Effect of Nanoscale Carbon Black, Ammonium Polyphosphate, and Microcrystalline Cellulose on Properties of Polypropylene Composites

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The effects of nano-sized carbon black (CB), ammonium polyphosphate (APP), and microcrystalline cellulose (MCC) were tested relative to the mechanical and thermal properties of polypropylene (PP)-based composites. Composites were produced by injection molding in nine different combinations by adding materials at the levels of 0% or 10% MCC, 0% or 15% APP, and 0% to 7% CB. With the use of APP, there was a decrease in tensile and flexural strength, while there was an increase in impact resistance. Compared to the control group, it was determined that with the use of CB and MCC, there was an increase in tensile modulus, flexural strength, flexural modulus, and impact strength, while there was a decrease in tensile strength and elongation at break values. The flexural strength and flexural modulus values of all PP composites were higher than the standard values for polyolefin-based plastic lumber decking boards. A decrease in the initial degradation temperature occurred with the addition of MCC. As the CB usage was increased and MCC was added, the amount of charred residue increased. Additionally, the use of CB and the addition of MCC increased the maximum and final degradation temperatures compared to the control sample. Considering the results obtained, it was concluded that the use of CB and MCC generally improved the mechanical and thermal properties of PP composites.

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Keywords: Carbon black; Ammonium polyphosphate; Microcrystalline cellulose; Thermoplastic composite

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INTRODUCTION

Natural fibers made of cellulosic materials offer numerous benefits, including improved physico-mechanical qualities, low density, biodegradability, renewability, and ease of availability. In polymer matrices, their potential as reinforcing fillers is significant because of the growing environmental issues worldwide (Merkel *et al.* 2014; Peng *et al.* 2014; Santos *et al.* 2015: Berthet *et al.* 2016). Lately, cellulose-based composites have found application in the automotive, building, and packaging industries, as well as dielectric materials for microchips, switches, connections, circuit board components, and transformer parts (Wagberg and Annergren 1997; Yang and Gardner 2011; Jayamani *et al.* 2015; Cavdar and Boran 2016). When compared to glass or aramid fibers, the addition of various cellulosic natural fibers from kenaf, sugarcane bagasse, palm fiber, banana fiber, jute, coir, linen, sawdust, hemp, or tea mill waste, cotton, recycled corrugated paper board, *etc*., have several benefits (Cavdar *et al.* 2011; Zulkifli *et al.* 2015; Boccarusso *et al.* 2016; Kili *et al.* 2023, 2024). In recent years, cellulose, a naturally occurring biopolymer, has been employed in place of inorganic fillers. Processing with acid hydrolysis eliminates the amorphous areas from the cellulose chain (Haafız *et al.* 2013; Rosa and Lenz 2013; Zulkifli *et al.* 2015).

When cellulose chains are hydrolyzed in an acidic solution, microcrystalline cellulose (MCC) is produced. This material has improved mechanical qualities, a large surface area, and increased thermal stability (Hoyos *et al.* 2013; Ifuku and Yano 2015). The MCC has some disadvantages despite these numerous benefits, such as it degrades thermally beyond 250 °C and is incompatible with hydrophobic polymer matrices (Hassan *et al.* 2014; Ifuku and Yano 2015). The characteristics of natural fiber composites are negatively impacted by the poor compatibility of cellulose with the polymer matrix (Peng *et al.* 2014; Boccarusso *et al.* 2016). Through altering the surface of cellulosic fibers and utilizing coupling agents and carrier systems in cellulose-based composites, this detrimental effect can be mitigated (Peng *et al.* 2014; Ifuku and Yano 2015; Boccarusso *et al.* 2016; Boran *et al.* 2016).

Each filler and additive added to the polymer matrix changes the mechanical properties of the composite material. Polymer composites are expected to meet certain mechanical standard values. According to the ASTM D6662 standard (Standard Specification for Polyolefin-based Plastic Lumber Decking Boards), the minimum flexural strength should be 6.9 MPa and the minimum flexural modulus should be 340 MPa.

One of the most significant polymer materials, polypropylene (PP), has many uses in furniture, cables, building materials, packaging, and interior design due to its low density, low toxicity, superior mechanical performance, and advantageous processing qualities (Zhang *et al.* 2017; Liang 2019; Xu *et al.* 2019). However, because of its entire aliphatic hydrocarbon structure, PP is combustible and burns quickly without leaving any residue, which frequently poses a serious risk to people's safety and limits the applications of this material in terms of safety (Peng *et al.* 2008; Subasinghe *et al.* 2018). As a result, the need to create flame-retarded polypropylene composites has grown.

Flame retardant additives, such as those based on phosphorus, have been included in polymer matrices to improve their thermal stability and charring, delay the burning rate, and reduce smoke and heat emission (Lu and Hamerton 2002; Schmitt 2007; Bolgar *et al.* 2008; Veen and Boer 2012; Attia *et al.* 2014; Duan *et al.* 2016; Lim *et al.* 2016). Ammonium phosphate (APP) may be utilized with a variety of polymer types and is not harmful to health when compared to other phosphorus-based additives (Boccarusso *et al.* 2016). When compared to other halogen flame retardants, APP, a halogen-free flame retardant, does not emit more smoke (Schmitt 2007; Veen and Boer 2012; Lim *et al.* 2016).

Environmentally friendly flame retardants may be easily included to create flame-retarded polymeric materials. Intrinsic flame retardants (IFRs) are a form of halogen-free flame retardant that have garnered a lot of attention due to their favorable characteristics including low toxicity, low smoke, and low corrosion (Sun *et al.* 2017; Li *et al.* 2018; Yin *et al.* 2018; Liu *et al.* 2019). IFR systems typically consist of three components: an acid supply, which acts as a catalyst for the development of char, a carbon source, which forms char, and a gas source, which creates foam. Their active groups respond by crosslinking and then carbonizing when the material is heated over a specific temperature or exposed to fire. This produces a foamed carbon layer that shields the underlying material from heat and flame. For example, ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (ME) are used in a typical IFR system (Camino *et al.* 1989). Because of its unique molecular makeup, APP is sometimes seen as both an acid source and a gas source at the same time. However, because PER is a polyhydric short molecule compound, it has several drawbacks (poor heat stability, moisture sensitivity, rapid migration to material surfaces, *etc*.), which frequently lead to a decline in mechanical performance and a reduction in flame retardancy effectiveness (Tian *et al.* 2013). Great effort has been made to create new charring agents to replace PER to solve this issue (Hu *et al.* 2004; Li and Xu 2006; Peng *et al.* 2008).

It has been shown that fabricating polymer/nanofiller composites has become an effective way to increase their thermal and flame retardancy because of the advancement of nanotechnology (Feng *et al.* 2017; Song *et al.* 2017). Several materials have demonstrated strong flame-retardant effects, including clay (Zhang *et al.* 2006), carbon nanotubes (CNTs) (Kashiwagi *et al.* 2004; Song *et al.* 2013a), fullerene (C60) (Song *et al.* 2008, 2011a, 2013b), graphene (Song *et al.* 2011b; Fang *et al.* 2019), and layered double hydroxide (LDH) (Li *et al.* 2018a; Li *et al.* 2018b), *etc*.

One of the most popular carbon nanomaterials is carbon black (CB). Carbon black has permanent conductivity, strong thermal stability, and is abundant. In previous studies, CB, as a nanoscale flame retardant, has been incorporated into pure PP, PP/CNT, and PP/carbon fiber (CF) systems with improvement in thermal stability, flame retardancy and electrical properties. In such studies, CB was found to play an important role in trapping radicals and forming a network in PP composites (Yang *et al.* 2015; Wen *et al.* 2012).

There has been no sufficient study on the effect of CB on cellulosic material-filled PP composites. The present study utilized CB not only as a nanoscale synergist, but also as a carbon source in the IFR system. This study aimed to investigate the synergistic effect of the combination of CB, MCC, and APP on the mechanical and thermal stability of PP based composite material.

EXPERIMENTAL

Materials

Microcrystalline cellulose (MCC) as filler and polypropylene (PP) as a polymeric matrix were used in composite production. In addition, maleic anhydride-grafted polypropylene (MAPP) (Licomont AR 504 by Clariant) as a coupling agent was used. Polypropylene (product code: EH102) (density = 0.905 g/cm^3, melt flow index at 230 °C/2.16 kg = 11 g/10 min) was supplied by Petkim Petrochemical Company in Turkey. The melting point, tensile strength in yield, flexural modulus at 23 °C, Izod impact strength at 23 °C (notched), and Rockwell hardness of the polypropylene (PP) were (DSC) 163 °C, 35 MPa, 1450 MPa, 20 J/m, and 96 R-scale, respectively. The size distribution of MCC supplied by Merck KGaA (Germany) is given in Table 1. The APP (Exolit AP 435) used as fire retardant was supplied by Ataman Chemicals. Carbon black (30 nm size) was supplied by the Nanografi company (Ankara, Türkiye).

Table 1. Size Distribution of Microcrystalline Cellulose (MCC)

Size	Distribution Rate
Sieve analysis (< 20 μm)	≤ 20%
Sieve analysis (> 160 μm)	≤ 2%
Sieve analysis (20 to 160 μm)	≥ 80%

Methods

Injection molded polymer composite manufacturing

Composites were manufactured in 9 different combinations using injection molding methods. The combination of composites produced is given in Table 2.

The materials PP, CB, MAPP, and MCC or without MCC were mixed at 60 rpm, for 2 min. To create a homogenous blend, PP, CB, MCC, and MAPP were dry-mixed in a high-intensity mixer according to the provided formulation. Subsequently, these mixtures were combined in a single screw extruder on a laboratory scale, operating at a screw speed of 40 rpm and a temperature range of 200, 195, 190, 185, and180 °C between the feed and die zones. Samples that had been extruded were cooled in a pool of water before being ground into pellets. Prior to injection molding, the pellets were oven-dried to an oven-dry weight of 103 °C (± 2). To create standard test samples, dried pellets were injected into the HDX-88 injection molding machine (temperatures: 180,190, and 200 °C from the feed zone to the die zone; pressure: 102 kg/cm^2; injection speed: 80 mm/s; screw speed: 40 rpm). After waiting for 35 seconds for the material to cool and solidify in the injection mold, the test samples were removed from the mold. The samples were conditioned in a climate chamber with a temperature of 20 °C and 65% relative humidity before testing.

Table 2. Material Combination of Composite Samples Produced

Samples	PP[a]	MCC[a]	APP[a]	CB[a]	MAPP[a]
PP (control)	97	-	-	-	3
0CB	82	-	15	0	3
3CB	79	-	15	3	3
5CB	77	-	15	5	3
7CB	75	-	15	7	3
0CB/MCC	72	10	15	0	3
3CB/MCC	69	10	15	3	3
5CB/MCC	67	10	15	5	3
7CB/MCC	65	10	15	7	3

a: Values are in percentage by weight (wt%); PP: polypropylene; MCC: microcrystalline cellulose; APP: ammonium polyphosphate; CB: carbon black; MAPP: polypropylene grafted maleic anhydride

Determination of Mechanical Properties

Test samples’ tensile, flexural, and impact strength values were ascertained in accordance with ASTM D 256 (2010), ASTM D 790 (2010), and ASTM D 638 (2010) (5.0 mm/min), respectively. Tensile and flexural properties were tested using a Zwick/Roell model Z010 universal mechanical testing machine, which has a 10 kN load capacity. Impact testing was conducted using a Zwick HIT 5.5P testing machine.

Determination of Thermal Properties

Through thermogravimetric analysis, the impact of CB and MCC on thermal stability—the material's capacity to withstand changes in physical structure, chemical irreversibility, or polymer chains at elevated temperatures—as well as other thermal parameters of PP composites were investigated. The samples were performed in a Shimadzu TGA-50 thermal analyzer, which ran on nitrogen at a flow rate of 20 mL/min and a heating rate of 10 °C/min. For the analysis, 10 mg of powdered test samples were utilized. The samples were heated to 800 °C from room temperature.

Statistical Analysis

The software IBM SPSS (Statistical Package for Social Sciences) version 21.0 was used to conduct statistical analysis. To identify the homogeneity groups of the composites, the Duncan’s mean separation test and the analysis of variance test (ANOVA) were selected with a significant level ($p < 0.001$).

RESULTS AND DISCUSSION

The mechanical properties of CB-, APP-, and MCC-filled PP composites are given in Table 3. Additionally, Table 3 demonstrates homogeneity ($p < 0.001$) among the composites’ groups.

Table 3. Mechanical Properties of Manufactured Composites

Samples	TS (MPa)	TM (MPa)	EaB (%)	FS (MPa)	FM (MPa)	IS (kJ/m^2)
PP (Control)	*26.48^{e**} (0.46)***	522.60^{a} (42.06)	450^{f} (0.1)	36.95^{bc} (0.95)	1047.77^{a} (34.67)	2.61^{a} (0.07)
0CB	23.88^{a} (0.97)	636.22^{b} (44.44)	450^{f} (0.1)	36.13^{ab} (0.79)	1146.61^{b} (20.19)	3.43^{c} (0.62)
3CB	25.64^{d} (0.66)	719.07^{cd} (72.11)	8.33^{de} (0.96)	39.56^{e} (0.44)	1263.53^{c} (19.49)	3.12^{bc} (0.37)
5CB	24.36^{abc} (0.43)	698.24^{bc} (48.38)	7.40^{cd} (0.68)	39.44^{e} (0.82)	1268.84^{c} (26.25)	2.88^{ab} (0.11)
7CB	23.93^{ab} (0.44)	717.85^{cd} (59.96)	7.06^{bc} (0.75)	38.42^{d} (0.66)	1252.69^{c} (41.85)	2.86^{ab} (0.08)
0CB/MCC	23.82^{a} (0.37)	690.95^{bc} (37.73)	8.78^{e} (1.93)	35.85^{a} (0.92)	1212.56^{bc} (35.83)	3.08^{bc} (0.34)
3CB/MCC	24.65^{bc} (0.30)	775.14^{de} (24.64)	6.20^{ab} (0.50)	37.29^{c} (0.64)	1282.25^{c} (79.29)	3.06^{bc} (0.07)
5CB/MCC	24.69^{c} (0.35)	827.42^{e} (30.94)	5.90^{ab} (0.82)	37.88^{cd} (0.47)	1284.47^{c} (11.66)	3.05^{bc} (0.15)
7CB/MCC	24.64^{bc} (0.45)	903.60^{f} (54.67)	5.25^{a} (0.50)	40.02^{e} (1.01)	1510.45^{d} (120.50)	2.98^{ab} (0.10)

TS: Tensile strength, TM: Tensile modulus, EaB: Elongation at break, FS: Flexural strength, FM: Flexural modulus, IS: Impact strength, * Values indicate mean, **The letters indicate homogeneity groups, *** Values in parentheses indicate standard deviation

It was determined that the use of MCC and CB significantly affected tensile strength. Figure 1 shows the tensile strength (TS), tensile modulus (TM), and elongation at break (EaB) graphs of composite samples. With the addition of APP to PP, a decrease in TS occurred. In samples without MCC filling, an increase in TS value was observed with the use of 3% CB compared to samples with 0% CB, and a decrease in the TS value was observed as the CB ratio was increased. It was determined that there was an increase in the TS value of the samples with the addition of 3% and 5% CB in the samples with MCC. Many flame-retardant fillers have the unfavorable effect of surface-treating the particles to enhance chemical interaction with the polymer matrix, which can reduce the mechanical qualities of polymers (Mouritz and Gibson 2006). Consequently, the TS of composites is influenced by the filler's dispersion in the polymer matrix or the interfacial adhesion between the filler and the matrix (Ramazani *et al.* 2008). According to literature, adding a coupling agent in addition to flame-retardants enhanced the interfacial adhesion between the filler and the matrix, preventing a significant loss of strength (Cavdar *et al.* 2016). In tensile tests and bending tests, strength is applied to the material in different directions. In the tensile test, force is applied parallel to the material surface, while in the bending test, force is applied perpendicular to the material surface. In the tensile test, the entire material is subjected to tensile stress. In the bending test, the upper surface of the material is exposed to compressive force while the lower surface is exposed to tensile stress. For this reason, some of the mechanical properties of the material decrease while others increase. The addition of CB with MCC increased the TM of the polymer composites (up to 73%). The composites became more rigid when MCC (10 wt%) was added as a filler to the polymer matrix (Kiziltas *et al.* 2013; Boran 2016; Trache *et al.* 2016). In comparison to the control PP, this resulted in a decrease in EaB values and an increase in TM for the composites.

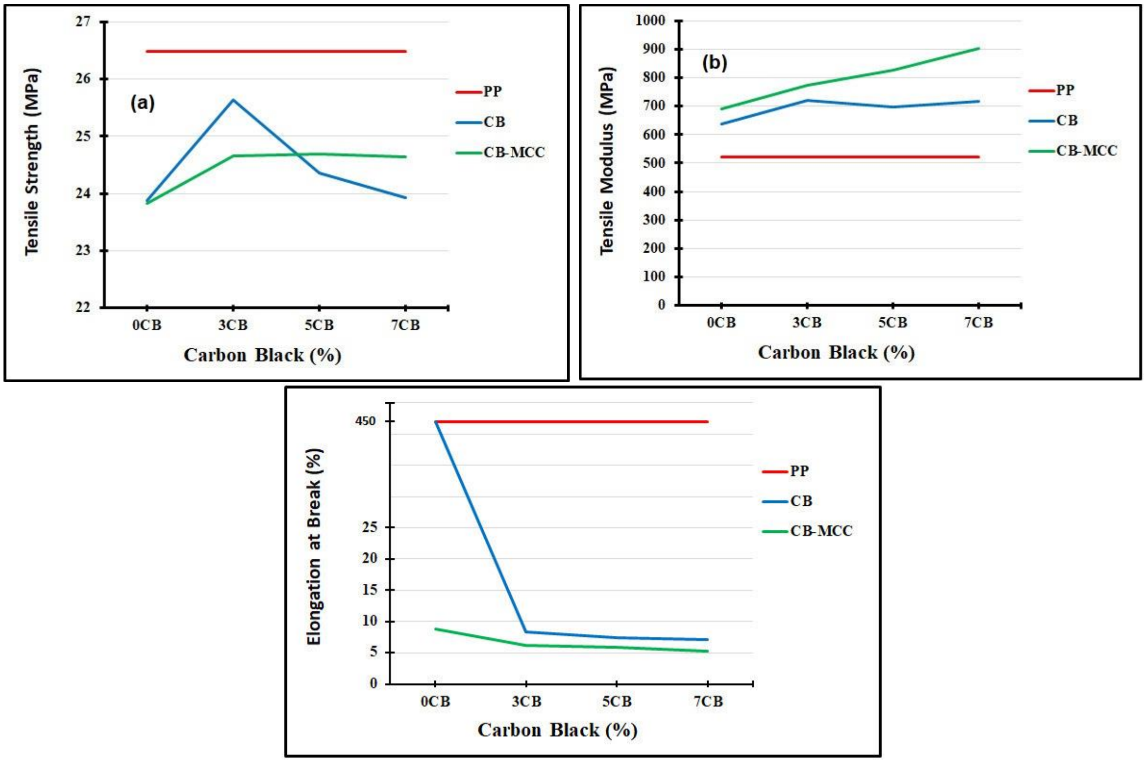

Fig. 1. Tensile strength (a), tensile modulus (b), and elongation at break (c) graph of composite samples

Statistically, the use of MCC and CB had a significant effect on flexural strength (FS). Figure 2 shows the FS, flexural modulus (FM), and impact strength (IS) graphs of composite samples. According to test results, the highest FS value was found in the 7CB/MCC group (40.01 MPa), and the lowest FS value was found in the 0CB/MCC group (35.85 MPa). Adding CB and MCC to the production increased the FS value compared to the control group. Additionally, it was determined that the FS increased as the CB ratio increased in samples with MCC. Researchers have stated that the crystalline nature and short microfibrils of MCC have improved most of the mechanical properties of polymer composites (Wunderlich 1990; Mouritz and Gibson 2006; Fonseca-Valero *et al.* 2015; Boran *et al.* 2016). It was determined that the use of MCC and CB had a statistically significant effect on FM values. The FM of the composites improved up to 44% with addition of MCC and CB. The highest TM and FM were obtained especially in the samples with MCC additive and 7% CB use.

The use of MCC and CB had a significant effect on impact strength. The highest IS value was found in the 0CB group, while the lowest IS value was found in the PP group. Impact strength, which is strongly correlated with toughness, is a measurement of a material's capacity to withstand breaking when stressed at a rapid rate (Panthapulakkal and Sain 2007). Impact strength has increased with the use of CB and MCC in PP composite production. According to the Duncan test, IS values of MCC groups were found to be similar.

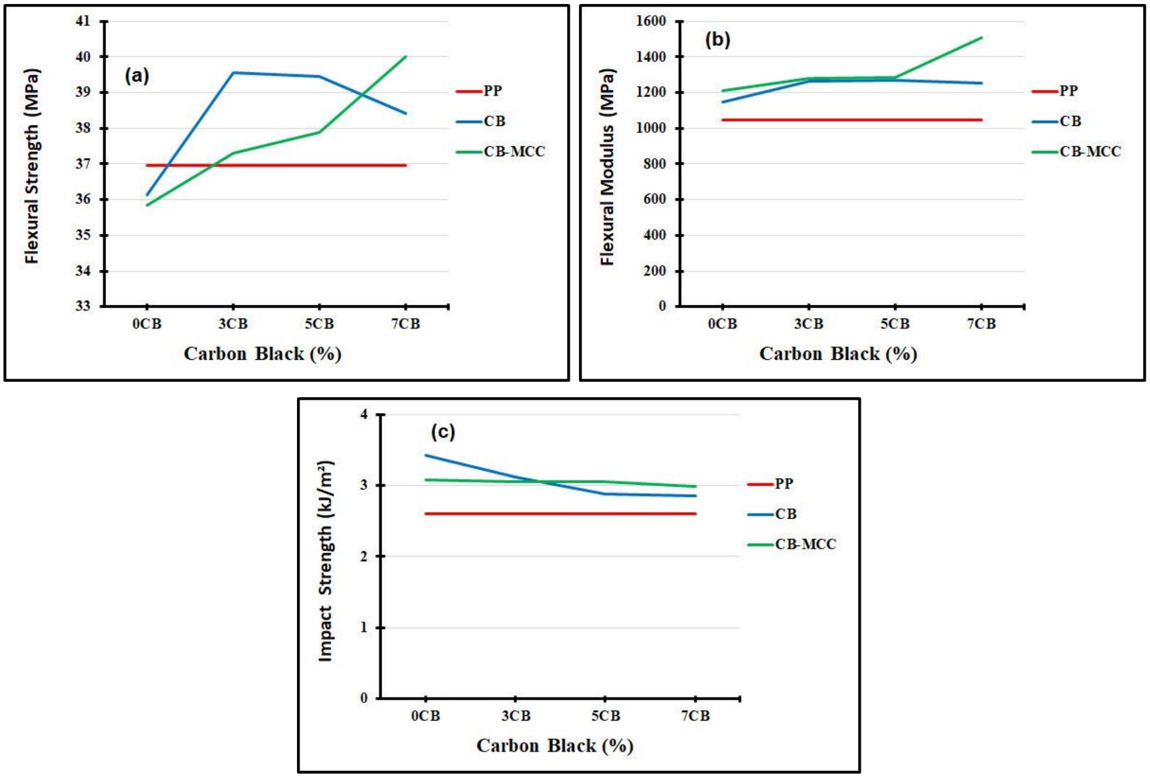

Fig. 2. Flexural strength (a), flexural modulus (b), and impact strength (c) graph of composite samples

Thermogravimetric analysis (TGA), which measures the sample's weight loss in response to temperature, gives precise information about the thermal characteristics and decomposition mechanism of the sample. Figure 3 displays the experimental TGA and DTG curves of CB- and MCC-filled PP composites under a nitrogen atmosphere. Table 4 provides a summary of the findings. The initial (T_{in}), maximum rate weight loss (T_{max}), and final (T_{end}) decomposition temperatures of the control PP composite were 434.7, 463.8, and 480.3 °C, respectively. Figure 3a and Table 4 show that at 800 °C and in N_2 atmosphere, the thermal degradation of the control PP composite resulted in just 1.1 wt% char residue. Compared to the PP composite, CB- and MCC-filled composites were found to have similar thermal behavior but a lower weight loss percentage. With the increase in CB usage rate, an increase occurred in the initial (T_{in}) and maximum weight loss (T_{max}) temperatures of the material. Similar results have been reported in the literature (Yang *et al.* 2019). An increase in the amount of residue was observed with the increase in the CB ratio and the use of MCC in the samples. When MCC-filled composites were exposed to a nitrogen environment, two stages of thermal degradation were evident (Fig. 3b). The first part of weight loss in the TGA curve of MCC -filled composites represented the decomposition of microcrystalline cellulose, corresponding to the temperature range of 289 to 320 °C. Char residue increased from 15.5% to 16.6%, 16.8%, and 18.7% at 800 °C, respectively, in the 0CB-MCC, 3CB-MCC, 5CB-MCC, and 7CB-MCC samples, indicating more char residue and a more compact char layer are formed under pyrolysis conditions (Cavdar *et al.* 2019).

Table 4. TGA and DTG Data of CB and MCC Filled PP Composites Under Nitrogen Atmosphere

Sample	T_{in} (°C)	T_{max} (°C)	T_{end} (°C)	Char at 800 °C (wt%)
PP	434.7	463.8	480.3	1.1
0CB	439.9	471.8	486.6	14.5
3CB	454.4	478.6	493.4	14.9
5CB	464.2	484.2	495.9	16.7
7CB	461.4	482.4	493.9	16.1
0CB-MCC	311.1	479.5	494.0	15.5
3CB-MCC	314.6	483.6	497.7	16.6
5CB-MCC	314.4	490.0	501.9	16.8
7CB-MCC	289.5	492.0	502.8	18.7

T_{in}: The initial degradation temperature; T_{max}: Maximum rate of weight loss temperature; T_{end}: The final degradation temperature

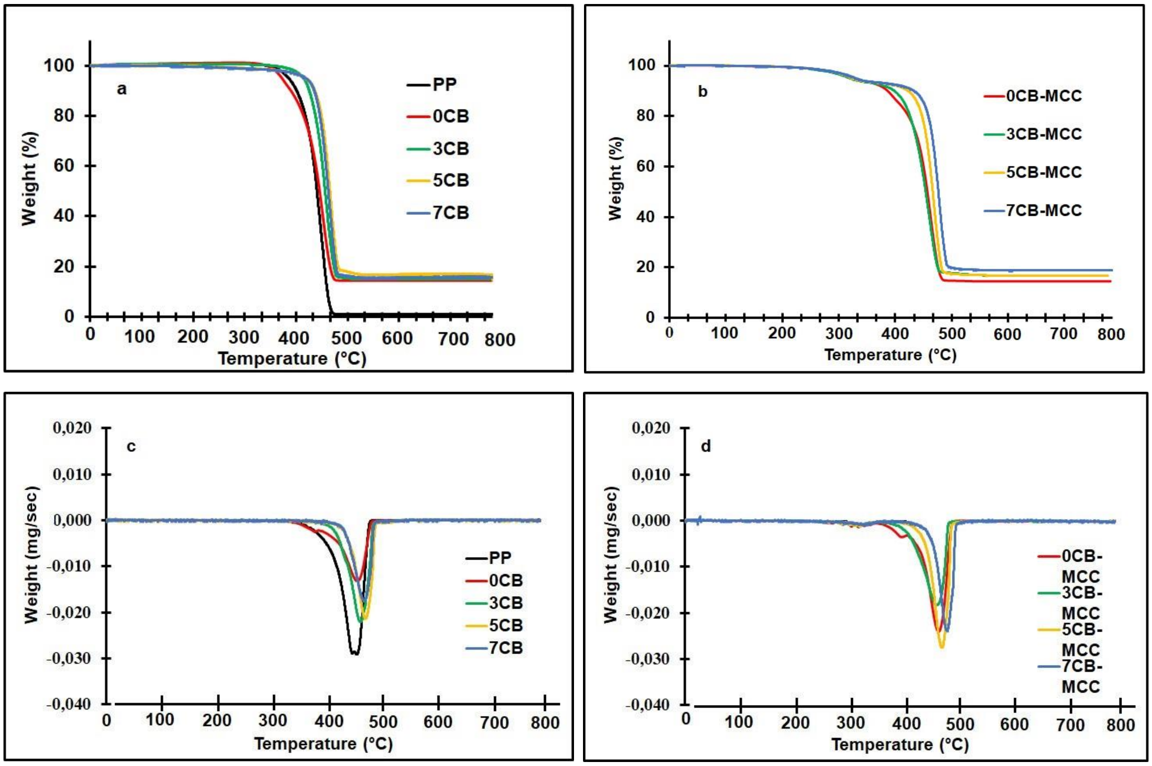

Fig. 3 (a, b) TGA and (c, d) derivation thermogram (DTG) curves of PP composites under nitrogen atmosphere

CONCLUSIONS

1. With the addition of carbon black (CB) and microcrystalline cellulose (MCC) to poly(propylene) (PP)-based composite materials, a decrease in tensile strength (TS) and elongation at break (EaB) values occurred, while an increase in tensile modulus (TM), flexural modulus (FM), flexural strength (FS), and impact strength (IS) were observed.
2. The ammonium polyphosphate (APP) addition in production caused a decrease in TS and FS.
3. The ASTM D6662 standard (2001) requires that plastic lumber decking boards based on polyolefins must have a minimum FS of 6.9 MPa and an FM of 340 MPa. The FS and FM values of PP composites were found to exceed these standards.
4. Both CB- and MCC-filled composites had higher thermal stability compared to control PP. According to TGA results, an increase in the maximum amount of char residue was observed with the use of CB and MCC in the composite material.
5. The initial degradation temperature decreased with the addition of MCC. An increase in $T_{\max}$ and T_{end} occurred with the increase in CB usage rate and the addition of MCC.

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