
THE EFFECT OF CALCIUM CARBONATE AT LOW VOLUME FRACTIONS ON THE MECHANICAL PROPERTIES OF POLYPROPYLENE/CALCIUM CARBONATE NANOCOMPOSITES

¹Chinedum Ogonna Mgbemena, ²Nelson Obinna Ubani, ³Chika Edith Mgbemena

¹Department of Mechanical Engineering, Nnamdi Azikiwe University, Awka

² Department of Mechanical Engineering, Michael Okpara University of Agriculture, Umudike

³ Department of Industrial/Production Engineering, Nnamdi Azikiwe University, Awka

Email: edumgbemena@yahoo.com

ABSTRACT

Polypropylene/Calcium Carbonate nanocomposites were prepared by melt compounding of the Polymer material and melt mixing with the Calcium carbonate nano-fillers at filler loadings of 5%, 10%, 15% and 20%. The samples evaluated were the stearic acid coated and uncoated nano-fillers. The results of the study showed that the addition of CaCO₃ nano-filler have resulted in the improvement of the mechanical properties of the Homo Polypropylene, mainly the Young Modulus. The tensile strength and elongation at break of Polypropylene was slightly reduced with the incorporation of the nano-filler. The Young Modulus increased for Calcium carbonate volume fractions for both the coated and the uncoated grades for filler concentrations up to 5%. Stearic acid coated fillers showed the highest Improvement in the above tensile properties at this low volume fraction .It is important to note that the maximum tensile strength occurred at 5% Volume fraction and as the volume fractions increased both the Tensile strength and elongation decreased and in contrast, the Young Modulus increased.

Keywords: Polypropylene, Calcium Carbonate, nano-filler, nanocomposites

INTRODUCTION

Polypropylene/Calcium carbonate nanocomposites are formed by the melt mixing and melt compounding of the polypropylene polymer with calcium carbonate nano-fillers at appropriate volume fractions or percentage weights of the fillers[1,2,9]. The term nanocomposite is used because the filler materials fall in the range of 1 to 100 nanometers (nm). One nm is equal to one-billionth of a meter (.000000001 m), which is about 50,000 times smaller than the diameter of a human hair. Scientists refer to the dimensional range of 1 to 100 nm as the nanoscale, and materials at this scale are called nanocrystals or nanomaterials. Calcium carbonate has a nanoscale of 44nm [3].

Nanocomposites refer to materials consisting of at least two phases with one dispersed in another that is called matrix and forms a three-dimensional network. It can be defined as multi-phase solid materials where one of the phases has one, two or three dimensions of less than 100 nano metres (nm) or structures having nano-scale repeat distances between the different phases that make up the material [4].

There have been many studies using nano calcium carbonate to enhance the properties of polymers. Among the techniques employed to disperse the nano filler include in-situ polymerization, melt mixing using internal mixers and melt compounding using twin-screw

extruders. In-situ polymerization technique has been used for PVC and PET, while melt mixing and melt compounding appeared to be the preferred method for PP [5].

Hanim et al [2] studied the effects of calcium carbonate nano- filler on the mechanical properties and crystallization behaviour of Polypropylene. In their study, PP/CaCO₃ nanocomposites were prepared using a co-rotating twin-screw extruder at filler loadings of 5, 10, and 15% weight. The mechanical properties of the nanocomposites are evaluated using impact, flexural and tensile test, while the crystallization behaviour was analyzed using Differential Scanning Calorimetry and Wide Angle X-ray Diffraction (WAXD) techniques. The impact strength and Modulus of PP showed some improvement with the incorporation of nano-filler while the tensile strength deteriorated. Scanning Electron Microscopy photomicrographs showed evidence of calcium carbonate agglomeration within the PP matrix, indicating that the level of shear stress generated during melt compounding was far from adequate to break-up the CaCO₃ nano filler. WAXD results showed the appearance of β -phase PP in the nanocomposites with 10 and 15-weight percentage CaCO₃. The influence of CaCO₃ nano filler on the crystallization behaviour of PP were also investigated using a DSC. Incorporation of CaCO₃ shifted the crystallization exotherms of PP towards higher temperatures, indicating that the nano filler has acted as a nucleating agent for PP. The reduced values of half crystallization times also implied that the introduction of CaCO₃ has accelerated the crystallization rate of PP. In their work, stearic acid coated calcium carbonate nanofiller were used to ensure uniform dispersion in the PP matrix.

Xie et al ,[12] successfully synthesized PVC/CaCO₃ nanocomposites via in-situ polymerization technique with filler loadings of 2.5, 5.0 and 7.5 weight percentage. Their studies found that the toughness and stiffness of PVC were simultaneously improved with the addition of 44nm sized CaCO₃ filler. Uniform filler dispersion was obtained using the technique employed and they concluded that the toughness effect observed was attributed to the debonding/voiding of the nano CaCO₃ particles and the deformation of the matrix material surrounding the nano particles.

Di Lorenzo et al [3] successfully polymerized poly (ethylene terephthalate) (PET) with coated and uncoated CaCO₃ particles of 40 – 80 nm size. They found that stearic acid coated CaCO₃ resulted in a stronger polymer-filler interaction compared to the uncoated grade. The strong interfacial adhesion between the phases resulted in significant increase in the glass transition temperature (14°C shift) and melting temperature (8°C shift) of the nanocomposites.

Chan et al [1] prepared PP/ CaCO₃ nanocomposites by melt mixing in a Haake mixer using various mixing time (15, 30 and 45 minutes) with filler loadings of 4.8, 9.2 and 13.2 volume percents. The dispersion of Calcium carbonate nanoparticles in PP was good for filler content below 9.2% volume. Their Differential Scanning Calorimetry results indicated that the nano CaCO₃ are very effective nucleating agent for PP. Tensile tests showed that the modulus of the nanocomposites increased by approximately 85%,while the ultimate stress and strain as well as yield stress and strain were not much affected by the presence of CaCO₃ nanoparticles. The results of the tensile test can be explained by the presence of the two-counter balancing forces: the reinforcing effect of the CaCO₃ nanoparticles and the decrease

in the spherulite size of the Polypropylene. Izod impact tests suggested that the incorporation of CaCO_3 nanoparticles in PP has significantly increased its impact strength by approximate 300%. J-integral tests showed a dramatic 500% increase in the notched fracture toughness. Micrographs of scanning electron microscopy revealed the absence of spherulitic structure of PP matrix. In addition; DSC results indicated the presence of a small amount of β -phase PP after the addition of the CaCO_3 nanoparticles.

EXPERIMENTAL

Materials and Sample Preparation

The PP was melted from its pelletized form at a temperature exceeding 180°C in a mixing chamber. Measured amounts of Calcium Carbonate were added to the melted PP by volume fractions and stirred continuously for 10 minutes to ensure a uniform dispersion of the mixture. The compounded mixture was cast in an aluminum mould that has been treated with a mould releasing agent and dried. The composite was allowed to cure and was later de-moulded. The above procedure was repeated for the stearic acid coated Calcium Carbonate previously done (i.e. at 5%, 10%, 15%, and 20% volume fractions). The fabricated material has a dimension of 85mm x 35mm x 10mm [13].

Table 1: Combination of composites taken for experiments by volume fractions.

Specimen Code	PP	Coated CaCO_3	Uncoated CaCO_3
PPC – 0	–	–	–
PPC – 1	0.95	0.05	0.05
PPC – 2	0.90	0.10	0.10
PPC – 3	0.85	0.15	0.15
PPC – 4	0.80	0.20	0.20

The densities of the polypropylene, CaCO_3 and stearic acid are 0.90g/cm^3 , 2.55g/cm^3 and 0.847g/cm^3 respectively.

Tensile Testing of the Samples

The tensile experiment was performed on ABBA Universal Testing Machine at a laboratory temperature of 25°C with a cross head speed of 100mm/minute according to ASTM D638. The tensile test is a destructive characterization technique. Tensile testing was performed to determine elastic modulus, ultimate stress, and ultimate strain for all samples.

The mechanical properties are determined from a stress vs. strain plot of the load and elongation data. A minimum of six samples were tested in each case for the coated and uncoated specimen at their various volume fraction.

RESULTS AND DISCUSSIONS

The test values presented below were averages. For each volume fraction, six samples were tested. Plots were made to show the relationship between the Tensile strength, Modulus of elasticity (Young Modulus) and elongation.

Table 2 Tensile test results for the coated PP/CaCO₃ specimen (Average Result)

Specimen Code	Volume Fraction % (filler)	Tensile Force, KN	Elongation	Tensile Strength, MPa	Engineering Strain $\epsilon = \Delta L/L$	Young Modulus GPa	Percent Elongation
PPC – 0	0	294	5	122.5	0.0625	1.2500	6.25
PPC – 1	5	336	3	140	0.0375	0.0131	3.75
PPC – 2	10	108	3	45	0.0375	0.0138	3.75
PPC – 3	15	226	2	94.2	0.025	0.0146	2.50
PPC – 4	20	158	1	65.83	0.0125	0.0154	1.25

Table 3 Tensile test results for the uncoated PP/CaCO₃ specimen (Average Results)

Specimen Code	Volume Fraction % (filler)	Tensile Force, KN	Elongation	Tensile Strength MPa	Engineering Strain $\epsilon = \Delta L/L$	Young Modulus GPa	Percent Elongation
PPC – 0	0	294	5	122.5	0.0625	1.250	6.25
PPC – 1	5	320	4	133.3	0.0050	2.666	5
PPC – 2	10	90	4	37.5	0.0050	0.750	5
PPC – 3	15	211	2.5	87.92	0.0313	2.809	3.13
PPC – 4	20	150	1.9	62.50	0.0240	2.604	2.40

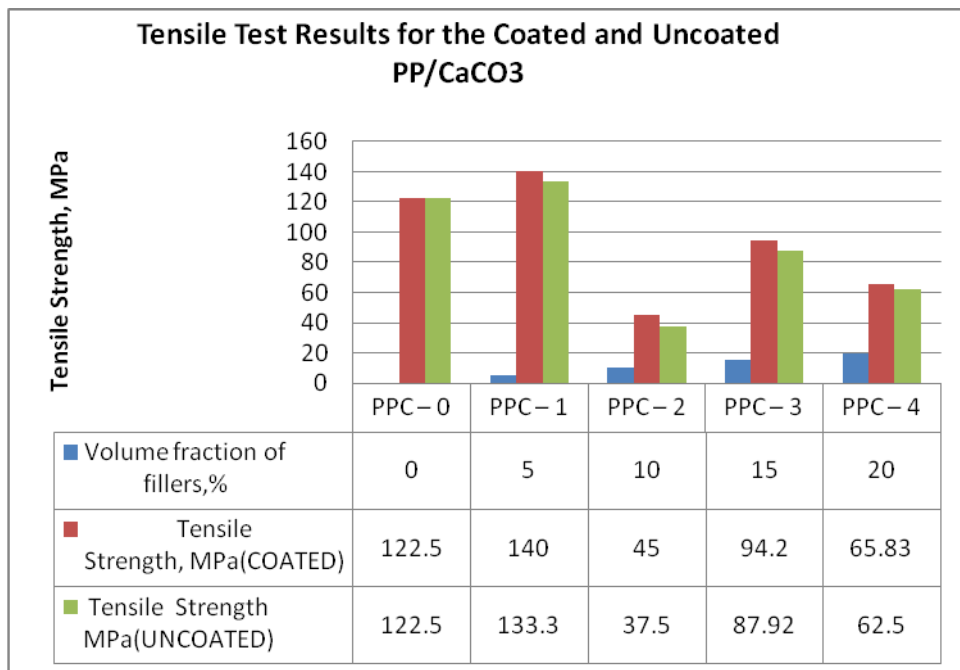


Figure 1: Tensile Test Results for the Coated and Uncoated PP/CaCO₃ nanocomposites.

The Modulus of elasticity of the nano- filled composite may be predicted using the following equations

[1, 9]:

$$E_c = E_p \phi_p + E_f \phi_f \tag{2}$$

$$E_c = \frac{E_p E_f}{E_p \phi_f + E_f \phi_p}$$

(3)

$$E_c = E_m [1 + 2.5\phi + 14.1\phi^2] \tag{4}$$

Equation (4) was developed by Guth and Gold [6] to predict the modulus of composites containing spherical fillers with filler concentrations less than 10%.

Where E_c = Modulus of elasticity (Young’s Modulus),

E_m = Modulus of Elasticity of the Polymer matrix.

ϕ = volume fractions of the fillers.

Subscripts c, f, p represent the composites, filler and polymer.

According to Hanim et al [2], equations 3 and 4 are best suited for predicting the Young’s Modulus of the Composite for concentrations up to 10% volume fractions.

Table 4: Calculated Modulus of Elasticity of PP/CaCO₃ for the coated sample

Specimen Code	Volume Fraction of Filler (%)	Equation(2) (GPa)	Equation(3) (GPa)	Equation(4) (GPa)
PPC-0	0	1.96	1.96	1.96
PPC-1	5	3.16	2.06	2.27
PPC-2	10	4.36	2.16	2.73
PPC-3	15	5.57	2.28	3.32
PPC-4	20	6.77	2.41	4.05

Equation (2) which is the Rule of Mixtures was the most inaccurate to predict the Young Modulus of the PP/CaCO₃ nanocomposites revealing that it is invalid for this composite. Equations (3) and (4) showed a good agreement up to filler contents of 5%.

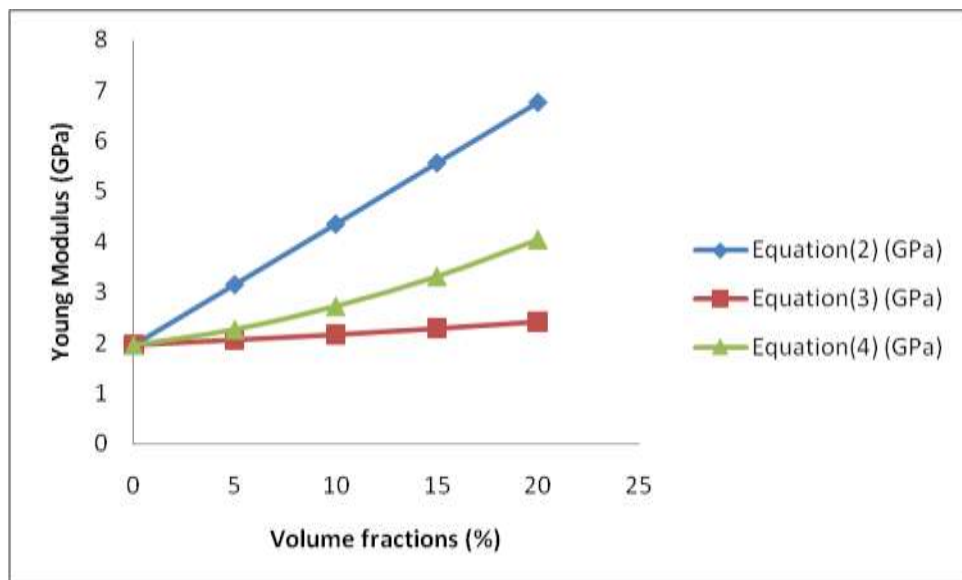


Figure 2: Young Modulus of nanocomposite as a function of filler content

CONCLUSION

Results revealed that the tensile strength increased as the volume fractions increased up to 5% (140MPa) for the coated and (133.3MPa) for the uncoated samples. The tensile strength decreased as the volume fraction increased beyond 5%-20%. This shows that the addition of CaCO₃ filler improved the tensile strength of the composites at low volume fractions but lowered the tensile strength at higher volume fractions

The Young Modulus (Modulus of Elasticity) which is a measure of stiffness or toughness of the material recorded an optimum value at 5% volume fraction from the three methods listed for predicting the Modulus of Elasticity of the composites. It is believed that the stearic acid aids in the dispersion of the fillers in the polymer matrix and also prevents the absorption of stabilizers into the filler. The strength of nano-filled polymer composite depends on the interfacial adhesion between the matrix and the filler which facilitates the transfer of a small section of stress to the filler particle during deformation.

ACKNOWLEDGEMENT

The author would like to express his thanks to Cutix PLC Newi for their kind permission to use their Laboratory to carry out this work.

REFERENCES

Chan C.M, Wu J, Li J.X, and Cheung Y.K, (2002) "Polypropylene/Calcium Carbonate Nano composites", *Polymer*, **43**, 2981-2992.

Hanim. H, et al (2008). "The Effect of Calcium carbonate Nano-filler on the mechanical properties and crystallization behavior of Polypropylene", *Malaysian Polymer Journal (MPJ)* Vol **3**, No. **12**, p 38-49.

- Di Lorenzo M. L, Enrico M. E, and Avell M (2002) "Thermal and morphological Characterization of Poly(ethylene terephthalate)/ Calcium Carbonate Nano composites", *Journal of material service*, **37**, 2351-2358.
- Manias, E Nature (2007) "Nanocomposites" nature material pp **6, 9 -11**
- Ritchie, R.O. (1993) "Mechanical Behavior of materials lecture notes" *University of California, Berkeley. Rhoads*.
- Guth E.J., (1945) "Theory of Filler Reinforcement", *Journal of Applied Physics*, 16, 20-25.
- Karger-Kosis, J. (editor) (1995), "Polypropylene: Structure, Blends and Composites". UK, Chapman & Hall, Chapter **1**, 1-4.
- Mickell P.Groover (2007) "Fundamentals of Modern manufacturing Engineering", John Wiley and Sons Inc, USA pp **182-184..**
- www.nexant.com/products/csreports/index.asp? Retrieved on 21st July 2009.
- Xie X.L, Q.X. Liu, R.K.Y.Li, X.P. Zhou, Q.X. Zhang, Z. Z. Yu and Y.Mai, (2004) "Rheological and Mechanical properties of PVC/ CaCO₃ Nanocomposites prepared by In-situ polymerization", *Polymer*, **45**,6665-6673.
- Mgbemena C.O (2010), "Evaluation of the Mechanical properties of Polypropylene/Calcium Caronate nanocomposites at various creep conditions ".*Master of Engineering thesis, Department of Mechanical Engineering, Nnamdi Azikiwe University, Awka*.