



Asian Journal of Scientific Research

ISSN 1992-1454

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Research Article

Nano CaCO₃ Incorporation with Polypropylene to Reduce Film Water Vapor Permeability for Packaging Application

Fatema Al-Attar and Meshal Al-Samhan

Petroleum Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait

Abstract

Background and Objective: The Polyolefin market mainly polyethylene (PE), polypropylene (PP) has experienced tremendous growth over recent years in the packaging industry. The objective: of the study was to investigate the influence of incorporating different wt% nano-CaCO₃ with PP on permeability, thermal and mechanical properties in the presence of maleic anhydride (MAH) compatibilizer. **Materials and Methods:** PP and the nano-CaCO₃ were mixed and compounded in twin screw extruders set at temperatures varying from 180-200°C and 150 RPM, later all prepared samples were rested to dry for one day before subjected to testing, all experimental results were analyzed by statistical arithmetic mean. **Results:** The nano-CaCO₃ additive has decreased the permeability of the PP and averaged just above 7.5 g/m² × 24 hrs for water vapor, higher values of nanofiller content indicated less moisture protection. The testometric tensile results of the prepared samples showed a noticeable influence of the nano filler at all selected concentrations and PP nanocomposite Young's modulus showed lower values than the pure PP indicating good creasing response. Thermally, Thermogravimetric Analysis (TGA) results showed a decrease in the starting decomposition temperatures for the PP nano-CaCO₃ this attributed to the decrease in the additional strength in the nanoparticles interface with the matrix. **Conclusion:** the study showed that the PP nanocomposite film prepared with low content of nano-CaCO₃ has improved the barrier property for water vapor sensitive packaging while other properties such as mechanical and thermal properties kept at a stable and good standard.

Key words: Nano CaCO₃, Polypropylene, Packaging, Permeability, Nanocomposite, Barrier, Thermomechanical

Citation: Al-Attar, F. and M. Al-Samhan, 2020. Nano CaCO₃ incorporation with polypropylene to reduce film water vapor permeability for packaging application. Asian J. Sci. Res., 13: 275-283.

Corresponding Author: Meshal Al-Samhan, Petroleum Research Center, Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The packaging industry over recent years has experienced tremendous growth in using polyolefin, mainly polyethylene (PE), polypropylene (PP) and other materials include polyvinyl chloride, polyvinylidene chloride, polystyrene, polyamide. One of the primary advantages of polyolefin is its properties which can be improved through the use of nano additives or polymers blending¹. PP is a very versatile and adaptable polymer as its properties can readily be enhanced with the inclusion of various types of fillers^{2,3}. Polypropylene is a semi-crystalline polymer that is recognized as a principal packaging material, due to high strength, good processing properties and low cost^{4,5}. These advantages aid both homopolymer and copolymer PP grades to be one of those most versatile polymers available and can penetrate the packaging industries^{6,7}. However, PP exerts some disadvantages, including poor mechanical properties, a high molding shrinkage factor and low fracture toughness, which limit broadening PP application⁸. The basic objective of packaging is to protect the product while in transit, therefore, modifying barrier property by controlling permeability is essential to give the packaging material the ability to resist the ingress of moisture, air, light and micro-organisms. However, these required enhancements to PP cannot be separated from other properties as the nano additives can impact other major packaging properties such as thermal and mechanical.

Barrier property adjusting methods include coatings using special materials, or the application of multilayer combinations of plastic techniques to reduce water and gas diffusion of the package^{9,10}. However, packaging materials are not the only factor that can influence the barrier properties, others, like food contact and environmental conditions such as temperature and relative humidity can also have an impact on the package breathing level. Therefore, the modification and toughening of PP have become one significant study in the field of polymeric materials in the last two decades. The most common practice in enhancing PP properties is the use of fillers/nano-fillers that can alter the properties of PP to fit specific applications^{11,12}. Different type of fillers are utilized for PP enhancement, the most common includes carbon nanotubes, graphite platelets, carbon nanofibers, natural fibers and nano-CaCO₃, the selection of these fillers is subjected to cost and targeted application. In the literature, there are several reports about using microscale CaCO₃ as a filler to improve PP properties^{13,14}. The addition of nano-CaCO₃ filler has markedly improved both mechanical and thermal

properties and this improvement is attributed to the heterogeneous nucleation effect of the filler^{15,16}. Some researchers also reported using nano-CaCO₃ with a different surface modifier such as sodium stearate, silane and titanate¹⁷. Different types of materials require packaging with a certain permeability that can ensure the best environment for the packaged product to maintain associated properties for the longest period possible (shelf life) such as in the pharmaceutical and cosmetic products. To counter this, barrier packaging is used, bags with tailored properties can withstand high temperatures and rough handling will be ideal for dry products such as nuts, medication pills and pet food. Mechanically the repeated bending and creasing of the film can affect the permeability and consequently the shelf life, similarly for elevated temperature during storage or shelving, the thermal stability is another factor that can directly affect the permeability packaging material^{18,19}. For example, aluminum pouches and foils cannot withstand elevated temperature which eventually results in the contents quickly being spoiled. Therefore, any enhancement technique for the barrier properties should not weaken the mechanical and thermal properties^{20,21}.

This paper focuses on the influence of incorporating different wt% (2,5,8,11) of nano-CaCO₃ with a PP to enhance the PP barrier property for packaging application without compromising the thermal and mechanical properties of the prepared PP nanocomposite. Maleic anhydride (MAH) compatibilizer was used to overcome PP non-polar chemical structure that leads to poor interaction with the typically polar fillers such as nano-CaCO₃.

MATERIALS AND METHODS

Study area: This work was carried out at Kuwait Institute for Scientific Research (KISR) in the Petroleum Research Center (PRC) laboratories over two years completed in late 2019 and all related data revision and analysis were completed in early 2020.

Materials: PP is available commercially in various grades. In this study, the HT031 grade was used and it was acquired directly from the EQUATE petrochemical company, Kuwait. The high purity nano-CaCO₃ and MAH were all acquired from international manufacturers through KISR's store department. Compatibilizer MAH was used to improve the interfacial adhesion between CaCO₃ and PP. Bi-functional molecules such as maleic-anhydride grafted PP (PP-g-MAH) are commonly used as compatibilizers for PP and CaCO₃.

Sample preparation: Following the standard blending procedure stated in the literature²²⁻²⁴ and following the procedure at the petrochemical and polymer laboratories of the PRC, the required samples were prepared. Blends were prepared using a twin-screw extruder (model latch LTE 26/40) at speeds ranging between 150 and 200 rotations per min (RPM). Prior to compounding and eliminating moisture, the PP additive-free samples were dried at 40°C for 24 hrs. whereas, the nano-CaCO₃ samples were dried at 50°C in an air-circulated oven for 5 hrs. Blending to compound the ingredients of different wt% of nano-CaCO₃ (2,5,8,11) took place at temperatures varying from 180-200°C (temperature recorded at the die head of the barrel). Using laboratory desiccators, the final samples after compounding were conditioned under the ambient temperature for 24 hrs then all prepared samples were cut in standard shapes for each test.

Experimental details: The PP and the PP/nano-CaCO₃ samples were tested for certain properties as follows:

- **Barrier properties (permeability test):** The water vapor transmission rates of the PP composite were determined by Gintronic GraviTest. The following parameters were used in the PC-software to complete the automation of the measuring process. Wetcup method was selected, the temperature set at 23 °C, humidity at 50%, air velocity at 2.5 m/s, weighing interval for 45 min and sample surface area equal to 50 cm². The permeability calculation was based on the following equation

$$\text{Permeance} = \text{WVT} / \Delta p = \text{WVT} / S (R1-R2) \quad (1)$$

where, Δp is vapor pressure difference, in. Hg, WVT is calculated water vapor transmission, S is saturation vapor pressure at test temperature, in. Hg, R1 is relative humidity at the source expressed as a fraction (the test chamber for desiccant method; in the dish for water method) and R2 is relative humidity at the vapor sink expressed as a fraction

Permeance experiments were performed three times and the mean values have been reported

- **Mechanical properties (Tensile):** mechanical test was essential to evaluate the mechanical properties of the prepared samples, that is, the tensile strength. Tensile testing was carried out according to ASTM D 638, using a Testometric tensile testing machine (Instron 5984) under ambient conditions with crosshead speeds of 500 mm/min

- **Thermal properties:** The thermal stability of the prepared samples was determined by Thermogravimetry using the Shimadzu DTG-60 Thermogravimetric Analyzer (TGA). This test determines the changes in the sample weight with an increase in temperature, as the onset temperature which is directly calculated from the TGA traces corresponding to the temperature at which the weight loss begins

RESULTS AND DISCUSSION

In this study the main objective of adding nano-CaCO₃ to pure polypropylene is to alter the barrier property of the prepared film by reducing water vapor permeability. This reduction in water vapor transmission of the film is very essential for food packaging applications. However, the enhancement in the barrier property for the prepared PP nanocomposite film should synergies with good mechanical and thermal properties of the film to ensure appropriateness for food packaging.

Film permeability test: the permeability of the prepared samples was evaluated for water vapor transmission. Pure PP and the prepared PP nanocomposite with different wt% of nano-CaCO₃ (2,5,8,11) were subjected to water vapor transmission (WVTR) for 24 hrs in the Gintronic Grave test, while maintaining other variables such as temperature and humidity fixed at 23°C and 50% respectively. Figure 1 and 2 PP mixed with 5 and 8 wt% nano-CaCO₃ show an increasing trend of WVTR over time indicating that the polymer matrix of the prepared film is more susceptible to water vapor in comparison with other samples with different concentrations. Where in Fig. 3 it can be noticed that the film maintained a low and steady water vapor transmission rate, however, in Fig. 4 the PP nanocomposite film with 2 wt% nano CaCO₃ content demonstrated the best barrier for the water vapor transmission resulting in an average water vapor permeability of 0.75 g/m² × 24 hrs. This could attribute to the distribution of the selected nano wt% in the prepared film which tightened the polymer matrix and reduced water vapor molecules transfer in comparison with pure pp structure²⁵.

Furthermore, Fig. 5 illustrates the calculated permeability of pure PP in comparison with the prepared PP nano-CaCO₃ composite films. It is noticed that at high 5 and 8 wt% of nano additives the prepared film has less moisture protection and consequently, unsuitable for dry environment packaging. However, in the case of high nano-CaCO₃ content (11 wt%) the PP composite demonstrated good water vapor tightness,

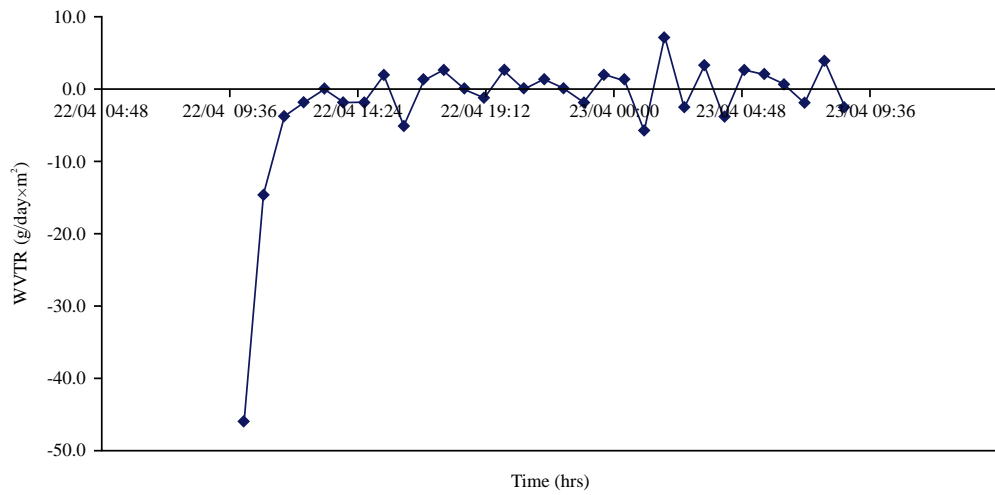


Fig. 1: Water vapor transmission rate of PP-NaCO₃-MAH 93-5-2

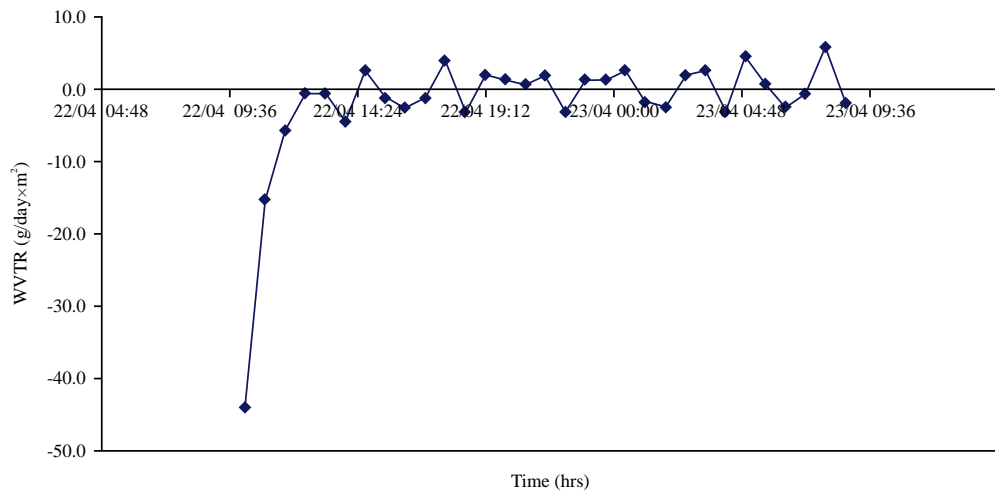


Fig. 2: Water vapor transmission rate of PP-NaCO₃-MAH 90-8-2

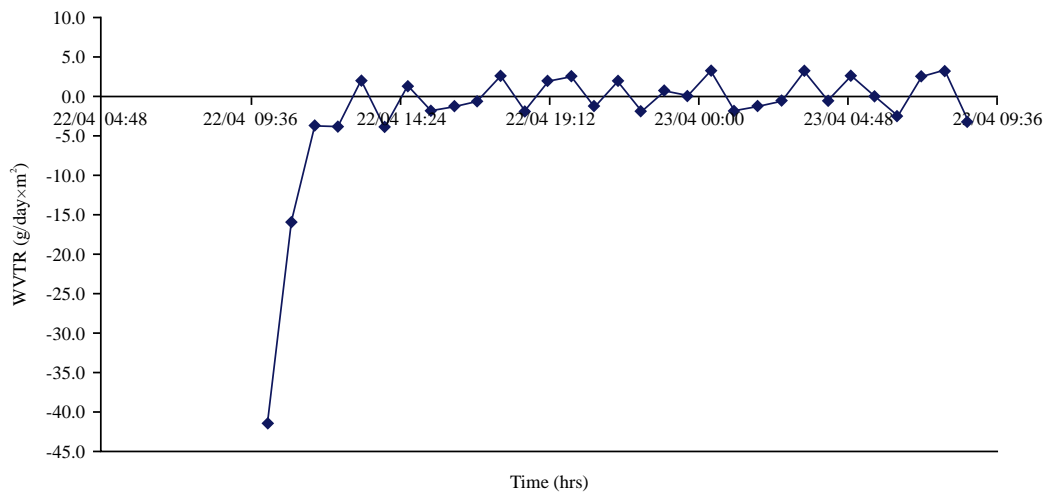


Fig. 3: Water vapor transmission rate of PP-NaCO₃-MAH 87-11-2

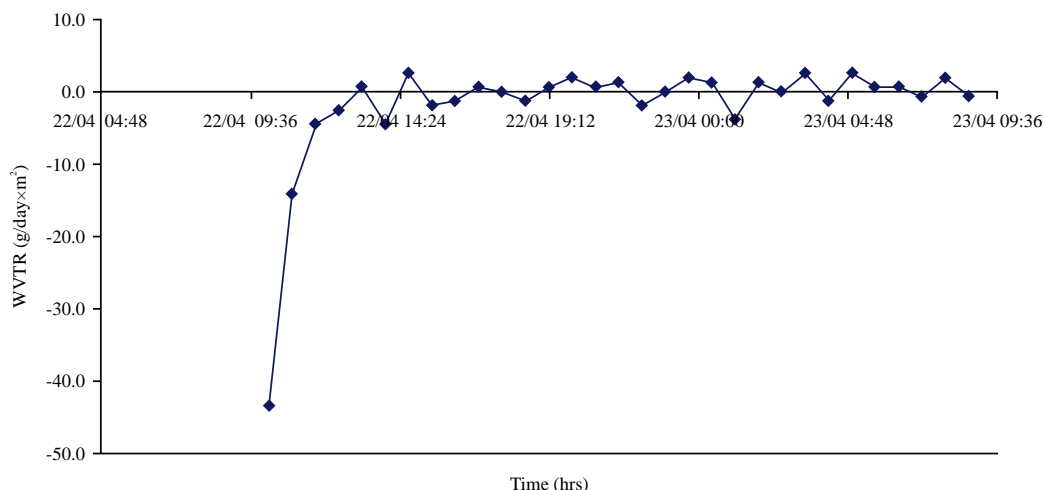


Fig. 4: Water vapor transmission rate PP-NaCaCO₃-MAH 96-2-2

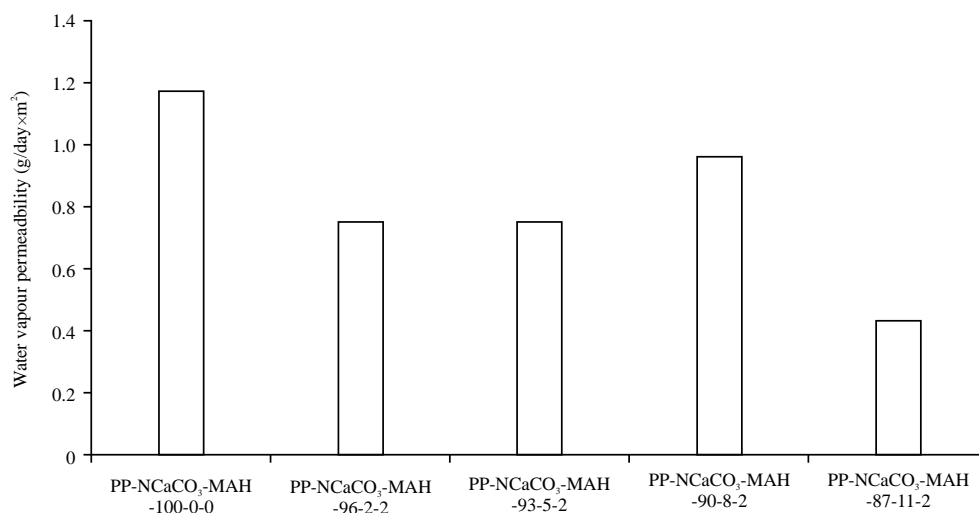


Fig. 5: Calculated permeability (g/m² × 24 hrs) of pure PP and PP nanocomposite with different concentrations of N-CaCO₃

this could be attributed to the exfoliation at high content leading the polymer matrix to restructure differently due to the high concentration of the additive²⁶. In general, the calculated permeability for all PP mixed with nano-CaCO₃ were reduced and averaged just above 7.0 g/m² × 24 hrs. this finding is of high value for the objective of understanding the impact of nano-CaCO₃ on PP. Moreover, the change in permeability in the prepared nanocomposite film is equal to 39% reduction for water vapor permeance in comparison with pure PP. As mentioned earlier in the paper other property like mechanical and thermal have to synergize with the results of permeability property to confirm the desired enhancement.

Film mechanical properties assessment: The mechanical properties of the PP nanocomposite samples were studied

using a Testometric Machine (model Instron 5984) under ambient conditions with crosshead speeds of 500 mm/min, using ASTM D 638²⁷. The Young's modulus and tensile strength were evaluated for the prepared samples with different nano-CaCO₃ wt% in comparison with pure PP. The Young's modulus property results are calculated using Eq. 2:

$$E = \frac{\sigma}{\epsilon} \dots \quad (2)$$

where, E is Young's modulus, σ is uniaxial force per unit surface and ϵ is the strain.

Figure 6 shows the results of Young's modulus and tensile strength for the prepared PP nanocomposite films with 2, 5, 8 and 11 wt% of nano-CaCO₃. The low modulus values for the

prepared samples in comparison with the pure PP indicating that the incorporating nano-CaCO₃ has enhanced the flexibility of PP, this finding is important for crease during handling and transportation to avoid changes in permeance of moisture for packaging application. In addition, it is noticed in the presented modulus value for 11 wt% nano content the PP nanocomposite behaved inconsistency with the trend of other nano contents indicating that the polymer matrix bonded in a different manner with the nano-CaCO₃ resulting in changed crystallinity of the polymer^{28,29}. This behavior of the prepared film with high nano-CaCO₃ wt% synergies with the finding in the permeability part.

On the other hand, for the tensile strength Fig. 6 illustrate that the reduction in tensile values for the different wt% of nano-CaCO₃ are almost similar ranging from 34.2 to 36.1 (MPa), demonstrating that low dosage of nano-CaCO₃ can give the same changes in the tensile strength for the prepared PP nanocomposite film. In relation with the other properties, it is important to remark that the PP nanocomposite had an insignificant reduction in tensile strength (the limit between plasticity zone and rupture zone) making the nanocomposite at the selected nano filler directly dependent on other properties results.

Overall, mechanical properties for the prepared PP nanocomposite film has demonstrated stable tensile strength and good reduction in the young's modulus at low nano concentration^{30,31}. Houang *et al.*²³ has explained that the nucleation role of nano additives in the crystallization of PP which results in polymer mechanical property changes. Moreover, from cost-effectiveness prospect using 2 wt% of the nano-CaCO₃ is a appropriate for PP mechanical film enhancement in terms of stable tensile strength and Young's modulus reduction.

Film thermal stability: Studies in the literature have shown that the permeability of water vapor PP and PP nanocomposite is impacted by the thermal stability of the material³², thus understanding the influence of the nanofiller additives on the polymer composite thermal property is essential.

The data related to the term oxidative stability of the prepared samples were collected from the TGA analysis. The pure PP onset degradation was recorded at 350°C and final degradation at 482°C with smooth and stable curve as shown in Fig. 7. As the degradation mechanism involves mainly chain scission of the material yielding the combustible gases, water, amines and gaseous aromatic compounds, etc. and the blank samples have no matrix. Therefore, the degradation curves reached full decomposition (0% weight).

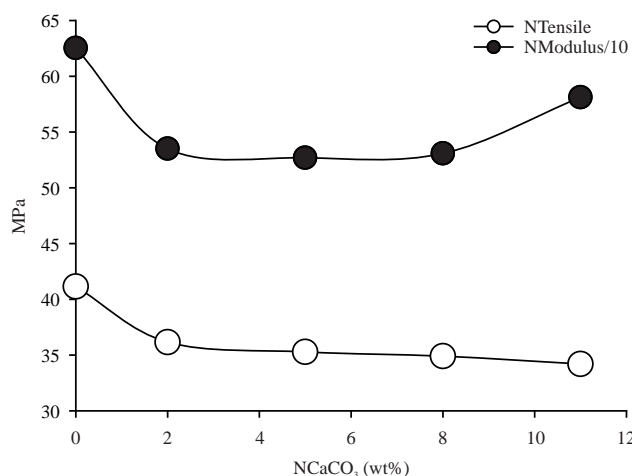


Fig. 6: Young's modulus and tensile strength of the pure PP and PP with different wt% of NCaCO₃

Figure 8 illustrates the TGA results of both pure PP samples and the prepared PP nanocomposite samples and the difference in enhancements associated with the different concentrations of the nano-CaCO₃. The PP nanocomposite showed similar behavior of early degradation temperature in comparison with the pure PP. The decrease in starting decomposition temperature for the PP with nano-CaCO₃ could be attributed to the decrease in the addition strength in the PP interface and the nanoparticles. This argument is supported by the observation of the double stage on-set degradation for most of the PP nanocomposite results. This is attributed to the existence of proper interface interaction, the particles are able to restrain/ease the movement of the polymer chain, making it less difficult for the breaking of the polymer chains occurring at lower temperature³³. Therefore, the prepared nanocomposite showed lower on-set temperature than pure PP. Moreover, it is noticed that sample with high nano content 8 and 11 wt% experience unstable double stage decomposition at 600°C before reaching final decomposition at 6 and 7%, respectively, which can be ascribed to chain breaking due to the high concentration of the additive.

In addition, with the incorporation of 2% wt nano-CaCO₃, the polymer matrix has shown end-set thermal stability reaching 2% weight final decomposition. Finally, PP/nano CaCO₃ demonstrated good thermal stability-indicating the homogeneity of the mix and a good dispersion of nano CaCO₃ despite the reduction in the onset temperature.

Finally, it is important to mention that the onset of weight loss is often used to define the upper-temperature limit of thermal stability. However, in many cases degradation has

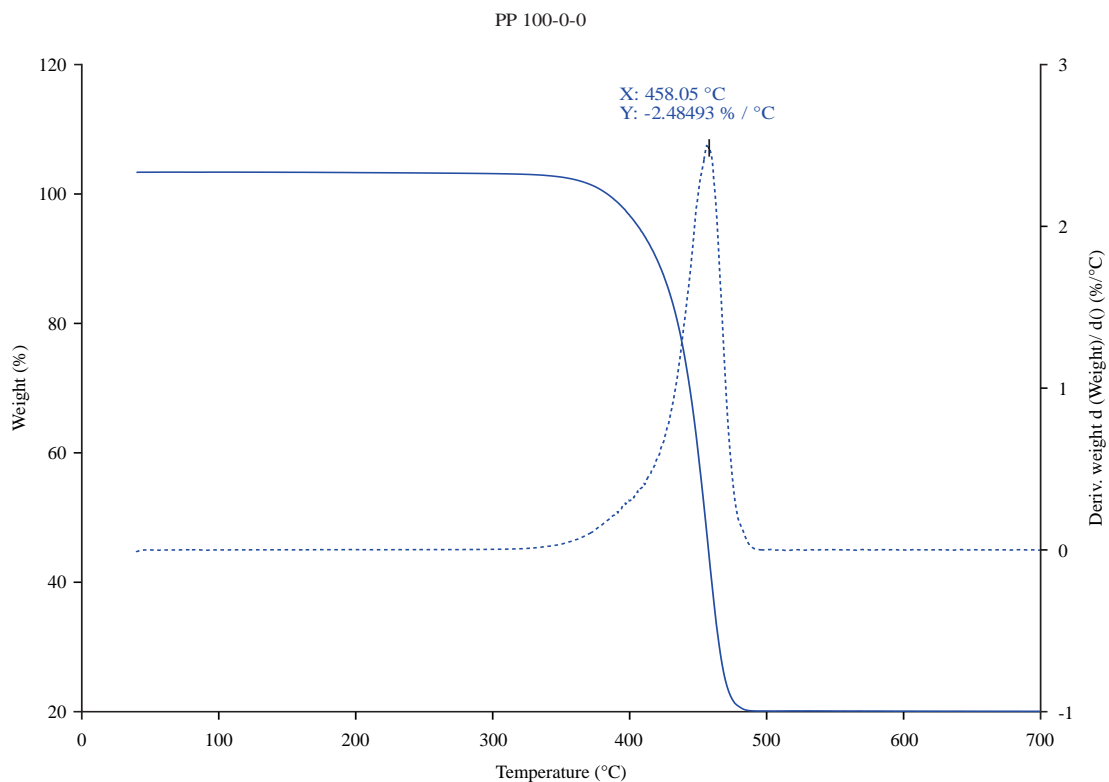


Fig. 7: Thermal degradation of blank PP sample

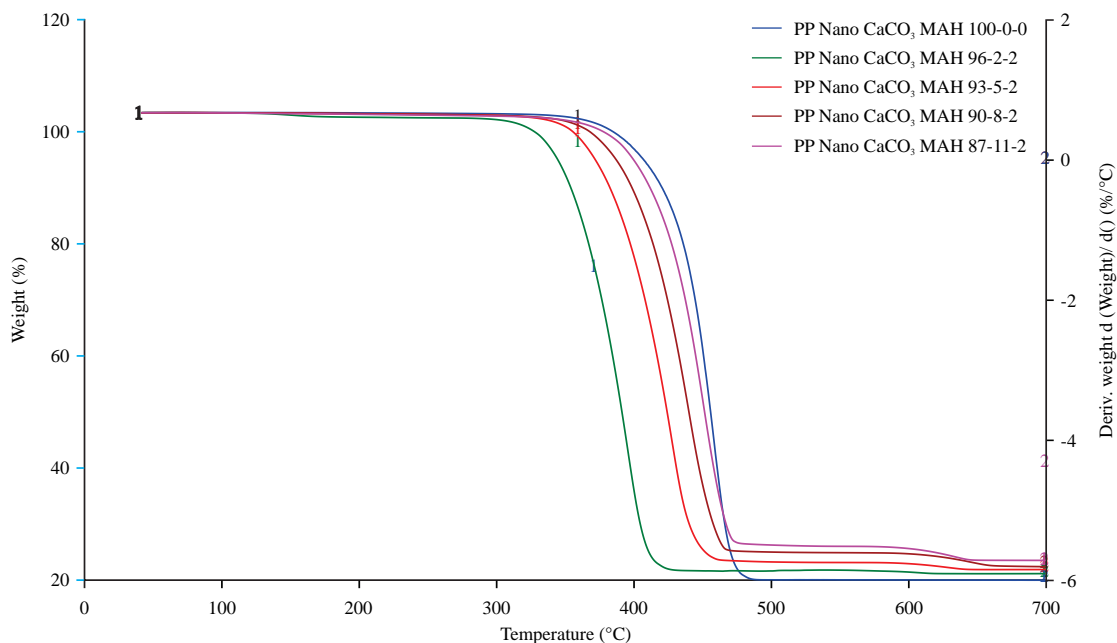


Fig. 8: TGA PP samples with different concentration of NCaCO_3 at 2% MAH

already taken place without a detectable weight loss, for example, by chain scission or crosslinking reactions. Thus, the prepared PP composites were less temperature-resistant

(above 300°C), yet stable at the lower range. Furthermore, the onset and end set degradation temperatures for most of the samples showed a similar trend in the decomposition

mechanism and any additional weight loss could be indicative of the evolved gaseous by-products.

CONCLUSION

The study has provided a clear understanding of PP nanocomposite performance when nano-CaCO₃ was used as a property enhancer. Test results and discussion were focused on the barrier, mechanical and thermal performance of the PP nanocomposite with different wt% of CaCO₃. The selected nano-CaCO₃ filler has reduced the water vapor permeability of PP especially at low wt% (2-5). Mechanical and thermal properties for the prepared nanocomposite films, both have confirmed the suitability of the selected nanofiller for enhancing PP packaging properties.

Conclusively, in terms of availability and cost nano-CaCO₃ is a cost-effective nanofiller that can be used to enhance the barrier property of mono PP while keeping mechanical and thermal properties stable.

SIGNIFICANCE STATEMENT

This study revealed that 2-5 wt% is the optimum nano-CaCO₃ concentration to enhance mono PP barrier property against water vapor, while mechanical and thermal property kept stable. Comparing the results of all tests in this study has advanced the understanding of the PP nanocomposite polymer matrix behavior in bonding with the nanofiller. This study will help the researchers to investigate further in the direction of interface region changes due to different compatibilizer (MAH) concentrations which can grantee polymer property enhancement. Thus a new compounding technique for enhancing mono polypropylene may be achieved.

ACKNOWLEDGMENT

I would like to acknowledge the principal adviser of this study Dr. M. Al-Samhan for his positive contribution at all stages of the study. I also would like to extend my thanks to the Equate petrochemical company for its support and raw material data accessibility without which this paper would not be completed.

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