Improvement of chemical, thermal, and mechanical properties of Polypropylene (PP) - Cellulose microcrystalline composites (CMC)

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Abstract

A research paper focuses on investigations of the improvements on chemical and thermal, and mechanical properties of polypropylene (PP) by adding cellulose microcrystalline fillers (CMC). The CMC powder was used as reinforcement in pure PP with various weight percentages 5, 10 and 20 % respectively. The melt mixing process was used to prepare (PP/ CMC) composites. The structural changes of PP/CMC composites were investigated by Fourier transform infrared (FTIR) spectra. The results of the Thermogravimetric analysis (TGA) exhibited that the higher addition of 20% CMC into the pure PP slightly improved both the residue yields and thermal stability. The tensile strength of 20% CMC into pure PP was slightly increased and elongation reduced, compared with pure PP.

Keywords: Polypropylene, Cellulose Microcrystalline, TGA, Tensile Strength

INTRODUCTION

In recent years, considerable research effort has been undertaken to develop new composite materials derived from natural filler and thermoplastic matrix due to the increase in applications of the resulting products associated with cost reduction and environmental consideration [1–3]. Cellulosic Fillers are extracted from very abundant plants. They are now fast evolving as a potential alternative to traditional ones like calcium carbonate, and glass for various applications [4-7] Indeed, natural fillers have several advantages like low density, high specific properties, nonabrasive to processing equipment, low cost, and most importantly biodegradability [8-11]. Polypropylene is a commodity polymer that is using in broad applications in the packaging, textile, automobile, and furniture industries because of its excellent processability, recyclability and low cost [12,13]. There is still need to understand the behavior of the thermoplastic materials with anatural organic filler such as wood flours [14-17]. This study evaluated the thermal

degradation of regular and wheat straw flour filled recycled thermoplastic composites. This study also examined and evaluated the effect of different contents of cellulose microcrystalline (CMC) when combining with polypropylene (PP) and on the chemical, thermal, and mechanical properties.

EXPERIMENTAL

Materials

The used PP polymer is provided from Saudi Polymer Company commercialized under the trade name HGZ-120SP. Polypropylene polymer has a melt flow index of 4g per 30 min at 237 °C. The Cellulose Microcrystalline is provided from Sigma-Aldrich Chemical Company, UK. The chemical structures of used materials are mentioned in figure 1.
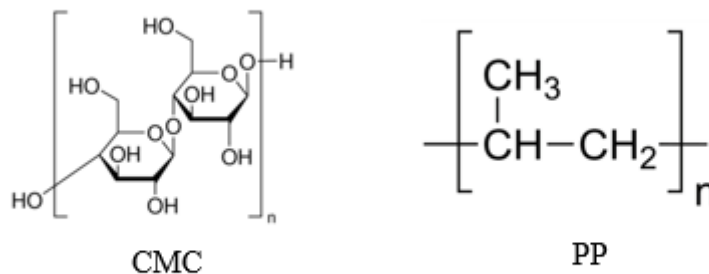

Figure 1. The chemical structures of used materials

Preparation of PP/CMC Composites

CMC was dried in an oven under vacuum at 50ºC overnight, to reduce the humidity content to less than 5 wt %. Composite samples based on PP and different materials 5, 10, 20 wt. % of CMC were mixed by melt blending in a The Thermo Scientific HAAKE Rheomix QC lab mixers (UK) internal mixer. The processing parameters used are the following: temperature 190°C, rotor speed 80 rpm, and a residence time 30 min. The mixed composite samples were dried overnight under vacuum at 80ºC and poured in metal molds in a Carver hydraulic press at 200 °C to obtain films of about 5 mm of thickness. The composite films were cut off and tested for chemical, thermal and mechanical measurements.

Fourier transform infrared (FTIR) spectroscopy

FTIR analysis of neat PP and PP/CMC composite samples was carried out by PerkinElmer Spectrometer FTIR, Model Two Perkin Elmer (Germany) and the attenuated total reflectance (ATR) method was applied. The sample was scanned in the frequency range of 4000–700 cm^{-1} with a resolution of 4 cm^{-1}.

Thermogravimetric analysis

Thermogravimetric (TGA) measurements were carried out using a Perkin Elmer (Switzerland) MT5 thermogravimetric analyzer. The range weight of specimens is between 5–10 mg and a heating rate of 10 ºC min-1. PP and PP/CMC composite samples were heated from room temperature up to 600 ºC to determine the complete thermal degradation of PP and PP/CMC composites. All tests were performed under nitrogen atmosphere.

Tensile tests

Uniaxial tensile tests were conducted with a Universal Instron Machine, UK. Model AT/CT M500) tensile testing machine equipped with a 1 KN load cell. Specimens were tested according to ASTM-D638 in the dimensions 100mm, 10mm, and 2.5mm length, width, and thickness respectively at a crosshead speed of 10 mm / min.

RESULTS AND DISCUSSION

FTIR analysis

The comparison of FTIR spectrum of neat PP, PP/CMC composites is shown in Figure 2. The main characteristic peak of neat PP and PP/CMC composites is listed in Table 1. The peaks at the range 3000–2800 cm-1 were contributed by (C–H) stretching vibrations in PP chains. The peaks found at 1457 and 1376 cm-1 were assigned to (– CH2) and (– CH3) bending vibration in PP. Moreover, 3 small peaks located at 1170, 990, and 975 cm−1 were due to (– CH3) symmetric deformation vibration and –CH3 rocking vibration of PP. The broad peak of around 3300 cm-1 on PP/CMC composites was attributed to (– OH) group from CMC. Furthermore, the absorption peak at 1601 cm-1 assigned to (C=C) stretching from hemicelluloses and the broad absorption peak at 1043 cm-1 was exhibited at the (C–O–C) and (C–O) groups from the main carbohydrates of cellulose microcrystalline. Regarding the FTIR spectrum, a new peak at 1737 cm-1 on PP/CMC composites.
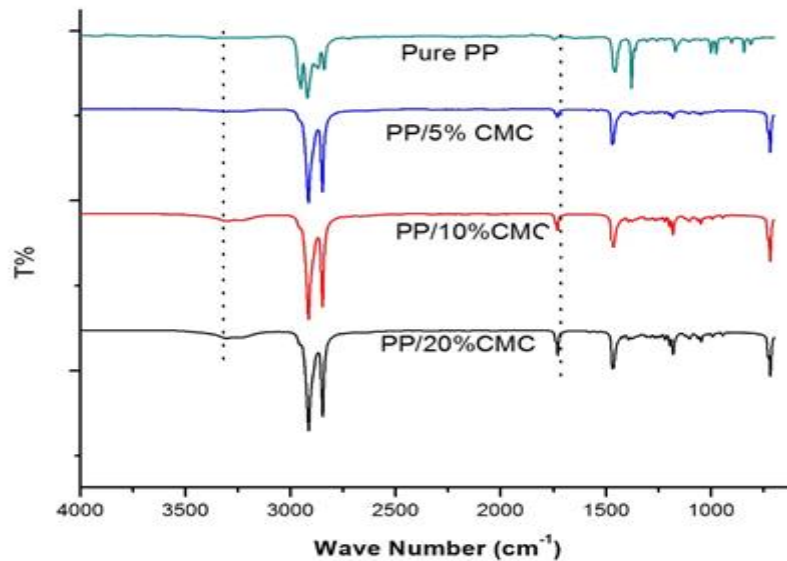
Figure 2. FTIR spectrums of pure PP, and PP/CMC composites

Thermogravimetric Analysis

Thermal Degradation of PP and PP/CMC Composites

TGA thermograms supported the thermal degradation of composites materials under a nitrogen atmosphere, and the heating rate for all samples was about 10 °C/min. Figure 3 shows the TGA thermograms of neat PP compared to those of PP/CMC composites, and the onset of degradation (T onset) gives more information accordingly to TGA curves in figure 3. The summary of the thermal stability for each sample explaining the onset temperature (Tons), the temperature at 50 % weight loss (T50), maximum temperature (Tmax), and residue for each sample are exhibited in table2. From Table 2, 20 %CMC into PP shows higher thermal stability than PP matrix. Moreover, it is observed that the thermal degradation of PP occurs in the temperature range of 375–476.5ºC while the largest amount of thermal degradation of PP/ 20% CMC takes place in the range 386 – 485.5 ºC. According to Table 2, 20% CMC into PP sample has the higher initial decomposition (Tonset = 375 ºC) comparing with PP without filler (Tonset = 375 ºC). The PP-CMC composite samples exhibited more resistant to weight loss (residue) that were 11.6, 12.5, 14.2 % of 5, 10, 20 wt. % of CMC, compared with PP (11%). These results indicated that presence of higher content of CMC 20 % , reduced the effects of accelerated thermal degradation.
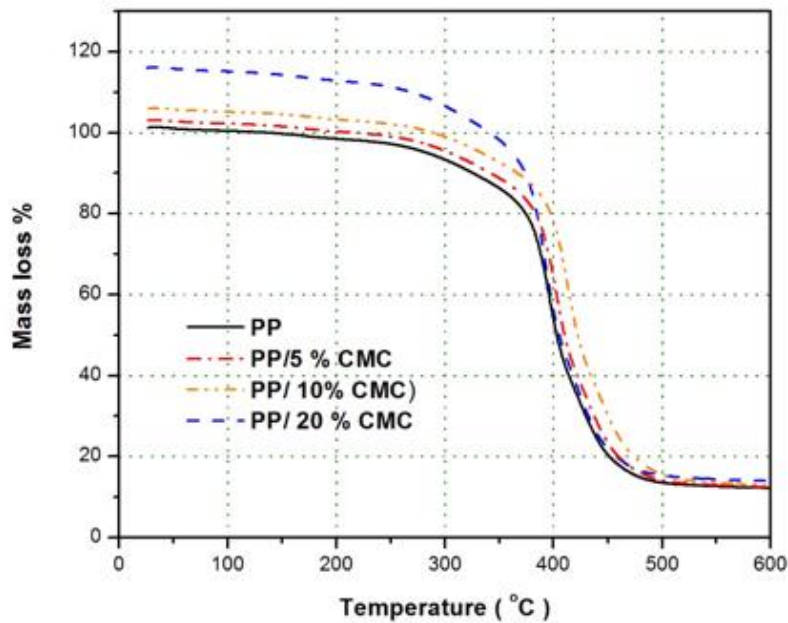
Figure 3. TGA thermograms of PP/CMC composites recorded at different loading rates 5, 10, 20 wt. % compared to neat PP.

Table 2. TGA results of PP and PP/CMC composites

Samples %	T_{onset} (±0.1 °C)	T_{50} (±0.1 °C)	T_{max} (±0.1 °C)	Residual yield %
Pure PP	375	390	476.5	11.2
PP/5 % CMC	376.5	393.2	477	11.6
PP/10% CMC	380	396.4	481.5	12.5
PP/20% CMC	386	399.5	485.4	14.2

Mechanical Properties of Nanocomposites

To further analyze the influence the content of CMC filler on the mechanical properties of the PP composite, the composite samples were tested by the tensile instrument.

The results of the tensile tests are shown in figure 4. CMC content into PP increased tensile strength and reduced strain at break. The fracture strain was seen to CMC down. Figure 4 demonstrates the comparison of the tensile stress versus strain for pure PP and PP /CMC composites. Figure 5 shows that the addition of CMC fillers for 5 wt. %, 10 wt. %, and 20 wt. % to the PP composite induced a rise in tensile strength 27.2 MPa, 28.1 MPa, and 33.8 MPa, respectively, compared with pure PP that shows the lowest value 54.5 MPa of tensile strength (figure 5). As in the case of the strain at break was decreased from 8.5% for PP to 8.2%, 7.65%, and 5.5 % for CMC content 5 wt. %, 10 wt. %, 20 wt. %, respectively (Figure.6). While the surface functionality and dispersion of the material is initially inadequate, the excellent addition of CMC (20 wt. %) improved the mechanical properties of the PP. The interfacial properties between PP and CMC fillers were enhanced in tensile strength and contributed to the slight increase in average tensile strength of their corresponded composites.
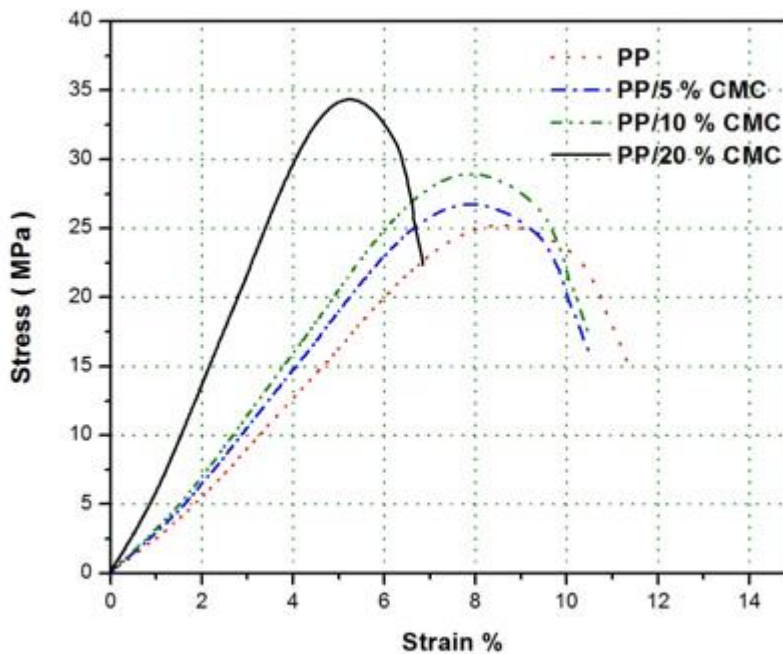

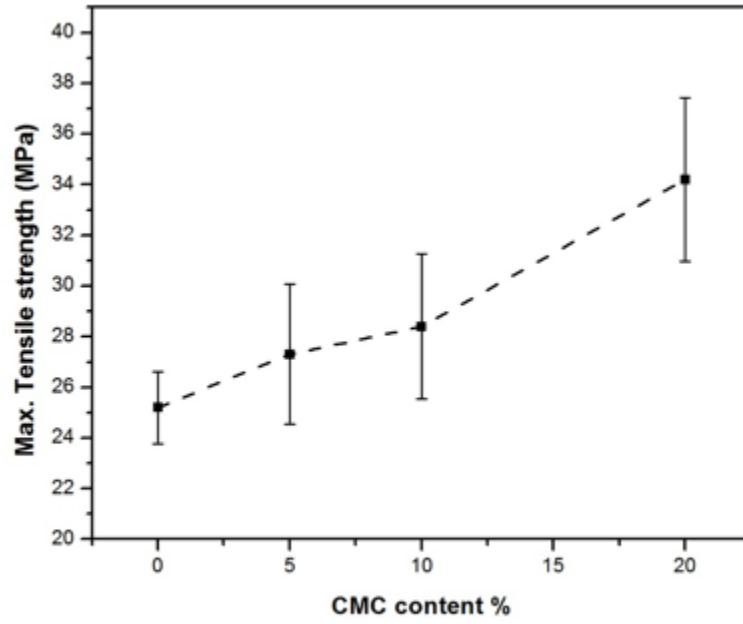**Figure 4.** Stress – strain curves of PP and PP-CMC composites

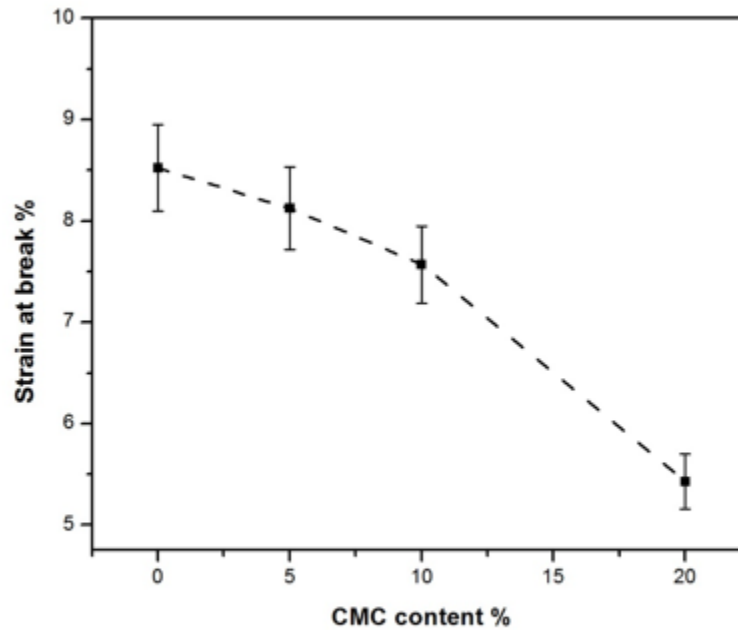**Figure 5.** Maximum tensile strength of PP/CMC composites

Figure 6. Strain at break of PP/CMC composites

Conclusion

The following conclusions were summarized from the above studies:

1. The PP/CMC composites increased chemical interaction with increasing CMC content.

2. The PP/CMC composites exhibit an early thermal decomposition, but they showed higher thermal stability at a higher temperature. The thermal stability of PP/CMC composites with MAPP improved as the T50 %, Tmax, and residue content at 600 ℃ increased.

3. The increase in CMC content decreased the tensile strength and the elongation at break of PP/CMC composites but increased in the tensile strength. Improved the tensile strength and tensile modulus of PP/CMC composites.

References

[1] M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne, Short natural fiber reinforced polyethylene & natural rubber composite: Effect of silane coupling agent and fibers loading, Composites science and technology, 67 (2007) 1627-1639.

[2] M. Biswal, S. Mohanty, S.K. Nayak, Banana fiber-reinforced polypropylene nanocomposites: Effect of fiber treatment on mechanical, thermal, and dynamic-mechanical properties, Journal of Thermoplastic Composite Materials, 25 (2012) 765-790.

[3] A.K. Bledzki, O. Faruk, Wood fiber reinforced polypropylene composites: effect of fiber geometry and coupling agent on physicomechanical properties, Applied Composite Materials, 10 (2003) 365-379.

[4] K.S. Chun, S. Husseinsyah, H. Osman, Utilization of cocoa pod husk as filler in polypropylene biocomposites: effect of completed polypropylene, Journal of Thermoplastic Composite Materials, 28 (2015) 1507-1521.

[5] Y. Cui, S. Lee, B. Noruziaan, M. Cheung, J. Tao, Fabrication and interfacial modifications of wood recycled plastic composite materials, Composite Part A: Applied science and manufacturing, 39 (2008) 655-661.

[6] N. Follain, C. Joly, P. Dole, C. Bliard, Properties of starch-based blends. Part 2. Influence of polyvinyl alcohol addition and photocrosslinking on starch based materials mechanical properties, Carbohydrate Polymers, 60 (2005) 185-192.

[7] S.H. Imam, P. Cinelli, S.H. Gordon, E. Chiellini, Characterization of Biodegradable Composite Films Prepared from Blends of Polyvinyl Alcohol, Cornstarch, and Lignocellulosic Fiber, Journal of Polymers and the Environment, 13 (2005) 47-55.

[8] K. Jarukumjorn, N. Suppakarn, Effect of glass fiber hybridization on properties of sisal fiber–polypropylene composites, Composites Part B: Engineering, 40 (2009) 623-627.

[9] R. Jayasekara, I. Harding, I. Bowater, G.B.Y. Christie, G.T. Lonergan, Preparation, surface modification and characterization of solution cast starch PVA blended films, Polymer Testing, 23 (2004) 17-27.

[10] R. Malkapuram, V. Kumar, Y.S. Negi, Recent development in natural fiber reinforced polypropylene composites, Journal of Reinforced Plastics and Composites, 28 (2009) 1169-1189.

[11] S. Mousazadeh, A. Shakouri, M. Hojjat, S.G. Etemad, S.Z. Heris, Rheological behavior of starch–poly(vinyl alcohol)–TiO2 nanofluids and their main and interactive effects, Journal of Applied Polymer Science, 133 (2016) n/a-n/a.

[12] D. Nawapat, W. Thawien, Effect of UV-treatment on the properties of biodegradable rice starch films, International Food Research Journal, 20 (2013) 1313-1322.

[13] S.K. Nayak, S. Mohanty, S.K. Samal, Influence of interfacial adhesion on the structural and mechanical behavior of PP-banana-glass hybrid composites, Polymer Composites, 31 (2010) 1247-1257.

[14] M. Sain, B. Kokta, Effect of solid–state modified polypropylene on the physical performance of sawdust–filled polypropylene composites, Advances in Polymer Technology, 12 (1993) 167-183.

[15] M. Sain, S. Park, F. Suhara, S. Law, Flame retardant and mechanical properties of natural fiber–PP composites containing magnesium hydroxide, Polymer Degradation, and Stability, 83 (2004) 363-367.

[16] H. Salmah, F. Amri, H. Kamarudin, Properties of chitosan-filled polypropylene (PP) composites: The effect of acetic acid, Polymer-Plastics Technology and Engineering, 51 (2012) 86-91.

[17] X. Tang, S. Alavi, Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability, Carbohydrate Polymers, 85 (2011) 7-16.