RECYCLING OF PHENOLIC MOLDING COMPOUNDS AS FILLER IN PARTICULATE COMPOSITES

Fabien Bernardeau[1], Didier Perrin[1], Anne-Sophie Caro[1], Jean-Charles Benezet[1] and Patrick Ienny[1]

[1]C2MA, Ecole des Mines d'Alès, 6 avenue de Clavières, 30319 ALES Cedex
Email: Patrick.ienny@mines-ales.fr, Web Page: http://c2ma.mines-ales.fr/

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Abstract

A new recycling method for phenolic molding compound (PMC), a thermoset plastic, is developed in this work. It consists in using the comminuted molding compound as filler in a thermoplastic in order to improve its mechanical properties. The effect of several important parameters of these particulates composites on the mechanical properties have been studied, such as the particle size distribution (PSD) of the filler and the loading percentage. It appears that PMC filled polypropylene has about the same tensile properties has CaCO3 filled polypropylene. They are almost independent of the PSD of the filler. However, the PSD has a deep influence on impact strength, which increases with decreasing size of the filler. No adhesion is observed between the neat filler and the matrix. When an adhesion promoter is added, an increase in mechanical properties is observed. It can be correlated with a decrease of the volumetric strain, related to less damage and cavitation in the material.

1. Introduction

Nowadays, recycling takes an important place in our society. Due to the increasing amount of waste produced every year, important research and industrial effort are dedicated to the development of technic to valorize waste materials. Amongst these materials, plastic are particularly problematic. While most of them are technologically recyclable (thermoplastic material), some are not (thermoset and rubber material) because of their reticulate structure. Direct mechanical recycling is therefore not possible for those.

Phenolic molding compounds (also known as BakeliteTM) are a particular kind of thermoset material based on phenol and formaldehyde condensation. A few research papers and patents describe valorization schemes for these materials, based on thermal recycling [1]–[4], chemical recycling [5]–[7] and mechanical recycling [8]–[15]. However, due to their complexity and the low-value of retrieved products, their industrial viability seems questionable.

A mechanical recycling option is developed in this work, based on the use of comminuted PMC as filler in a thermoplastic matrix. Indeed, polymers are often reinforced with mineral fillers in order to improve their mechanical properties. Due to their high rigidity in comparison with most common thermoplastics, we can expect such reinforcing action from PMC fillers. In this kind of particulate composite, several parameters are known to have a major impact on the material properties, such as loading content, particle size distribution of the filler, dispersion or adhesion at the filler/matrix interface [16]. In order to understand the role of the PMC as filler and optimize the properties of the composite, they have been studied thoroughly in this work.

In particular, filler/matrix adhesion plays a major role in the mechanical performance of the composite. Several methods have been proposed to assess the strength of adhesion, and in particular the stress at which debonding between filler and matrix occurs. These methods are in-situ tensile experiments, acoustic emission and volume strain measurements [17]. In this work, the effect of an

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anhydride maleic grafted polypropylene coupling agent on the adhesion is evaluated by volumetric strain measurements.

2. Materials and method

2.1. Materials

Phenolic molding compounds (PMC) used in this study was recovered from WEEE casing. They were identified via FTIR analysis and manually sorted from other plastic parts. Further analysis showed that all these PMC samples shared the same material composition, corresponding to a normalized phenolic molding compound composition (PF2A1 in ISO 800 or PF WD40MD5 in ISO 14526-3). This corresponds to a phenol-formaldehyde resin filled with about 40w% of wood floor and less than 5w% of mineral (mainly calcium oxide and silica).

In order to prepare the PMC waste, all contaminant (metal insert, paper) were removed from the parts. A pre-crushing was done manually in order to reduce the pieces to an appropriate size (<5cm) for further comminution. The pre-crushed parts were washed two times in water in order to remove dust and remaining contaminant, and then they were allowed to dry for 24h at 80°C.

A Polypropylene 576P was kindly provided by Sabic. It is a PP homopolymer with narrow molecular weight distribution and a MFI of 19 (230°C, 2.16kg). A Polypropylene grafted with maleic anhydride (PP-g-MA) Orevac CA100 from Arkema was also used in this study. In order to compare the properties of the PMC filled composites with commercially available fillers, a calcium carbonate Piketty (d_{50} = 6 µm) and a talc Luzenac A30 (d_{50} = 18 µm) were used.

2.2. PMC filler preparation

The PMC pre-crushed pieces were comminuted and prepared in a three-step process. The first step consisted in a coarse grinding, the second in a micronization, and the third in a sieving in order to tailor the PSD. 4 particles size distribution were produced for this study. They were characterized with a Beckman Coulter LS 13 320 laser diffraction particle size analyzer equipped with a Tornado Dry Powder System (Fig. 1).

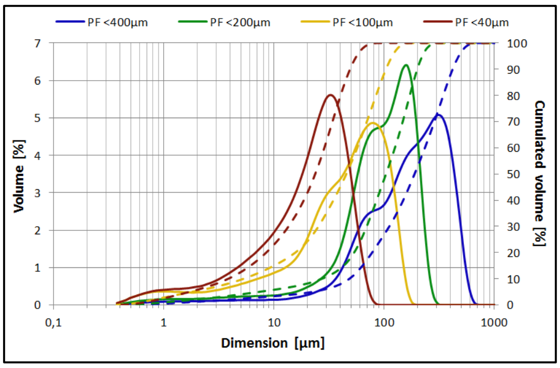

Figure 1. Particles size distributions of the phenolic molding compound fillers used in this study.

Table 1. Particle sizes of the PMC fillers.

Sieving mesh	d10	d25	d50	d75	d90
400 µm	48	93	188	313	418
200 µm	27	61	104	158	200
100 µm	5,7	23	50	84	114
40 µm	3,8	11	24	37	49

Median particles diameters ranging from 24 µm to 188 µm were obtained (Table 1).

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2.3. Composite compounding and injection molding

Particulates composite were prepared by extrusion. All materials (thermoplastic matrix, micronized phenolic molding compounds, additives) were dried at 80°C for 24h in an air circulating oven prior to compounding. Loading percentage of 10%, 20% and 40% (by weight) were achieved (respectively 6.7%, 13.9% and 30.1% by volume). A Clextral BC21 co-rotating twin screw extruder was used. For PP materials, temperature was set to 220°C at the primary feeding port, and to 210°C at the extrusion head. A rotation speed of 250rpm was used. An overall extrusion rate of 5kg/h was set for all composite. PMC fillers were fed in a port located in the middle of the barrel. PP-g-MA was dry-mixed with polypropylene before processing. The extruded material was cooled in a water bath and granulated.

After compounding, extruded materials were dried at 80°C during 24h. The pellets were then injection molded with a Krauss Maffei KM50-T180CX. Dog bone samples (ISO 1A according to ISO 527-2) were injected for mechanical testing.

2.4. Mechanical testing

Mechanical tests were performed on ISO 1A samples. All measurements were carried out at 23°C ± 2°C and 50% ± 5%. Tensile tests were carried out according to ISO 527 with a Zwick Z010 equipped with a 2.5 kN load cell and a Clip-on extensometer. A pre-load of 0.8MPa was applied to samples priori to testing. The elastic modulus was measured at a 1 mm/min crosshead speed until a 0.3% deformation was achieved (measured with the Clip-on extensometer). Ultimate properties were then measured at a crosshead speed of 50 mm/min. 5 samples were tested for each formulation. Impact strength was measured with an impact tester Instron CEAST 9340 according to ISO 179. 80mm long bar were sawn in the central part of ISO 1A samples (10 for each formulation). Samples were tested un-notched in standing position.

In order to measure the volumetric strain during tensile test, an optical extensometer associated with a Charge-Coupled-Device (CCD) camera was used. The image processing by Digital Image Correlation (DIC) technique is applied to the image sequences and led to the evolution of the in-plane strain components. As image signature, a random speckle pattern of paint blobs was created on the surface of the ISO 1A sample. If we assume transverse isotropy for the material, we can deduce that both transverse strains are equal. It yields to the calculation of the logarithmic volumetric strain from the plane strain tensor. The dependence of the volumetric strain to the axial strain rate also being studied, tensile tests were performed at 5, 50 and 250 mm/min.

3. Results and discussion

3.1. Tensile and impact tests of neat PMC/PP composites

An increase of the elastic modulus is observed with increasing loading percentage of the filler (Fig. 2). This behavior is expected, as the phenolic molding compound has a higher elastic modulus (7.8 GPa) than the PP matrix. Interestingly, unlike some proposed model for particle filled polymers, the relationship between modulus and mass fraction is almost linear.

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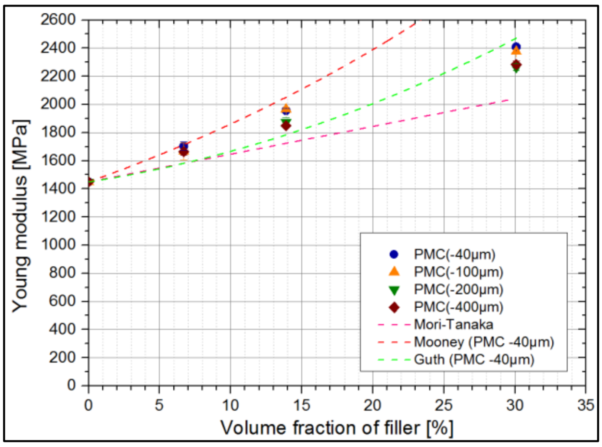

Figure 2. Young modulus of PMC filled PP for different loading percentage and particle size distribution of the filler

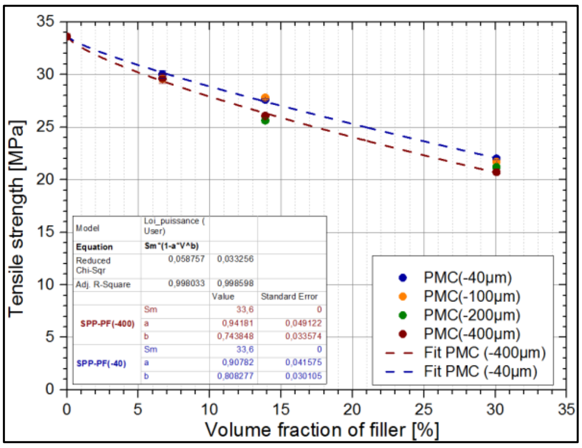

Figure 3. Tensile strength of PMC filled PP for different loading percentage and particle size distribution of the filler

It can be seen that, while the same modulus is measured at 6.7% volume fraction for all filler PSD, the modulus at 13.9 $\%_{\mathrm{volume}}$ and 30.1 $\%_{\mathrm{volume}}$ is slightly higher for the two smaller particle size distributions, i.e. d_{50} = 50µm and d_{50} = 24µm.

Most models fail to fit the observed increase of Young modulus. The Mooney model (Eq. 1), well adapted for rigid mineral filler [18], predicts higher modulus, especially at high filler content. This might indicate that the PMC filler cannot be considered to be infinitely more rigid than the matrix. The Mori-Tanaka model for spherical particles, which takes in account mechanical properties of filler and matrix, predicts lower modules than those observed experimentally. The best fit is obtained with Guth model (Eq. 2) for non-spherical fillers [18], associated with a shape factor of 1.6. Measured shape factor (obtained by image analysis) for PMC range from 1.4 to 1.5, which is close.

$$E_C = E_M \exp \frac{2.5\,V_f}{1-SV_f} \qquad (1)$$

$$E_C = E_M(1 + 0.67pV_f + 1.62p^2V_f^2) \qquad (2)$$

$$\sigma_C = \sigma_M\,(1 - a\,V_f^{\,b}) \qquad (3)$$

With E_C the composite modulus, E_M the matrix modulus (EM = 1450MPa), V_f the volume fraction of filler, S the crowding factor, p the shape factor, σC and σM the tensile strength of composite and matrix, a a parameter related to the interfacial adhesion, and b a parameter related to the mode of fracture.

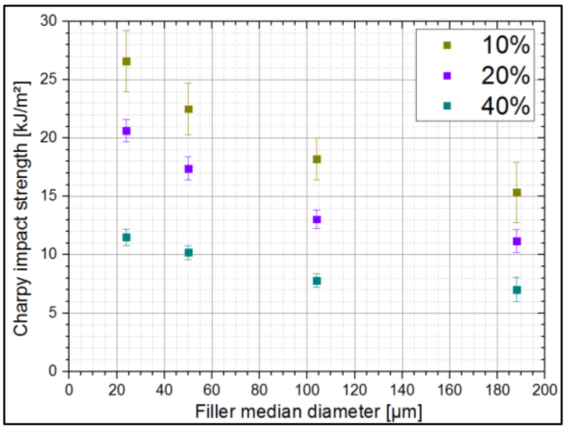

Figure 4. Charpy impact strength of PMC filled PP for different loading percentage and particle size distribution of the filler

The tensile strength decreases with increasing filler content (Fig. 3), which is again an expected behavior for particulate composites with little interfacial adhesion. As for the Young modulus, the tensile strength is almost the same at 6.7% volume fraction for all filler's PSD. For 13.9% $_{\mathrm{volume}}$, a higher tensile strength is measured for PSD with d_{50} = 50µm and d_{50} = 24µm.

Power law (Eq. 3) have been used to fit the tensile strength behavior [19]. Two set of parameters are

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found for the smaller and bigger PSD. Interestingly, the a parameter, which generally depends on the adhesion in the composite, is equal to 1.21 when there is no adhesion and decreases with increasing adhesion. It is found to be equal to 0.91 and 0.94. That might indicates that some adhesion exists at the interface.

A different behavior is observed with Charpy impact test (Fig. 4). First, the impact strength of all composites is lower than for neat PP (a_{cu} = 92 ± 12 kJ/m²). It decreases with loading content. However, the effect of particle size distribution is more obvious than in tensile test. It can be seen that the impact strength increases greatly as the particles size decreases. For example, at 6.7%$_{volume}$ loading, the impact strength of the composite filled with d_{50} = 24 µm particles is 74 % higher than the one filled with d_{50} = 188 µm particles. This effect is less pronounced at 30.1% loading.
Surface of rupture of samples after tensile test were observed with ESEM. Two areas can typically be sorted on these surfaces: a localized area with a high level of polymer matrix deformation, where cavitation occurred, probably initiating the breaking of the sample, and a larger area with little localized deformation, where the break propagated in a brittle way (Fig. 5).

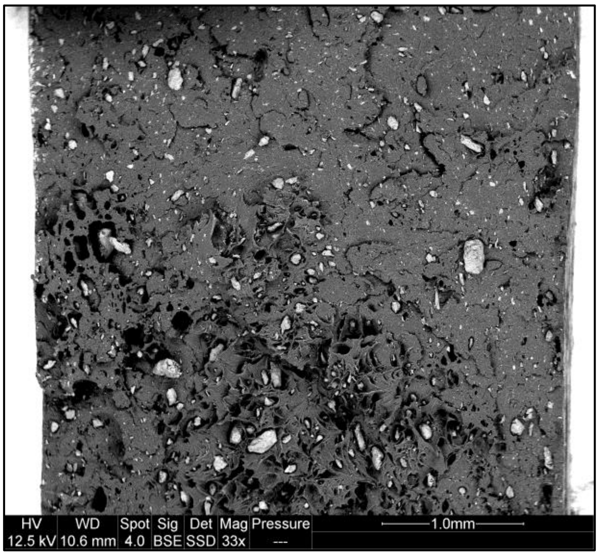

Figure 5. ESEM image of the surface of a sample loaded with 6.7% of PMC at d_{50} = 50 µm after tensile test (left-down corner: area of localized yielding)

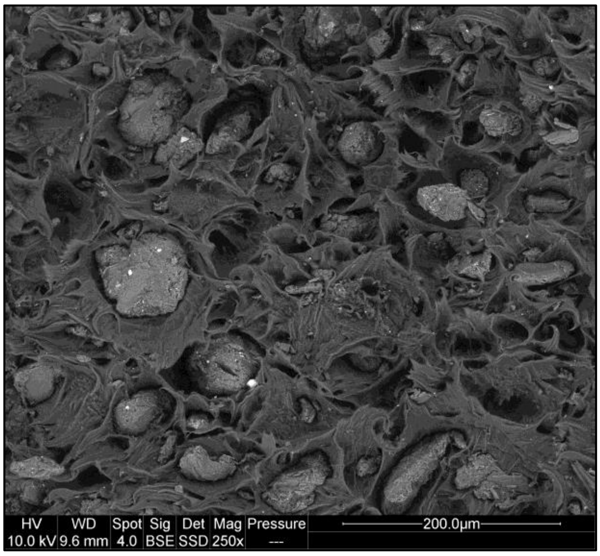

Figure 6. ESEM image of the surface of a sample loaded with 13.9% of PMC at d_{50} = 50 µm after tensile test

Obviously, very little or no adhesion exists between the PP matrix and the phenolic fillers (Fig. 6). This can be explained by the difference in polarity of these two polymers, the PP being an apolar plastic, and the phenolic resin being slightly more polar, because of phenolic hydroxyl for example. Some pictures show that some mechanical adhesion might occur, due to the roughness of the surface of the filler.

The low adhesion could explain the loss of mechanical properties observed in these composites. In tensile test, the main phenomena is the decrease of the tensile strength, which is mostly dictated by the filler loading percentage, and is very little affected by the size of the filler. This decrease of the tensile strength in particulate composite is generally attributed to the decrease of the load bearing section due to the formation of cavity around the fillers.

On the other hand, the effect of the size of the particles is obvious on impact test results. The main difference between these two mechanical tests, apart from the geometry, is the material deformation speed. At low speed (tensile test), the effect of particles size seems to be hidden by the plasticity of the

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matrix, which accommodate the cavity created by the fillers through deformation mechanism. At higher speed (impact test), the ductility of the matrix is lowered, and its behavior probably becomes more brittle. Therefore it cannot accommodate the cavity created by the stress concentration around fillers.

3.2. Effect of PP-g-MA on the mechanical properties

In order to improve the adhesion between the filler and the matrix, an adhesion promoter (PP-g-MA) was added to the composite. It is a polypropylene grafted with anhydride maleic, a polar component. 3% by weight were added to composites with $10\%_{weight}$ and $20\%_{weight}$ of PMC and with two particle size distributions (< 40µm and < 100µm). PP-g-MA addition leads to an increase of both tensile strength and Charpy impact strength (Fig. 7 and Fig. 8).

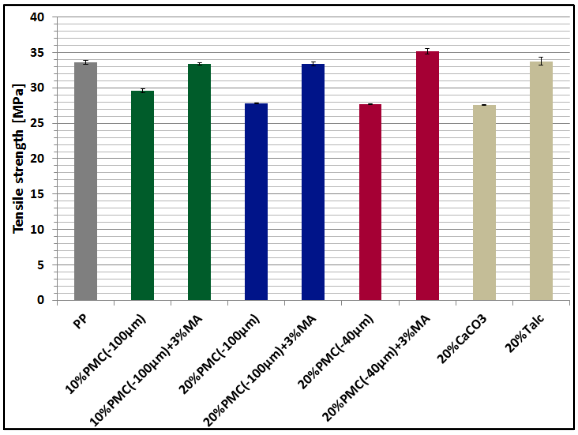

Figure 7. Tensile strength with and without PP-g-MA

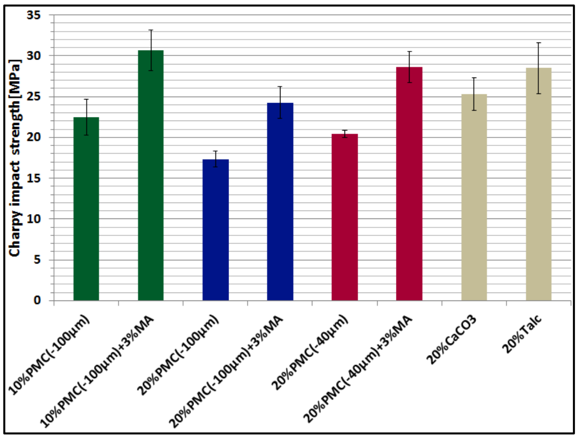

Figure 8. Charpy impact strength with and without PP-g-MA

In tensile mode, the modulus is not modified by the addition of PP-g-MA (for $10\%_{weight}$ PMC (-100µm), E=1666±59 MPa without PP-g-MA and E=1688±36 MPa with; for $20\%_{weight}$ PMC (-100µm), E=1966±15 MPa without PP-g-MA and E=1897±38 MPa with). However, it increases the tensile strength almost to the same value (or higher) as the PP for all formulations. This could be associated with either a better adhesion between the filler and matrix or a more dissipative behavior of the matrix when PP-g-MA is added, leading to less cavitation and less load bearing section reduction. Impact strength also increases with PP-g-MA. Unlike tensile strength, there seems to be a dependence of amount of PP-g-MA added on the impact strength.

The PMC filled composites were compared with $CaCO_3$ and Talc filled composites. With no PP-g-MA added, the tensile properties (modulus and tensile strength) are very similar to a $CaCO_3$ filler PP. The PMC therefor plays an inert filler role. When PP-g-MA is added, similar tensile and impact properties as Talc filled PP are observed. In this case, a semi-reinforcing role is ensured by the PMC.

3.3. Volume strain measurement

In order to better understand the effect of PP-g-MA, volume strain was measured during tensile test by DIC. This technique has been proposed to study the mechanism of deformation of composite materials [20]. Indeed, while at small strain induced by low stress, only hydrostatic stress results in a volume increase (volumetric strain associated with the elastic response), at higher strain, other mechanism of deformation can occur, such as cavitation, leading to higher volume increase. In the case of filled polymers, fillers can act as nuclei for cavitation either due to the lack of adhesion at the interface, or

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stress triaxiality located between nearby particles. Volume strain measurement can therefore be used to assess adhesion at the matrix/filler interface. The evolution of volume strain during a tensile test at 50 mm/min was therefore measured for neat PP, PP with 20%$_{\text{weight}}$ PMC and PP + 20% $_{\text{weight}}$ PMC + PP-g-MA (Fig. 9).

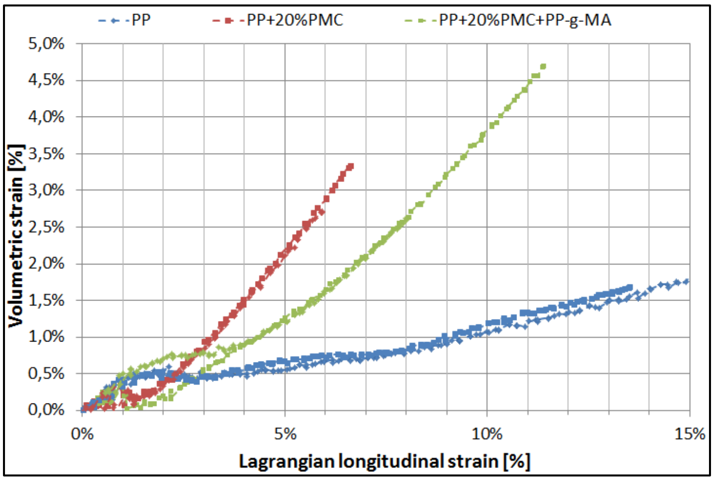

Figure 9. Volumetric strain during tensile test at 50 mm/min for polypropylene and filled PP

Two stage of volumetric strain increase can be identified on the curves. The first one, up to 1% of longitudinal deformation, corresponds to the elastic regime of the material optionally followed by a step of plastic deformation as evidenced by the observation of an isochoric behavior. In the second step, an important increase in the volumetric strain occurs. It corresponds to the damaging of the material occurring during the plastic deformation of the material. It can be seen that composites undergo much higher volumetric strain that neat PP with increasing longitudinal strain. Cavitation can be an explanation for this phenomenon. When PP-g-MA is added, the volumetric strain is diminished in comparison with the composite without PP-g-MA for the same level of longitudinal strain. That would indicate that the cavitation process is diminished, either due to a better adhesion between the filler and the matrix, or a change in behavior of the matrix by adding PP-g-MA. Whereas in the case of the composite without PP-g-MA, no change in the slope of the curve can be seen in the plastic domain, an increase of the slope at about 6 % of longitudinal strain can be seen for the composite with PP-g-MA. This change might indicate a debonding process. Before the change of slope, the volume strain is higher than for neat PP, indicating that some damaging process was already occurring.

4. Conclusion

A novel approach to phenolic molding compound recycling was proposed in this work. The effect of this type of filler on the mechanical properties of a polypropylene matrix was investigated. While the addition of PMC filler lowered impact and tensile strength, the addition of PP-g-MA allowed obtaining similar properties as talc filled polypropylene. Thus, it appeared that PMC waste could be used as a viable filler of polymeric materials.

The study also concerns the composite with high reinforcement content. Mechanical solicitation of these materials leads to constraints triaxiality phenomena inherent to the microstructure (and the effects of dispersion of the fillers). This locally generates a high hydrostatic pressure at the base of the growth cavity and damage to the composite structure as it has been observed experimentally in this work. Also other work is underway on the numerical modeling by homogenization of PMC filled polypropylene where the mechanical behavior of the matrix is based on the coupling of an elastic-visco-plastic law with a damage model by growing type of cavities as the model of Gurson [21].

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