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STATE OF THE ART IN CALCITE AND POLYOLEFINS RECYCLING

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Abstract: *The article outlines several aspects regarding the efficient recycling of polyolefin wastes and crystalline calcium carbonate-based second raw materials (calcite) in order to obtain composite materials with improved properties. Several bottlenecks regarding the compatibility of the polymer with the inorganic filler are addressed, with detailing the up-to-date available solutions, as well as several other issues, related to calcium carbonate particles aggregation and abrasivity diminishing in order to obtain composites with improved mechanical properties and stability. The need for new ecologic and chemically stable compatibilising agents defines the research in this domain still an open and permanently improving issue.*

Key words: *polyolefins, calcite, polymer wastes, recycling.*

1. State of the Art

Owing to an increased use of polyolefins and other plastics and to a more increasing environmental and liability awareness, especially regarding packaging, automotive and other related industry branch, much attention is paid nowadays to reuse, recover and dispose of these types of materials [11], [12], [18].

Polyolefins (among which polyethylene and polypropylene are the most frequent) are used in many different products with varying demand of durability [19].

Since the lifetime of a product depends on the usage and of the stabilising system used, it may be noted that it is possible to stabilise polyolefins so that they maintain their mechanical properties for a large period of time.

An unmodified polyolefin product takes many years to degrade in the natural environment, thus contributing to waste build-up [6], [11].

In order to handle polyolefin waste, several alternatives are available, such as depositing, incineration, recycling and composting.

At European level, the EU28 directive states that the majority of the wastes should be recycled by other means than traditional depositing (60%).

However, according to the *Consultic* database (Figure 1), for the large majority of the European countries, the waste depositing rate is significantly higher than the recommended value.

In Romania, although progress has been made in this direction, the majority of polyolefin wastes (>60%) are handled through depositing in landfills.

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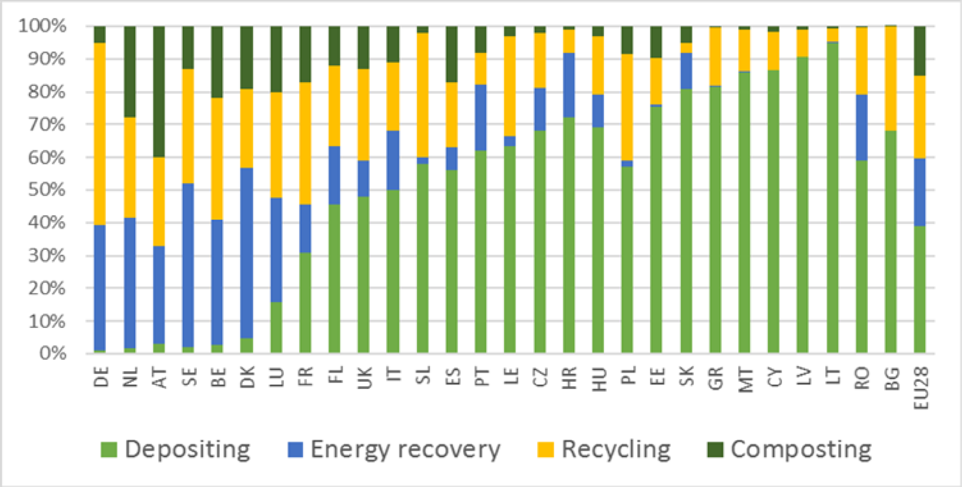

Fig. 1. *Polyolefin waste disposal methods (2015)* [19]

While generally, energetic recovery (through incineration) possesses some environmental risks, due to the emission of toxic gasses and/or volatile organic compounds, and nowadays has a rather limited economical feasibility, recycling is an increasingly attractive waste handling method [8].

As for all thermoplastics, polyolefin scrap and well defined waste, such as heavy duty film, drums, containers etc., can be mechanically recycled into new applications [1-5].

In Romania, mechanical recycling through extruding, granulating and injection of the plastic waste is among the most frequently used recycling process.

The recyclability depends more on the application and the use of the product than on the polymer [19].

Recycling normally requires shredding, and washing operations, while the recycled material should generally be used in non-critical (e.g. non-food) applications.

Non-hydrated calcium carbonate in crystalline form (calcite) constitutes a base material, of metamorphic or sedimentary origins, frequently used in the construction industry, either as such (marble) or as an admixture with other types of silicate-based minerals (as in the composition of cement pastes and clinkers) [2], [10].

Calcite mining and process industry represent one of the most promising business areas of the mining sector, with a mean growth in the world production of approximately 6% per year in the 2005-2015 periods. The international trading is approximately US$ 6 billion per year and around US$ 13 billion, taking into account the tools, equipment, and so forth [7], [10].

Taking into account that generally, only about 30% of calcite material is effectively used, the rest being discarded as chips, dust or slurry in the cutting, polishing, processing and grinding processes, with detrimental effect on the population health, flora and fauna, new efficient ways of calcite secondary raw material utilization are needed. Nowadays, only about 40% of the total amount of calcite wastes (100 billion tons/year) is being efficiently recycled, by their inclusion in cementitious materials, bricks or as filler in ceramic or polymer matrix composites [7].

Calcium carbonate is the fourth most frequently employed category of filler used for the production of thermoplastic matrix composites, especially polyolefin-based (polyethylene and polypropylene), after talc, silica and montmorillonite. The addition of calcite in the polyolefin (PO) matrix leads, in principle, to a diminishing of the final cost of the material and to the improvement of its mechanical properties (rigidity, hardness, impact resistance and flexural resistance), and could constitute an effective method to an efficient valorification of both polyolefin and calcite wastes [12-15].

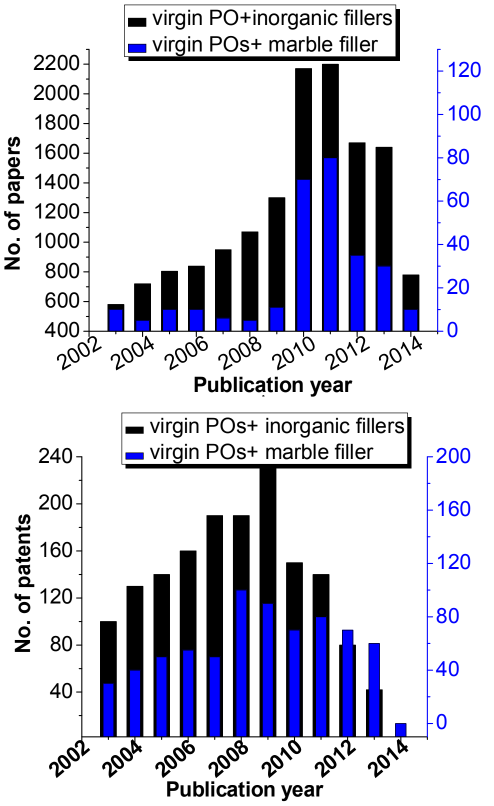

Fig. 2. *Number of publications dynamics in the domain of PO composites and inorganic fillers (10 years' span)*

The majority of the studies from the reference literature have indicated the use of amorphous calcium carbonate as filler for PO composites, while crystalline calcium carbonate (such as that resulted as waste from marble processing industry) has been used on a lower extent in obtaining composites with virgin PO matrix, as it can be seen from the dynamics of the number of publications in the domain, on a 10 years' span (Figure 2, source: Scopus database).

By analyzing the reference literature, it could be observed that there are few studies concerning the obtaining of composites with recycled polyolefin matrix and crystalline marble powder. Due to the recycled polyolefins (POw) lower both molecular mass and crystallinity, these materials could be actually more compatible with marble, in comparison to the virgin polyolefins. Using marble as filler presents some elements of difficulty. Firstly, the limited compatibility of the crystalline filler with the thermoplastic polymer matrix, as well as its tendency to agglomerate leads to the obtaining of brittle and low-wear resistance composite materials. Secondly, a high dispersion of the crystalline inorganic filler in the molten polymer is necessary.

Calcite powder is highly abrasive and determines the wear of the raw-material processing equipment [12], [13]. In order to limit the abrasivity of the calcite powder, the particles are ground at a diameter smaller than 5 μm and are treated at the surface with tensioactive compounds, in order to improve their dispersion and their compatibility with the thermoplastic polymeric matrix [14], [15].

Traditionally, stearic acid, calcium stearates, fluoro-alkoxysilanes or amino-alkoxysilanes are added in a weight ratio of 5%, reported to the calcite [12]. Recent studies employ the use of nano-sized calcite particles of 40-50 nm diameter and additives in a weight ratio of 8% reported to the calcite [15], [16]. Table 1 highlights some recent research in the domain of calcite and polyolefin composites obtaining, in terms of matrix filler and additives characteristics and ratios, as well as of the operational parameters used.

Table 1

Operational parameters for calcite-PO composites obtaining (reference literature study)

Matrix characteristics	**Filler characteristics**	**Compatibiliser**	**Operational parameters**	**References**
PP, $\rho = 0.9$ g/cm^3; MFI = 11 g/10 min at 190 °C	Marble dust; $d_{ap} = 2.7\text{-}2.95$ g/cm^3, 25% ratio reported to PP	Sodium palmitate at 1.3 and 5% loading reported to the filler	Twin screw extruder, $v_{mix} = 50$ rpm; $t_{mix} = 25$ min; $T_{mix} = 200$ °C	[13]
PP homopolymer, F41 type	Marble dust, 0-10% ratio reported to PP	Oleic acid at 7% loading reported to the filler	Twin screw extruder, $v_{mix} = 60$ rpm; $t_{mix} = 25$ min; $T_{mix} = 180\text{-}240$ °C	[3]
PP, $\rho = 0.91$ g/cm^3; MFI = 2.5 g/10 min at 230 °C	Marble dust, 20% ratio reported to PP	Stearic acid as coating agent for marble (8%) and p-tertbutyl aluminium benzoate	Twin screw extruder, $v_{mix} = 60$ rpm; $t_{mix} = 15$ min; $T_{mix} = 180\text{-}200$ °C	[4]
PP homopolymer F401 type, propylene-ethylene copolymer K8003 type	Marble dust, 10-15% ratio reported to PP	γ-aminopropyl-triethoxysilane 25% in acetone	Twin screw extruder, $v_{mix} = 140$ rpm; $t_{mix} = 45$ min; $T_{mix} = 180\text{-}200$ °C	[15]
PP block-copolymer, $\rho = 0.91$ g/cm^3; MFI = 2.16 g/10 min at 230 °C	Marble dust, 5-15% ratio reported to PP	Maleic anhydride-grafted PP, X1343 type, 2-4% loading reported to the matrix	Twin screw extruder, $v_{mix} = 200$ rpm; $t_{mix} = 45$ min; $T_{mix} = 230$ °C	[14]
PP block-copolymer, $\rho = 0.91$ g/cm^3; MFI = 2.22g/10 min at 230 °C	Marble dust, 25-35% ratio reported to PP	γ-aminopropyl-fluoroethoxysilane 15% in toluene	Twin screw extruder, $v_{mix} = 180$ rpm; $t_{mix} = 35$ min; $T_{mix} = 220$ °C	[15]
PP homopolymer F401 type	Marble dust; $D = 20$ µm at 10% ratio reported to PP	Calcium neoalkoxyzirconate (NZ12L)	Twin screw extruder, $v_{mix} = 250$ rpm; $t_{mix} = 35$ min; $T_{mix} = 200$ °C	[12]

where: MFI = melt flow index of polymer; D = average diameter of calcite particles; d_{ap} = apparent density of calcite powder; v_{mix} = mixing speed of PO-calcite receipt; t_{mix} = mixing time of PO-calcite receipt; T_{mix}= mixing temperature of PO-calcite receipt

As it can be seen from Table 1, the majority of the studies cited in the reference literature make use of fatty acids salts as coating agents and compatibiliser between calcite and polyolefins. Several authors reported however that calcium carbonate actually catalyses the decomposition of the fatty acid at temperatures above 150 °C, thus leading to composites with poor mechanical properties [17].

Alkoxysilanes and fluoroalkoxysilanes are generally regarded as efficient compatibiliser between PO and calcite, but they have the disadvantage of being economically inefficient due to their high price, and also possess an environmental risk, due to their dissolution in volatile organic solvents [15], [16].

Further research is still needed in order to find an efficient and ecologic compatibiliser between PO and calcite, with low specific consumption, optimum interfacial adhesion between the components and improved chemical and thermal stability.

2. Conclusions

The increasing worldwide demand for plastic products and crystalline inorganic raw material-based construction materials has led to the constant build-up of wastes in the environment, with detrimental effects on the biosphere.

Even if recent regulations enforce more efficient disposal methods for wastes, still a lot of effort has to be made in the domain of polyolefins and calcite wastes recycling, through obtaining composite materials with calcite as filler.

Several bottlenecks are to be addressed, such as the limited compatibility between the polymer and the filler, due to their profound dissimilar chemical nature, the high tendency of calcite powder to agglomerate, coupled with its high abrasivity, which leads to an increased equipment wear and specific energy consumption.

An ecologic and efficient compatibiliser, with high thermal and chemical stability could lead to the obtaining of high-value materials, with optimal mechanical properties and improved stability, thus leading to an efficient waste valorification technique and a sustainable society development.

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