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The investigation of the mechanical thermal and physical properties of using waste toner/MCC/old newspaper fiber in polypropylene hybrid composites

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Abstract

In this study, the effects of polypropylene (PP) composites produced by adding 10% old newspaper fibers (ONP), 5% microcrystalline cellulose (MCC), 3% polypropylene carbonate (PPC), and waste toner from 1% to 4% on the mechanical properties, physical properties, morphological, and thermal properties were investigated. According to the FTIR-ATR and SEM-EDS analysis results, it was determined that a significant part of the waste toner used in the study consisted of polystyrene co-acrylate, and the remaining part consisted of carbon black and trace amounts of silicate. In the research, it was determined that the flexural and tensile strengths of MCC/ONP/PP composites containing 1% waste toner and 3% PPC increased by 13% and 46%, respectively, compared to the control sample. Additionally, the samples with the lowest water absorption values were measured in composites containing 1% waste toner and 3% PPC. The highest crystallinity value (50.75%) was obtained with the use of 1% waste toner and 3% PPC in MCC/ONP/PP composites. However, with waste toner usage above 1%, the mechanical, thermal properties, and water absorption rate have slightly decreased. As a result of the study, it was concluded that up to 1% waste toner with 3% PPC can be used successfully in MCC/ONP/PP composites.

KEYWORDS

microcrystalline cellulose, old newspaper, polypropylene, waste toner

1 | INTRODUCTION

Nowadays, it has become quite common to use one or more materials in plastics in order to reduce costs and combine the properties of different materials. Some of these fillers are valuable additives to reinforce the properties of polymer matrix, such as minerals, wood flour, fibers, nanocrystalline, and microcrystalline cellulose.[1–6] Many waste such as textile, agricultural waste, paper mill waste, recyclable fiber, and so forth have the opportunity to be reused as filler.[7–13] Cellulose based composite materials have some advantages and disadvantages. They have high dimensional stability and work very little, are produced in desired sizes and shapes, have no cracking or fiber lift, have high resistance to insects and fungi, are biodegradable, are nontoxic and have low maintenance requirements.[5,14] They can also be produced from recyclable waste materials. However, they have low melting point, have low water resistant and insufficient interface adhesion.[5] Old newspapers are a good example of these resources, as they are a material that can be easily recycled.[15] The newspaper consists of mechanical pulp fibers containing cellulose, hemicellulose, and lignin. Due to its wood-like structure, the old newspaper fibers can be used as filler in these composites as in wood-plastic composites.[16–20]

Microcrystalline cellulose (MCC) materials, a cellulosic reinforcement in polymer matrices, obtained from different cellulosic and having a high specific surface area improve some properties of polymer composites by providing strong reinforcement in the polymer matrix.[21,22] The microcrystalline cellulose, which is produced by acid hydrolyzing cellulose chains, improves the end product's distinctive qualities, high surface area, greater thermal stability, and better mechanical properties.[23,24]

Waste toner, which is used as a variable in this study, is a product that can be considered as industrial waste and contains organic macromolecular compounds that can pollute the environment and threaten human health if it leaks out.[25] Toner powder, which is produced and used in large quantities worldwide each year, is made up of binder resin, colorants, iron oxide, load control agents, and other additives.[26] The resin (45%–90%) is the main component of toners, and it binds and fixes the toner to the receiver, which is usually paper, creating a permanent image.[26,27] Polymer, carbon black, and titanium dioxide are the three main components of toner.[28,29] There are countries that provide recycling programs for waste powder from toner cartridges, but the majority of these are applications that require consumer payment. This results in improper disposal of toner cartridges and the remaining toner powder in the environment.[26–28] The waste toner from the cartridges of copiers and printers is a big problem due to the presence of hazardous substances that cause health and environmental problems.[30] Therefore, how to recover the waste toner cartridges has become an important problem not only in terms of the reuse of resources but also in terms of environmental protection. Some problems arise when the waste toners are disposed of either by regular storage or by incineration. Plastics made from polymers have a very slow rate of decomposition in the environment or furan and dioxin gases are produced during combustion. In storage or incineration processes, residual toner leaks out, polluting the environment.[25]

In this study, it is aimed to minimize the damage to the environment by including the waste toner, which cannot be evaluated in accordance with our country's zero waste policy. Thus, the possibilities of using the old newspaper and the waste toner in different industries were searched and alternatives were presented. The microcrystalline cellulose has been also added to these natural fiber-plastic composites to produce composite materials with higher resistance properties. This is a novel study on the hybridization effect of the waste toner, and natural fibers including ONP and MCC into the PP matrix. In this work, the effects of the old newspaper fiber, waste toner, MCC addition on the mechanical, thermal, morphological properties, and the water absorption rate were investigated.

2 | EXPERIMENTS

2.1 | Materials

Polypropylene (PP) and polypropylene carbonate (PPC) as a coupling agent were obtained from by Petkim Petrochemical Company in Izmir, Türkiye. Microcrystalline cellulose (MCC) was purchased by Merck (Cas No: 9004-34-6), it was produced from cotton linter. The old newspapers (ONP) were supplied from Demirören Printing Center in Trabzon, Türkiye and they were stored in a dark-closed warehouse at room temperature. All newspapers used in the study were printed on the same day. The waste toner powders used in the study were obtained from printer toners that have partially completed their printing life.

2.2 | Preparation of fibers

The old newspaper was fibered using a Fritsch brand Willey mill. During the fibering process, the fibers were sized with a 0.25 mm sieve cassette located under the mill. The prepared old newspaper fibers were dried at 103°C for 24 h before composite production.

2.3 | Composite production

Polypropylene and other additives such as the old newspaper (ONP), microcrystalline cellulose, compatibilizer, and waste toner were mixed homogeneously in the ratios given in Table 1. The microcrystalline cellulose was also dried prior to extrusion. The mixture was fed into a laboratory single screw extruder. The processing parameters of the extruder; screw speed was set at 100 rpm, the zone temperatures were 170, 175, 180, and 185°C. The extruded pellets were cooled using a water bath and grounded in a mill. The hot press was used to mold the oven-dried grounded-pellets for 3 min at a pressure of 10 MPa and a temperature of 180°C. Prior to testing, the composites were

TABLE 1 The experimental design for the study.

Samples	PP*	PPC*	ONP*	MCC	Waste toner
C1	100	-	-	-	-
C2	85	-	10	5	-
C3	82	3	10	5	-
T1	81	3	10	5	1
T2	80	3	10	5	2
T3	79	3	10	5	3
T4	78	3	10	5	4

Abbreviations: MCC, microcrystalline cellulose; ONP, old newspaper fiber; PP, polypropylene; PPC, polypropylene carbonate.
*Values are percentage by weight (wt%).

conditioned in the climate room at 20°C and 65% relative air humidity for a week. The thickness of the produced composites is 3.5 mm.

2.4 | Mechanical properties

The Zwick/Roell Z010 Universal Tester with a 50 kN load cell conducted the flexural and tensile, in accordance with ASTM D 790[31] and ASTM D 638,[32] respectively. The flexural test was performed at a constant speed of 2 mm/min, while the tensile test was performed at a cross speed of 5 mm/min on an Universal testing machine (Zwick/Roell Z050, Germany) with a load cell capacity of 50 kN. A notching cutter was used to cut the notches for the Izod impact test (Ray-Ran Test Equipment Ltd., Polytest, UK) according to ASTM D 256.[33] They were examined using an impact testing device (Zwick, HIT5.5P; Germany). To determine average values, at least 10 samples from each group were measured.

2.5 | Thermal properties

2.5.1 | Differential scanning calorimetry analysis (DSC)

In this study, a Perkin Elmer (Model DSC 8000) device was used for DSC analysis. The samples were put inside the apparatus after being covered with an aluminum container. The temperature value was raised to 250°C during the test phase by adding 10°C/min, and the nitrogen gas flow rate was set to 20 mL/min. The composites were heated to 250°C before being allowed to cool again for analysis. After cooling, the samples were tested by reheating to 250°C. Under nitrogen gas conditions, it was measured in three steps: heating, cooling, and reheating. The degree of crystallinity (X_c) of the polymer was calculated using the Equation (1).[34]

$$X_c\,(\%) = \left(\frac{\Delta H_m}{\Delta H_0 \times W}\right) \times 100. \tag{1}$$

The heat fusion of composite and 100% crystalline polyethylene is denoted by ΔH_m and ΔH_0, respectively, and the plastic ratio is denoted by W. The ΔH_0 value of polypropylene was taken as 207 J/g in this study.

2.5.2 | Thermogravimetric analysis (TGA)

The TGA of composites was performed using a Perkin Elmer (Model STA 6000) test device and an alumina ceramic crucible in nitrogen. The weight of each sample was about 4–5 mg. The temperature was raised from room temperature to 600°C at a rate of 10°C/min, and the nitrogen gas flow was adjusted to 20 mL/min. The TGA graphs were created by measuring the change in sample weight depending on the temperature.

2.6 | Water absorption

The water absorption rate was calculated using the ASTM D 1037 standard.[35] The samples prepared in 50×50× composite thickness (mm) dimensions were weighed accurately to 0.01 g. Following that, the weighed samples were kept in water at 20 ± 2°C. The measurements were taken at 1, 2, 3, 4, 5, 6, 7, and 8 weeks. Ten replicates were tested for each group. Water absorption percentages for all composites were carried out using the Equation (2)

$$\mathrm{WA} = \left(\frac{\mathrm{my} - \mathrm{mk}}{\mathrm{mk}}\right) \times 100. \tag{2}$$

While WA means water absorption (%), my is initial weight of the sample (g), and mk is weight of the sample after soaking in water (g).

2.7 | Characterizations

2.7.1 | FTIR-ATR analysis

The attenuated total reflection (ATR) attachment integrated into Fourier transform infrared spectroscopy was used to examine the structure of the old newspaper fibers, MCC, and waste toner. The samples were dried at 60°C for 4 h before analysis. The FTIR spectra were recorded on the Fourier transform infrared (FTIR-ATR) spectra (Shimadzu IR Prestige-21/Pike Miracle ATR). All spectra in the wavenumber range 600–4000 cm^{-1} were recorded with a spectral resolution of 16 cm^{-1} and were averaged over 24 scans.

2.7.2 | Morphological properties

A scanning electron microscope (SEM) was used to examine the samples under a vacuum (ZEISS EVO LS 10, Carl Zeiss NTS GmbH, Germany). The samples were gold coated prior to analysis using the sputtering system. The SEM images of the waste toner and hybrid composites were captured at 1000× and 500× SEM micrograph magnifications at 10 kV, respectively. In addition, EDS analysis of the waste toner was measured at the same magnification.

2.8 | Statistical analysis

The statistical package software SPSS 21.0 was used to analyze the mechanical test results with one-way ANOVA and to determine homogeneity groups with Duncan test.

3 | RESULTS AND DISCUSSION

3.1 | FTIR-ATR characterization of materials

FTIR-ATR spectra of the waste toner, old newspaper, and microcrystalline cellulose are shown in Figure 1. It is seen that the waste toner used in the study form peaks in the 3100–3000, 1730, 1130, 760, and 700 cm^{-1} bands. The 3000 cm^{-1} band indicates C—H stretching and the peaks in the 700 and 760 cm^{-1} bands indicate out-of-plane deformation substitutions of polystyrene. The peak in the 1730 cm^{-1} band indicates the presence of ester carbonyl and the peak in the 1130 cm^{-1} band indicates the C—O—C stretch.[36] Additionally, the 1500–1450 cm^{-1} bands show C—H bending. According to these results, it can be said that the major resin of toner consists of polystyrene co-acrylate, as stated in the study of Merril et al.[36] In Figure 1, MCC and ONP fiber showed strong and wide band at 3335 cm^{-1}, which indicates the stretching vibration of the —OH group.[37,38] The band at 2918 cm^{-1} belongs to the symmetric and asymmetric C—H vibration of MMC and ONP fiber.[37,38] Additionally, peaks associated with the C—O tension of cellulose in the 1044 cm^{-1} band and the C—O—C symmetrical tension of cellulose in the 1120 cm^{-1} band were observed in the microcrystalline cellulose and old newspaper spectra.[39] In the spectrum of the old newspaper, unlike MCC, peak formation was also observed in 1510 and 1650 cm^{-1} bands due to the stretching vibration of the double bonds in the aromatic ring of lignin[40–43] and the C═O stretching vibration in the carbonyl structures.[43] In addition, due to the high hemicellulose content in the newsprint spectrum, peak formation was observed as a result of C═O stretching of unconjugated ketones, carbonyl, and aliphatic groups in the 1730 cm^{-1} band.[44]

Figure 2 shows the FTIR-ATR spectra of PP and hybrid composites. The FTIR spectrum of polypropylene presents asymmetric —CH_3 stretching at 2950 cm^{-1}, asymmetric —CH_2 stretching at 2920 cm^{-1} and shoulder at 2875 cm^{-1}, and the asymmetric and symmetric in-plane C—H (—CH_3) at 1455 cm^{-1}. The peak at 1376 cm^{-1} is assigned to —CH_3 group.[45]

In PP composites containing 10% old newsprint and 5% MCC as filler, cellulose and hemicellulose origin peak formations were observed in 1044 and 1730 cm^{-1} bands. With the addition of 1%, 2%, 3%, and 4% waste toner to the composite composition, an increase in the peak intensity was observed in the 700 cm^{-1} band that indicate out-of-plane deformation substitutions of polystyrene.

3.2 | Thermal properties of hybrid composite materials

Data on the thermal properties of filler, additives and composites are given in Table 2. Thermal Gravimetric Analysis (TGA) and Differential Thermal Gravimetric Analysis (DTGA) curves of the components in the composite are shown in Figure 3. The inflection point temperature of MCC (349.67°C) and ONP (374.82°C) was determined lower than toner (410.61°C) and PP (465.44°C). As can be seen from Figure 3, the MCC produces a cleaner peak, while the ONP creates a broader and shorter peak also that gives shoulders. This is because the MCC consists of pure cellulose, whereas the ONP, unlike MCC, contains hemicellulose, which pyrolysis faster, and lignin, which pyrolysis more slowly.[46]

The TGA and DTGA curves of the PP and hybrid composites are shown in Figure 4. It is seen that composites (C2, C3, T1, T2, T3, and T4) form two degradation steps. The first step is the pyrolysis of the MCC and ONP

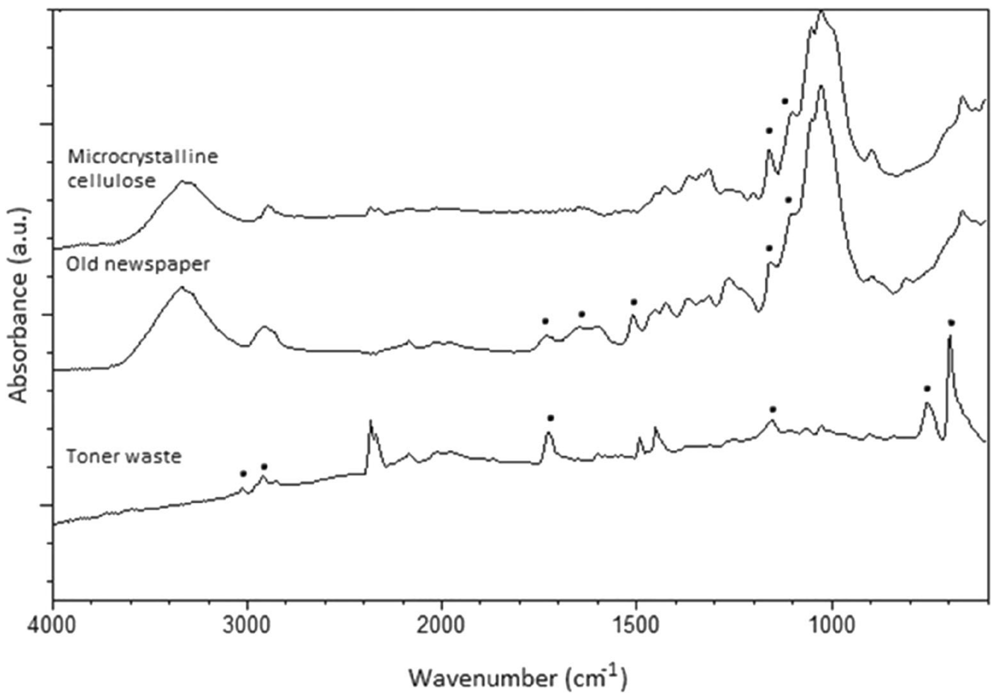

FIGURE 1 FTIR-ATR spectra of waste toner, old newspaper, and microcrystalline cellulose.

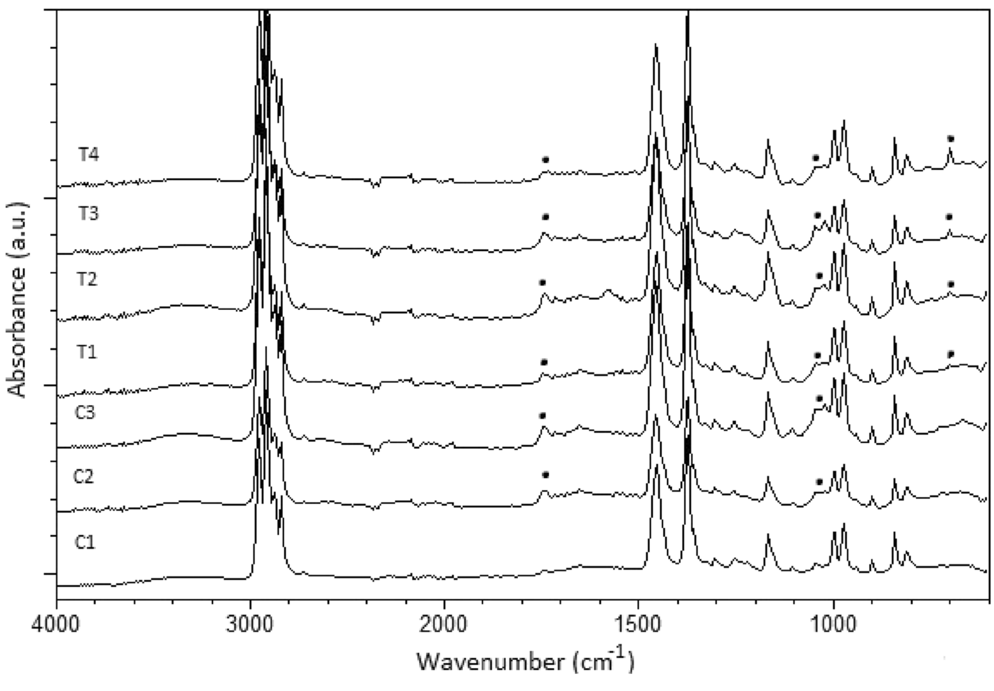

FIGURE 2 FTIR-ATR spectra of hybrid composites.

fibers, and the second step is the degradation step of PP and polystyrene co-acrylate. As mentioned before, polystyrene co acrylate is the resin in the waste toner. When the PPC was added to the hybrid composite as a compatibilizer, the inflection point temperature decreased from 365.96 to 351.62°C in the first degradation step, whereas the inflection point temperature of the PP increased from 465.44 to 469.22°C. Adding 1% waste toner to the composite content increased the inflection point temperature of the first degradation step from 351.62 to 373.99°C. However, with the increase in the amount of the waste toner, the inflection point temperature of the first degradation step decreased slightly to 370.09°C with 4% the waste toner. This may be due to the amount of carbon in the toner content and low amounts of polystyrene co acrylate slowing down the pyrolysis of the fibers. The inflection point temperature in the second degradation step of the composites containing 1% and 2% the waste toner increased from

TABLE 2 Thermal properties of filler, additives, and composites.

	First degradation step				Second degradation step			
	Onset temp. (°C)	Inflection point temp. (°C)	Endset temp (°C)	ΔY (%)	Onset temp. (°C)	Inflection point temp. (°C)	Endset temp (°C)	ΔY (%)
MCC	320.60	349.67	366.20	79.94	-	-	-	-
ONP	321.00	374.82	392.14	65.58	-	-	-	-
Toner	392.51	410.61	427.56	88.01	-	-	-	-
C1 (PP)	-	-	-	-	439.89	465.44	478.60	99.38
C2	342.72	365.96	375.13	11.35	444.98	465.44	481.96	77.49
C3	336.22	351.62	365.81	9.53	449.86	469.22	483.82	77.92
T1	343.43	373.99	381.87	9.51	444.47	470.06	484.10	79.43
T2	353.29	372.45	377.15	12.90	448.98	471.00	484.40	71.94
T3	345.47	371.28	379.39	9.01	445.36	467.39	483.51	77.18
T4	339.25	370.09	379.94	13.38	440.03	467.03	483.85	66.12

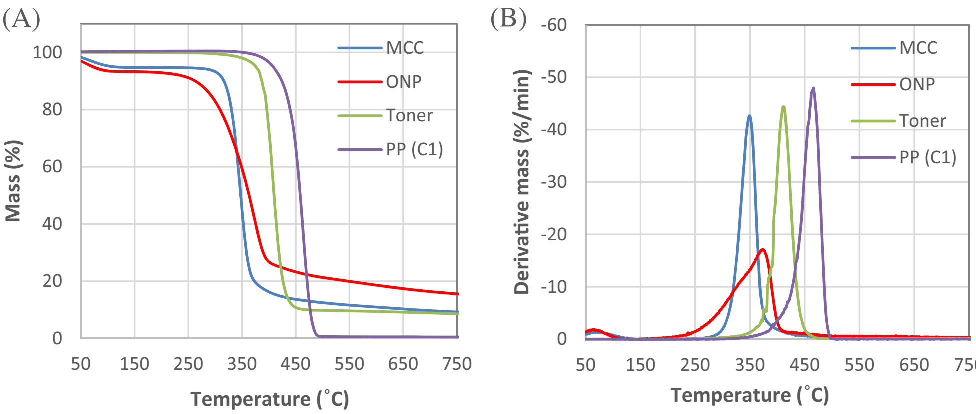

FIGURE 3 TGA (A) and DTGA (B) curves of the components in the composite.

469.22 (C3) to 470.06 and 471.00°C, respectively. On the other hand, the inflection point temperature of the samples containing 3% and 4% the waste toner decreased to 467.39 and 467.03°C, respectively. The reason for the decrease in the inflection point temperature of the second degradation step with the increased amount of the waste toner 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 3 shows the DSC results of the composites. It is seen that the addition of a compatibilizer to the ONP-MCC-PP composite increases the crystallinity from 41.27% to 49.27%. With the addition of 1% waste toner to the composite, the crystallinity increased up to 50.75%, but with a further increase in the waste toner ratio, the crystallinity decreased to 43.49%. Similar results were also found in the study of Hammani et al.[47] on the waste toner-added LDPE-HIPS composites. The reason for this may be that the waste toner acts as a heterogeneous nucleating agent due to its structure,[48] and also that the waste toner disperses into the amorphous regions, preventing the nucleation and growth of the crystal field, thereby reducing the degree of crystallinity.[49,50] Another reason for the decrease in crystallinity with the addition of toner is the increase in the polystyrene ratio in the composite composition. As can be seen from Table 3, the melting and crystallization peak temperatures decreased with the increase in the polystyrene co acrylate ratio due to waste toner. Similar results were also found in a study on polypropylene polystyrene blend.[51]

According to the thermal analysis results, it can be said that the optimum result was obtained with a composite consisting of 10% ONP, 5% MCC, 1% waste toner, 3% PPC, and 81% PP (T1 sample).

3.3 | Mechanical properties of hybrid composites

Table 4 shows the mechanical properties of ONP/MCC/toner reinforced PP composites. The lowest

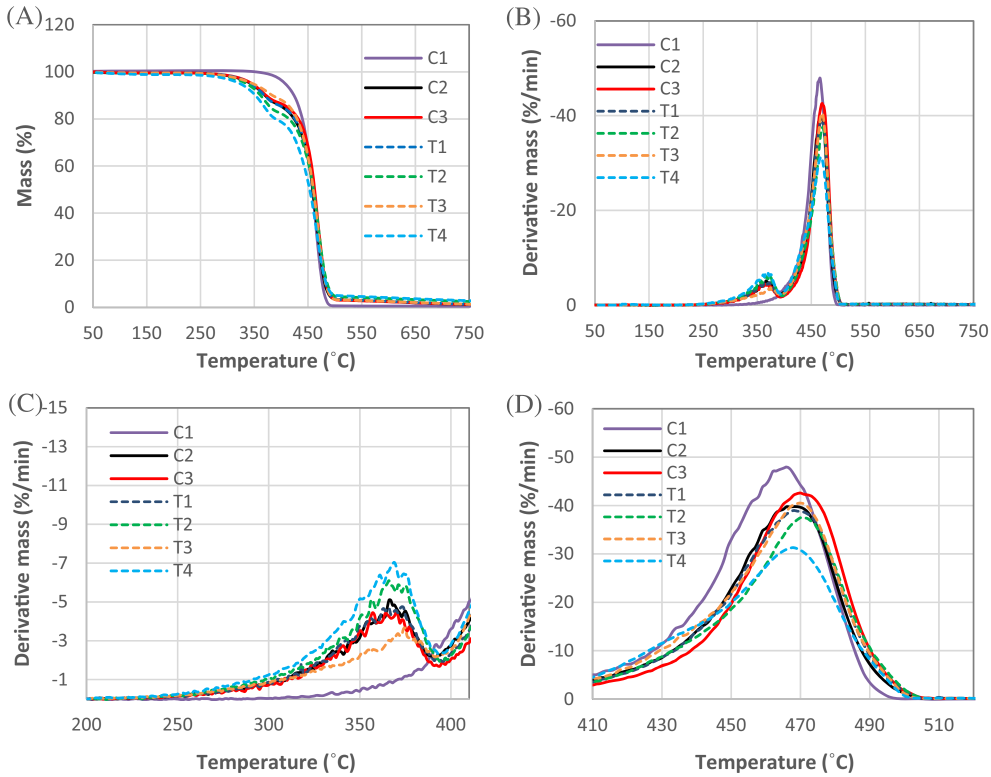

FIGURE 4 TGA (A) and DTGA (B–D) curves of hybrid composites.

TABLE 3 DSC results of hybrid composites.

	T_{cold} (°C)	Peak height cold (mW)	ΔH cold (J/g)	T_{melt} (°C)	Peak height melt (mW)	ΔH melt (J/g)	$X_{corr.}$ (%)
C1	106.91	−27.6691	−86.1589	162.62	14.4578	86.5639	41.82
C2	117.67	−19.6873	−75.0254	163.88	10.3211	73.8307	41.96
C3	117.51	−24.0550	−84.7705	162.79	13.9865	83.6294	49.27
T1	114.46	−28.6812	−89.1898	162.99	16.3890	84.0443	50.75
T2	117.34	−24.9912	−83.7440	163.05	12.4989	76.5360	45.65
T3	114.22	−22.5541	−79.3897	162.86	12.8941	76.2445	46.62
T4	115.47	−19.9621	−73.1043	162.68	11.1822	70.2212	43.49

tensile (19.34 MPa) and flexural (47.76 MPa) strength values were obtained from the polypropylene (C1) sample. The tensile strength and flexural strength of the PP hybrid composite (C2) reinforced with the ONP and MCC increased to 21.98 and 51.22 MPa, respectively. The tensile and flexural strengths of the ONP/MCC/PP composite (C3) reinforced with 3% the PPC as compatibilizer increased up to 28.08 and 53.38 MPa, respectively. The addition of the PPC improved by 45% in the tensile strength of the hybrid composites. Li et al.[52] state that the PPC had superior mechanical strengths on the recent researches and applications of PPC composites materials. Additionally, Ge et al.[53] reported that ultra-high mechanical strengths were obtained with natural fiber-reinforced polycarbonate materials due to the strong chemical structure of PPC. The moduli of tensile and flexural for the hybrid composites increased with the ONP and MCC due to being stiffer and more rigid than thermoplastic matrix.[14,54]

When the waste toner was incorporated by the mixture of ONP/MCC/PPC/PP, the mechanical properties affected depending on its loading ratio. The highest tensile (28.22 MPa) and flexural strength (54.00 MPa) values were obtained in the ONP/MCC/PP composite reinforced with 1% waste toner and 3% PPC. This result is in agreement with the crystallinity ($X_{corr.}$) values in the DSC results previously discussed in another study.[20] Peşman and Güleç,[20] in their study on the use of the waste paper fibers printed with different printing

TABLE 4 Mechanical properties of hybrid composites.

Samples	Tensile strength (MPa)	Tensile modulus of elasticity (MPa)	Flexural strength (MPa)	Flexural modulus of elasticity (MPa)	Impact resistance (J/m)
	***	**	***	***	*
C1	19.34 (b) ±4.91	3657.40 (ab) ±400.90	47.76 (c) ±1.32	1864.00 (d) ±62.29	2.96 (a) ±0.37
C2	21.98 (b) ±2.01	3610.00 (b) ±205.91	51.22 (b) ±2.75	2354.00 (ab) ±296.70	2.53 (a) ±0.50
C3	28.08 (a) ±2.23	3862.00 (ab) ±522.90	53.38 (ab) ±0.91	2388.00 (ab) ±122.76	2.96 (a) ±0.16
T1	28.22 (a) ±0.34	4178.00 (a) ±85.85	54.00 (a) ±0.92	2474.00 (a) ±109.45	2.82 (a) ±0.15
T2	27.46 (a) ±3.02	3770.00 (ab) ±327.34	53.34 (ab) ±1.17	2464.00 (a) ±70.92	2.76 (a) ±0.57
T3	27.12 (a) ±1.34	3774.00 (ab) ±294.59	47.58 (c) ±2.36	2084.00 (c) ±69.14	2.87 (a) ±0.17
T4	21.60 (b) ±0.96	3654.00 (ab) ±527.05	45.98 (c) ±1.14	2198.00 (bc) ±176.27	2.57 (a) ±0.18

Note: Different letters indicate statistically significant differences between the groups.
*$p > 0.5$; **p: 0.5–0.1; ***$p < 0.0001$.

techniques in the PP composites, obtained the highest physical and durability properties in composites using toner printed fibers. The main difference between the two studies is that one used the printed version of the toner on the fibers, whereas in this study, the fiber, waste toner, and PP were added to the extruder separately for the composite formation. Therefore, in the previous study, the toner coated on the fiber surface as a compatibilizer gave more effective results in terms of mechanical properties. However, in Peşman and Güleç's[20] study, the toner content printed on the fiber surface did not exceed 1% of the composite. Similarly, in this study, the use of up to 1% waste toner improved the strength properties of hybrid composites. On the other hand, it was determined that the tensile and flexural strength values decreased with increasing the amount of the waste toner by more than 1%. The reason for this may be that the polystyrene in the waste toner content is very low tenacity and brittle,[51] so the increased the waste toner after the optimum dosage reduces the mechanical properties of PP composites. Another possible reason is heterogeneously dispersed the waste toner in to polymer matrix when it was high loading. This situation is a common problem for nanoscale powder-reinforced polymer composites, especially when used in a single screw extrusion process.[55,56]

As shown in Table 4, the notched impact resistance of the hybrid composites was less affected by the addition of toner. The increase in toner content only slightly decreased the impact resistance behavior of the hybrid composites. However, the difference between the composite groups is not statistically significant, and all composites are in the same homogeneity group according to the Duncan test.

3.4 | Water absorption of hybrid composites

Figure 5 shows the water absorption rates of hybrid composites after 1 day, 1, 2, 3, 4, 5, 6, 7, and 8 weeks, respectively. The water absorption percentage of the PP hybrid composite reinforced with 10% the ONP and 5% MCC (C2) reached the second highest value. The reason for this is that the ONP and MCC, which contain hydrophilic hemicellulose and cellulose, swell by taking in water from the gaps formed due to their incompatibility with plastic. However, with the addition of 3% PPC as a compatibilizer to the composite content (C3), the water absorption percentage decreased by almost half. This is due to the PPC's very high barrier properties and biocompatibility. In other words, the use of the PPC reduces the void structure in the composite. The lowest water absorption percentage was obtained with 1% the waste toner addition to the PP hybrid composite composition (T1). It is thought that adding a sufficient amount of the waste toner to the composite causes a more homogeneous distribution and reduces water absorption by filling the remaining voids in the composite. However, adding more than 1% the waste toner to the composite composition increased the water absorption percentage. When added 4% waste toner in PP matrix was observed that the water absorption value was significantly increased. If amount of waste toner in composite was higher than the optimum dosage it may lead to a more irregular distribution through agglomeration and increases the void structure of the composite, causing the hydrophilic fibers to swell. This result is also supported by Dönmez Çavdar et al.[57]

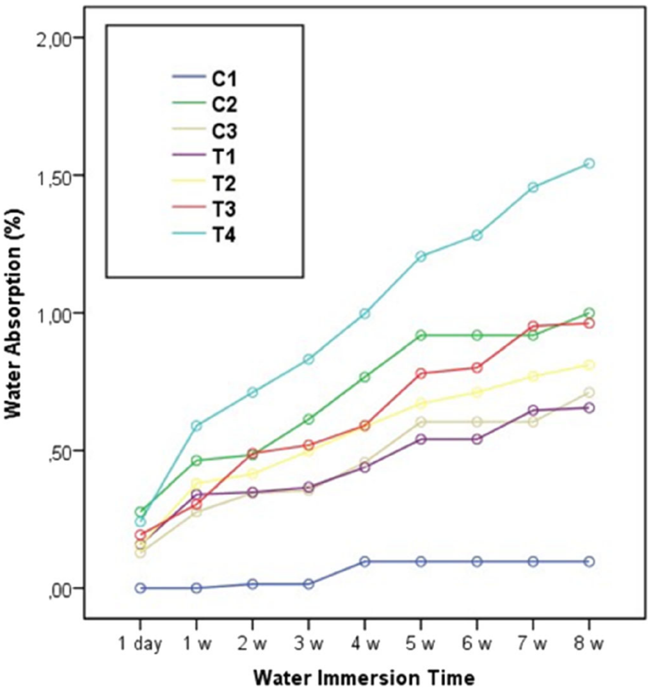

FIGURE 5 The water absorption percentage of hybrid composites.

3.5 | SEM analysis of hybrid composites and EDS analysis of waste toner

Figure 6 shows the SEM image and EDS spectrum of the waste toner at 1000× magnification. As seen in Figure 6, the particle diameter of the waste toner used in the study was measured as approximately 10 nm. In addition, in the EDS measurement taken at the same magnification, it was determined that the waste toner consisted of 90.57% carbon, 8.50% oxygen, and 0.65% silica. The analysis of the EDS results shows that carbon is the most abundant element in this composition with oxygen. The signal of carbon should mainly originate from the polymer phase.[47]

Figure 7 shows the micrographs of toner, C1, C2, C3, and T2 samples, respectively. A composite prepared without PPC showed the ONP fibers as well as gaps around them, which indicated that the interfacial adhesion between the modified fibers and the matrix was weak. The interface of ONP and PP became more and more ambiguous and no debonding of fibers was observed with increased toner loading shown in Figure 6E. The interfacial adhesion was enhanced since the toner connected with hydroxyl groups of the ONP fibers through ester and/or hydrogen bonding.

Due to the cellulose and hemicellulose on its surface, the ONP, like other lignocellulosic fibers, releases a significant amount of hydroxyl groups. These groups cannot chemically interact with the PP. By utilizing MAPP, coupling mechanisms between the OH groups of the fibers' hydroxyl groups and maleic acid can be established. These coupling mechanisms rely on the formation of hydrogen bonds and ester linkages as a result of chemical reactions between the MAPP anhydride groups and the fibers' hydroxyl groups.[58,59]

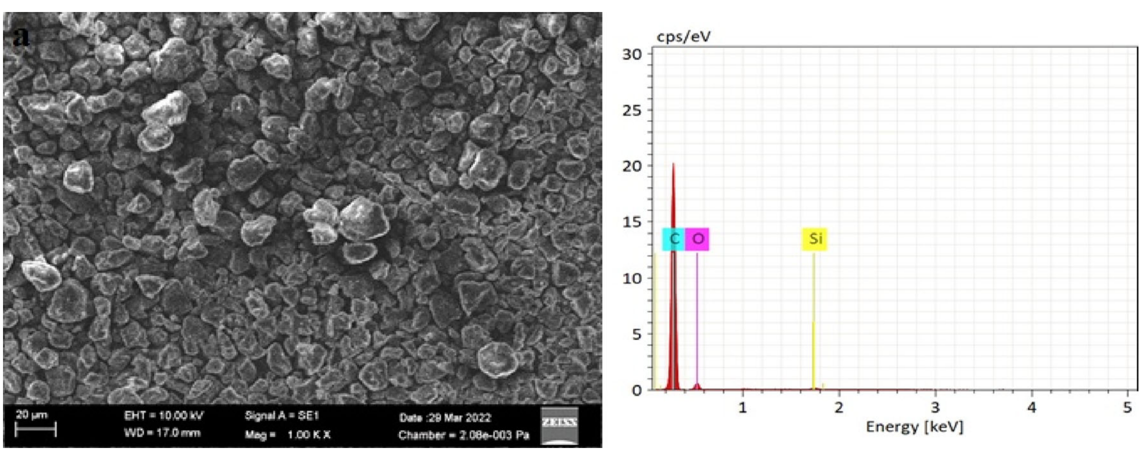

FIGURE 6 SEM image and EDS spectrum of waste toner.

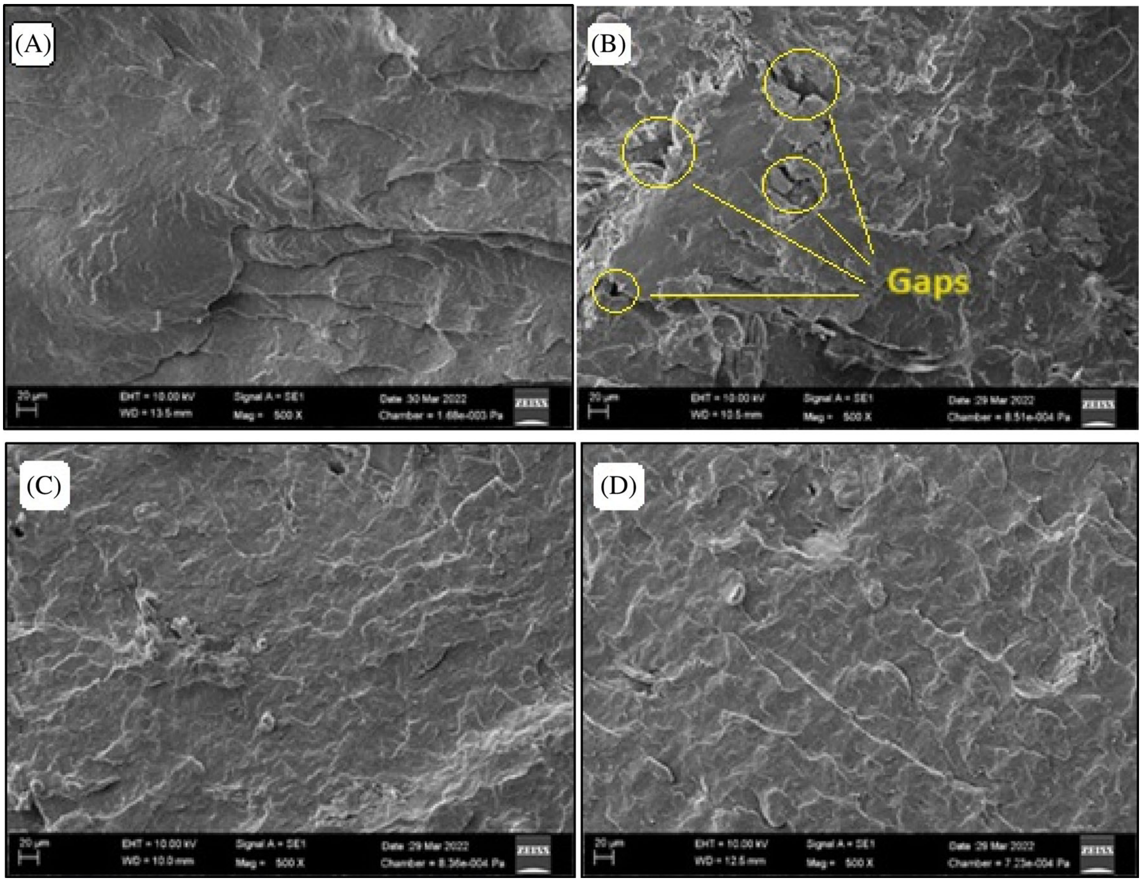

FIGURE 7 SEM photographs of hybrid composites; (A) C1 (PP); (B) C2 sample (with 10% ONP and 5% MCC addition); (C) the C3 sample (with 3% PPC, 10% ONP, and 5% MCC addition); (D) the T2 sample (with 3% PPC, 10% ONP, 5% MCC, 2% toner).

4 | CONCLUSION

In this study, the effects of waste toner usage in the ONP/MCC/PP composites on thermal, mechanical, physical, and morphological properties were investigated. Based on these results;

- According to FTIR-ATR and SEM-EDS results, it was determined that the main part of the waste toner consists of polystyrene co-acrylate resin, the remaining part is mostly carbon and traces of silica.
- As a result of the reinforcement of polypropylene plastic with 5% microcrystalline cellulose and 10% old newsprint fibers, the tensile strength increased from 19.34 to 21.98 MPa, and the flexural strength increased from 47.76 to 51.22 MPa. However, the water absorption increased.
- As expected, with the addition of PPC as compatibilizer to the MCC/ONP/PP composite, the tensile strength increased to 28.08 MPa, the flexural strength to 53.38 MPa and the crystallinity (X_c) to 49.27%. In addition, the WA values have also improved.
- Highest tensile strength (28.22 MPa), flexural strength (54.60 MPa), and crystallinity value (50.75%) X_c were obtained with composite consisting of 10% ONP, 5% MCC, 1% waste toner, 3% PPC, and 81% PP (T1). In addition, the lowest water absorption value was obtained with the composite containing 1% waste toner. The reason for this improvement was that the gaps formed in the composite matrix were filled with the optimum amount of waste toner (1%).
- However, with waste toner usage above 1%, mechanical, physical and thermal properties have slightly decreased. This may be because the waste toner, which is above 1%, is well above the sufficient amount to fill the voids formed in the matrix. Another possibility is that the polystyrene in the waste toner content is very low tenacity and brittle, therefore the increased waste toner after the optimum dosage reduces the mechanical properties of PP composites.

In conclusion, the hybrid composites of ONP/MCC/toner reinforced PP could be used in 3D material and automotive industries.

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CONFLICT OF INTEREST STATEMENT

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.

DATA AVAILABILITY STATEMENT

The data presented in this study are available on request from the corresponding author.

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