

## Modelling the Tensile Properties of HDPE Composite Materials with Poly (vinyl acetate) Coated Calcium Carbonate Filler

**Catalin CROITORU**

Transilvania University of Brasov, Romania, [c.croitoru@unitbv.ro](mailto:c.croitoru@unitbv.ro)

**Ionut Claudiu ROATA**

Transilvania University of Brasov, Romania, [ionut.roata@unitbv.ro](mailto:ionut.roata@unitbv.ro)

**Edit Roxana MOLDOVAN**

Transilvania University of Brasov, Romania, [edit.moldovan@unitbv.ro](mailto:edit.moldovan@unitbv.ro)

**Mihai Alexandru LUCA**

Transilvania University of Brasov, Romania, [luca.mihai@unitbv.ro](mailto:luca.mihai@unitbv.ro)

### Abstract

Amorphous calcium carbonate particles with average diameter of 56  $\mu\text{m}$  have been coated with poly (vinyl acetate) to improve their adhesion to a thermoplastic polymer matrix such as high-density polyethylene. The resulting composite materials, obtained by compression moulding of the coated calcium carbonate filler and polyethylene matrix at 140 °C present improved tensile strengths, in comparison with the reference material, obtained without poly (vinyl acetate) coating. The mechanical properties of the composite assembly have been modelled with Digimat-FE software, obtaining a satisfactory correlation between the experimental results and the simulated tensile strength.

### Keywords

composite materials, compression moulding, poly (vinyl acetate), mechanical strength

### 1. Introduction

High performance composite materials with polymeric matrix are ubiquitous today for many industry branches, such as construction, automotive, aeronautic, and so forth [1, 2]. Among the most frequently used materials for composite matrices are thermoplastic polymers (65.2 % of the total produced polymer composites) [3], from which polyolefins (polyethylene, polypropylene) account for 81 % of the total production [4].

Calcium carbonate (in its crystalline or amorphous forms) represents an inexpensive inorganic filler for plastic composites, having the advantage of high thermal stability, neutral colour (white), wide availability and relatively low cost [5, 6].

Due to the dissimilar nature of the plastic material (hydrophobic) and calcium carbonate filler (hydrophilic), their physical interaction is not optimal, often leading to poor mechanical performance of the assembly (delamination, debonding) [7].

The solution to obtaining optimal-bonded plastic-filler assemblies lies in the usage of various additives that can improve the interfacial adhesion between the filler and the thermoplastic polymer matrix, among which the most frequently used are fatty acids (stearic acid, oleic acid), fatty acid-derived salts (stearates, palmitates), long chain alkylsilanes and so forth [8, 9]. These are used to lower the surface tension of the inorganic phase (calcium carbonate in this case) and to optimally disperse the filler in the polymer matrix.

Often, several specialized software could be used as a rough estimate of the mechanical properties of composite materials, starting from the bottom-up engineering approach. Using of such software could be in some cases time-efficient, contributing to the optimization of production and choosing the optimum materials for fillers and matrices [10].

This paper reports the obtaining of high density polyethylene (HDPE) composites filled with 10% amorphous calcium carbonate through the compression moulding process. To enhance the interfacial

adhesion between the components, the calcium carbonate phase has been coated with poly (vinyl acetate), an inexpensive film-forming polymer.

To our knowledge there are no studies regarding the usage of this type of coated filler, in conjunction with polyethylene matrices. The mechanical properties of the composite material have been simulated with a specialized software, namely Digimat-FE.

## 2. Materials and Methods

### 2.1. Materials

High density polyethylene (HDPE) has been used as composite matrix (Sigma-Aldrich). The characteristics of the polymer are: density - 0.934 g/cm<sup>3</sup>, mass melt flow index - 3.21 g/10 min (according to ISO 1133, respectively ASTM D1238), respectively, melting temperature of 123.4 °C (determined by differential scanning calorimetry).

Amorphous calcium carbonate (CaCO<sub>3</sub>) with average particle diameter of 56 μm has been used as filler for the composite material (Sigma-Aldrich).

Poly (vinyl acetate) (PVAc) with gravimetric molecular mass M<sub>w</sub> of 100000 (Sigma-Aldrich) has been used as coating agent for the calcium carbonate as solution in toluene.

### 2.2. Composites obtaining

The calcium carbonate particles were coated with poly (vinyl acetate) according to the scheme depicted in Fig. 1. Briefly, the poly (vinyl acetate) powder has been dissolved by magnetic stirring in toluene (PVAc: toluene mass ratio of 1:4) at 80 °C under reflux. The carbonate powder has been dispersed and stirred in this PVAc solution for 1 hour, after which it has filtered, dried and de-agglomerated.

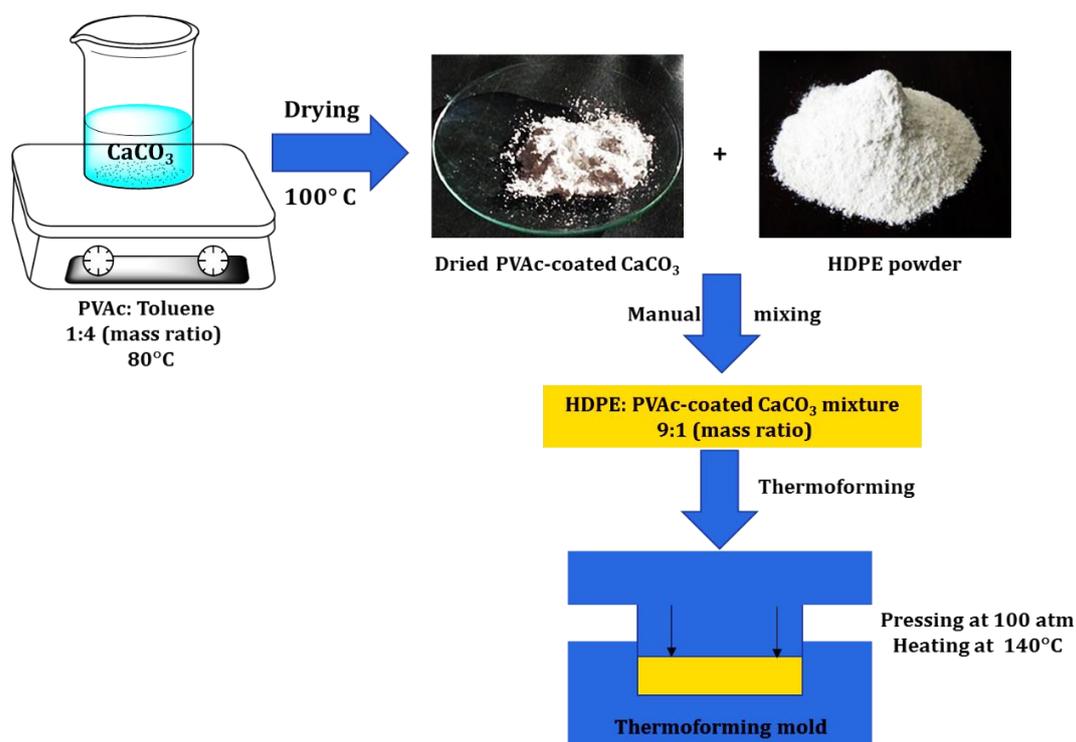


Fig. 1. Filler coating and composites obtaining procedures

The HDPE powder has been mechanically mixed with the coated calcium carbonate powder (10% filler, reported to the total amount of mixed solids), introduced in a thermoforming mould (dimensions 50×200×5 mm), pressed at 100 atm and heated at 140 °C for 1 hour, to ensure the complete melting of the polymer phase. Composites with uncoated calcium carbonate powder were obtained following the same protocol as above, and kept as reference materials.

Composite material strips with 10×100×5 mm have been cut for tensile mechanical tests. Prior to testing, all the probes have been maintained under constant relative humidity conditions (~54%) for seven days.

### 2.3. Composites characterization

For the tensile properties determining, a Zwick Roell Z010 universal testing machine has been used, with 5 mm/min traction speed (5 tests/sample, with coated filler and respectively reference).

The structure of the material has been simulated with the help of Digimat-FE version 2016 software. The parameters used for the mechanical properties simulation have been chosen as follows: for the coated filler - as constitutive law: elastic model, with isotropic elasticity and for the HDPE matrix - as constitutive law: elastoplastic model, plasticity model J2, exponential and linear isotropic hardening model. The computed tensile properties of the two components, coated filler, respectively HDPE matrix is depicted in Fig. 2a and 2b (stress is expressed in MPa).

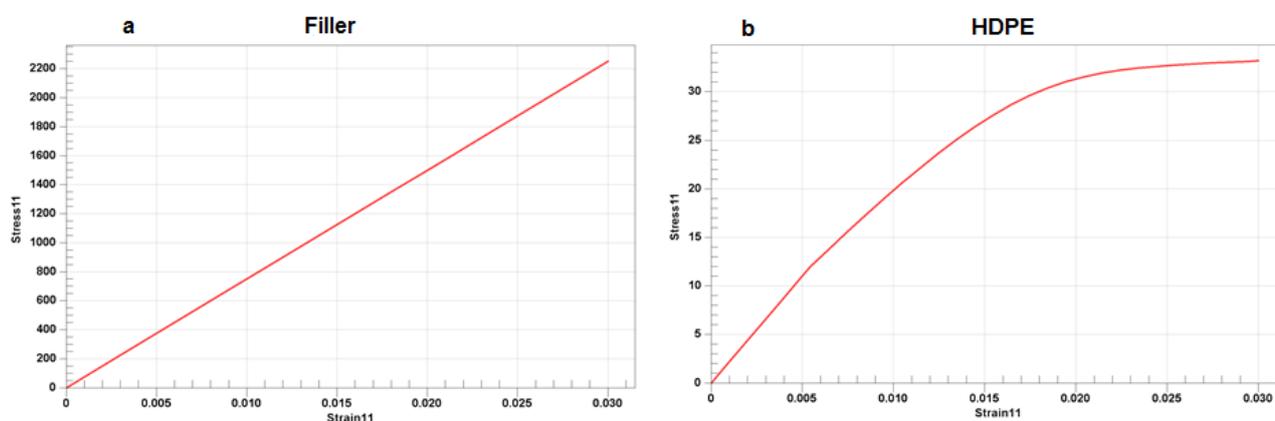


Fig. 2. Simulated stress-strain curves of a) filler and b) HDPE matrix

As filler-interface model, a perfectly bonded interface behaviour has been chosen, and the mechanical properties of the assembly were modelled by using periodic boundary conditions under conditions of uniaxial tensile loading.

### 3. Results and Discussion

The bulk of the composite has been generated according to the filler loading mentioned in section 2.2. Meshing has been performed with the non-conforming (voxel) model, with a total number of 125000 voxels, Fig. 3.

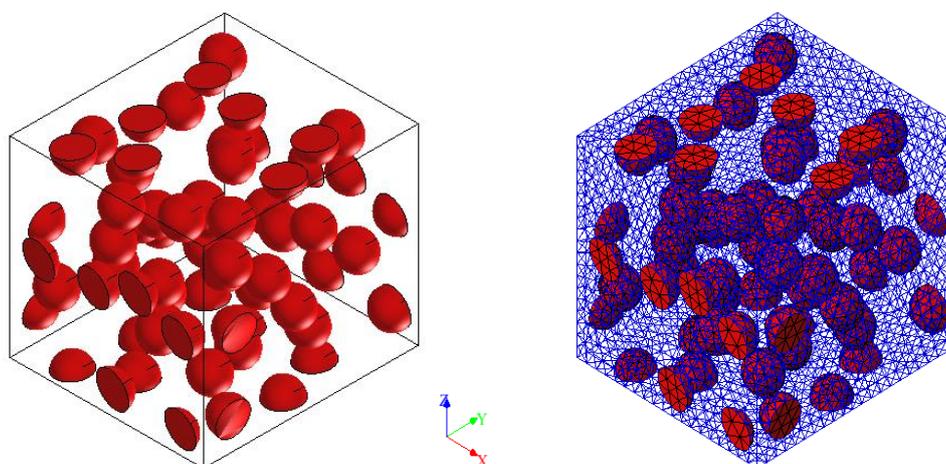


Fig. 3. Simulated filler inclusions (left) and meshing output of the composite assembly (right)

The experimental stress-strain curves for the composite with coated poly (vinyl acetate) filler and the reference material (uncoated filler) is illustrated in Fig. 4.

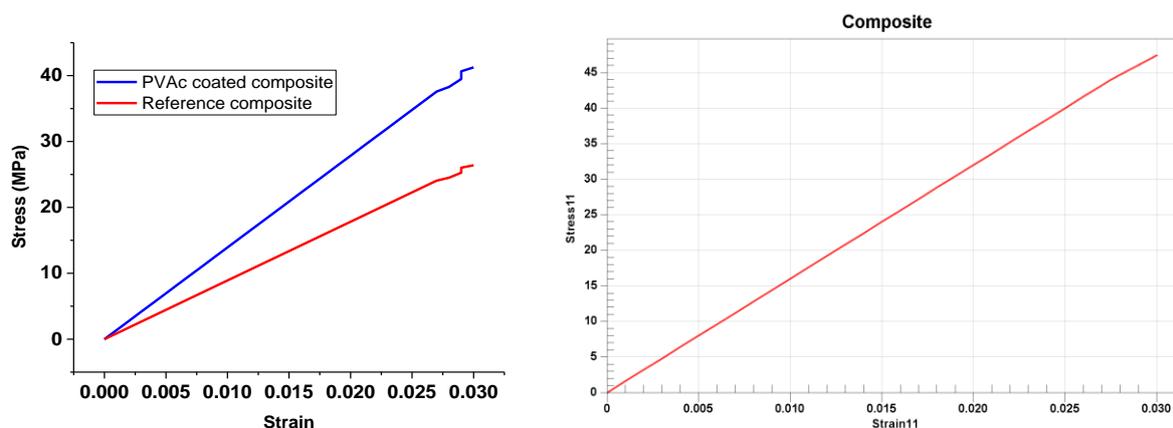


Fig. 4. Simulated filler inclusions (left) and meshing output of the composite assembly (right)

As it could be seen from Fig. 4, the coating of the filler material with poly (vinyl acetate) is beneficial. The coating improves the interfacial adhesion between the components, leading to a 20% increase in ultimate tensile strength, in comparison with the reference material (without modified filler).

The tensile stress-strain curves indicate a brittle-like behaviour for both type of materials, which is characteristic to discontinuous reinforcing agents-filled composites [3]. The ultimate tensile strength is still lower than that of pure HDPE (cca. 55-70 MPa [4], depending on the polymer characteristics and processing).

From Fig. 4 it could also be observed that the simulated stress-strain curve for the composite with coated filler resembles the experimental one, the difference being the 5% higher ultimate tensile strength. This difference could be accounted for the presence of several macro-defects in the thermoformed composite (such as porosity), unavoidable for compression moulding.

Following the mechanical properties simulation, it could be observed from Fig. 5 that the zone of maximum plasticity occurs in the (011) direction, where the presence of filler is minimal. This could be due to the crystallization inducing effect of the filler for the HDPE polymer phase, as reported also in other research. A higher crystalline to amorphous fraction in the polymer phase corresponds to a more rigid behaviour of the matrix. The values corresponding to the von Mises stress are uniformly distributed throughout the material.

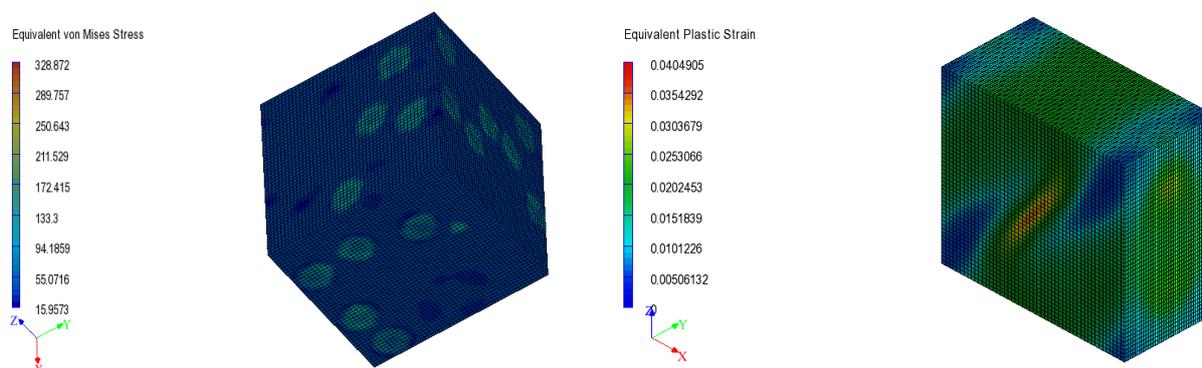


Fig. 5. Simulated von Mises stress (left) and equivalent plastic strain (right)

#### 4. Conclusions

Poly (vinyl acetate) has been used in this work to obtain a continuous coating on amorphous calcium carbonate particles to improve their bondability to a thermoplastic polymer matrix such as high-density polyethylene.

The reported procedure has led to the improvement in the tensile properties of the composite with up to 20%, reported to the reference material.

It has been demonstrated that the elastic approach for the filler inclusion (typically rigid in its uncoated form) generates a simulated output in Digimat-FE software which is able to successfully comply with the experimental tensile stress-strain curve.

Further studies are needed, to assess the tensile properties of material with higher filler to matrix ratios (20...50%) and to select other suitable cost-efficient polymers or small-molecular additives that could further improve the behaviour of the composite assembly.

### Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-0173.

### References

1. Elleithy R.H., Ali I., Ali M.A., Al-Zahrani S.M. (2010): *High density polyethylene/micro calcium carbonate composites: A study of the morphological, thermal, and viscoelastic properties*. Journal of Applied Polymer Science, ISSN 1097-4628, Vol. 117, is. 4, pp. 2413-2421, <https://doi.org/10.1002/app.32142>
2. Teixeira S.C.S., Moreira M.M., Lima A.P., Santos L.S., da Rocha B.M., de Lima E.S., da Costa R.A.A.F., da Silva, A.L.N., Rocha M.C.G., Coutinho F.M.B. (2006): *Composites of high density polyethylene and different grades of calcium carbonate: Mechanical, rheological, thermal, and morphological properties*. Journal of Applied Polymer Science, ISSN 1097-4628, Vol. 101, is. 4, pp. 2559-2564, <https://doi.org/10.1002/app.23920>
3. Chawla K.K. (1998): *Polymer Matrix Composites*. In: Chawla K.K.: *Composite Materials*. ISBN 978-1-4419-3124-5, pp. 133-163, Springer, New York, U.S.A., <https://link.springer.com/book/10.1007/978-1-4757-2966-5>
4. Wang R., Zheng S., Zheng Y.G. (2011): *Polymer Matrix Composites and Technology*. Elsevier, ISBN 978-0-85709-221-2, eISBN 9780857092229
5. Wang W.Y., Zeng X.F., Wang G.Q., Chen J.F. (2007): *Preparation and characterization of calcium carbonate/low-density-polyethylene nanocomposites*. Journal of Applied Polymer Science, ISSN 1097-4628, Vol. 106, is. 3, pp. 1932-1938, <https://doi.org/10.1002/app.26833>
6. Azizi H., Faghihi J. (2009): *An investigation on the mechanical and dynamic rheological properties of single and hybrid filler/polypropylene composites based on talc and calcium carbonate*. Polymer Composites, ISSN 1548-0569, Vol. 30, is. 12, pp. 1743-1748, <https://doi.org/10.1002/pc.20685>
7. Leong Y.W., Abu Bakar M.B., Mohd. Ishak Z.A., Ariffin A. (2005): *Effects of filler treatments on the mechanical, flow, thermal, and morphological properties of talc and calcium carbonate filled polypropylene hybrid composites*. Journal of Applied Polymer Science, ISSN 1097-4628, Vol. 98, is. 1, p. 413-426, <https://doi.org/10.1002/app.21507>
8. Ihli J., Kim Y.Y., Noel E.H., Meldrum F.C. (2013): *The Effect of Additives on Amorphous Calcium Carbonate (ACC): Behavior in Solution and the Solid State*. Advanced Functional Materials, ISSN 1616-3028, Vol. 23, is. 12, pp. 1575-1585, <https://doi.org/10.1002/adfm.201201805>
9. Cantaert B., Kim Y.Y., Ludwig H., Nudelman F., Sommerdijk N.A.J.M., Meldrum F.C. (2012): *Think Positive: Phase Separation Enables a Positively Charged Additive to Induce Dramatic Changes in Calcium Carbonate Morphology*. Advanced Functional Materials, ISSN 1616-3028, Vol. 22, is. 5, pp. 907-915, <https://doi.org/10.1002/adfm.201102385>
10. Doghri I., Ouaar A. (2003): *Homogenization of two-phase elasto-plastic composite materials and structures: Study of tangent operators, cyclic plasticity and numerical algorithms*. International Journal of Solids and Structures, ISSN 0020-7683, Vol. 40, is. 7, pp. 1681-1712, [https://doi.org/10.1016/S0020-7683\(03\)00013-1](https://doi.org/10.1016/S0020-7683(03)00013-1)