylor JH III. Forensic discrimination of photocopy and printer toners I. The development of an infrared spectral library. *Anal Bioanal Chem*. 2003;376(8):1272-1278.
46. Sprynskyy M, Gadzała-Kopciuch R, Nowak K, Buszewski B. Removal of zearalenone toxin from synthetics gastric and body fluids using talc and diatomite: a batch kinetic study. *Colloids Surf B Biointerfaces*. 2012;94:7-14.
47. Thwe MM, Liao K. Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Compos Sci Technol*. 2003;63(3–4):375-387.
48. Huda MS, Drzal LT, Mohanty AK, Misra M. The effect of silane treated- and untreated-talc on the mechanical and physico-mechanical properties of poly(lactic acid)/newspaper fibers/talc hybrid composites. *Compos Part B Eng*. 2007;38(3):367-379.
49. Reale Batista MD, Drzal LT, Kiziltas A, Mielewski D. Hybrid cellulose-inorganic reinforcement polypropylene composites: lightweight materials for automotive applications. *Polym Compos*. 2020;41(3):1074-1089.
50. Inacio AL, Nonato RC, Bonse BC. Recycled PP/EPDM/talc reinforced with bamboo fiber: assessment of fiber and compatibilizer content on properties using factorial design. *Polym Test*. 2017;61:214-222.
51. Zhu K, Guo X, Zhang Q, et al. Crystallization, rheological behavior and mechanical properties of carbon nanotube/metallocene polypropylene composites. *Mater Res Exp*. 2023;10:025301.
52. Ifuku S, Yano H. Effect of a silane coupling agent on the mechanical properties of a microfibrillated cellulose composite. *Int J Biol Macromol*. 2015;74:428-432.
53. Pesman E, Güleç T. The effects of ink presence on mechanical, physical, morphological and thermal properties of office and newspaper fiber-polypropylene composites. *Mater Sci*. 2019;25(2):195.
54. Wang D, Yu J, Zhang J, He J, Zhang J. Transparent bionanocomposites with improved properties from poly(propylene carbonate) (PPC) and cellulose nanowhiskers (CNWs). *Compos Sci Technol*. 2013b;85:83-89.
55. Muthuraj R, Mekonnen T. Carbon dioxide–derived poly(propylene carbonate) as a matrix for composites and nanocomposites: performances and applications. *Macromol Mater Eng*. 2018;303(11):1800366.
56. Kuroda S, Mizutani A, Ito H. Effect of talc size on surface roughness and glossiness of polypropylene injection molding application to automotive plastics. *Polym Eng Sci*. 2020;60(1):132-139.
57. Kuroda S, Mizutani A, Ito H. Influence of talc and rubber contents on surface replication of polypropylene injection molding application to automotive plastics. *J Polym Eng*. 2019;39(3):300-308.
58. Gurau L, Ayrilmis N. Effect of raw material composition of wood plastic composites on surface roughness parameters evaluated with a robust filtering method. *J Thermoplast Compos Mater*. 2019;32(4):427-441.
59. Kaneda R, Takahashi T, Takiguchi M, Hijikata M, Ito H. Optical properties of HDPE in injection molding and injection press molding for IR system lenses part II: Mold temperature and surface roughness effects on injection molding. *Int Polym Process*. 2017;32(2):237-244.
60. Trumic MS, Antonijevic MM. Results of fibre and toner flotation depending on oleic acid dosage. *Physicochem Prob Miner Process*. 2016;52:5.

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