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Thermomechanical Degradation of Filled Polypropylene

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Summary: The main problem in post-consumer plastics recycling is due to the thermomechanical stress acting on the melt during the reprocessing operations. The macromolecules break because of the temperature and of the mechanical stress. The extent of degradation is then correlated to the level of mechanical stress which, in turn, is proportional to the viscosity of the melt. The presence of fillers increases the viscosity of the polymers and then it is expected that the level of thermomechanical degradation of these systems is larger than that of the unfilled material.

In this work the thermomechanical degradation kinetic of a polypropylene sample is investigated as a function of the calcium carbonate content. It is shown that the decrease of viscosity, that is the decrease of molecular weight, is directly related to the increase of viscosity due to the filler content. The worsening of the mechanical properties are consistent with the change of viscosity.

Introduction

The huge amount of plastic products made of filled polymers makes the recycling of these post-consumer products an important tool in the plastic recycling industry. Nevertheless the industrial importance, only a few works in the literature dealt with this topic [1]. The degradation during the melt recycling operations, due to the presence of a thermomechanical stress acting on the melt, can strongly worsens the properties of the recycled material. This worsening occurs because of the change of molecular structure and morphology the degradation can induce.

The thermomechanical degradation is caused by the contemporary presence of high temperatures and mechanical stress. That increases with increasing the viscosity of the melt. For this reason filled polymers behaves in different ways during the melt

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reprocessing operations. Indeed, the presence of fillers increases significantly the viscosity of the molten polymer.

Polypropylene is one of the most used polymers, also as filled material. The recycling of filled polymer systems has been studied by a few authors [2-6].

In this work a study of the thermomechanical degradation of calcium carbonate filled polypropylene has been carried out in order to have information about the recyclability of this material when subjected to repetitive processing operations. Polypropylene is very prone to the thermal degradation but the presence of mechanical stress dramatically enhances its degradation kinetic. Calcium carbonate is one of the most used and cheap fillers for polymers and does not change its shape during melt operations. This last fact allows us to understand the effect of the fillers on the polymer matrix during these melt operations.

Experimental

A sample of extrusion grade polypropylene (D50S from Basel, Italy), PP, has been compounded with calcium carbonate ($D \approx 1.5$ μm) in different concentrations, namely 20 and 40% wt/wt. Polymer and filler have been mixed in a Brabender mixer at 210 °C, at a mixing speed of 50 rpm for about 5 min. The materials prepared in these conditions have been considered the "virgin" systems. Degradation tests have been carried out in the same apparatus extending the mixing time until 40 min. Pure polypropylene was subjected to the same treatment.

Rheological and mechanical tests have been carried out on specimens prepared by compression moulding. Rheological tests were performed at T=210 °C with a Rheometrics RDA II Dynamic in a plate-plate mode. Mechanical tests were carried out with an universal Instron machine mod 1122.

Discussions of the results

The viscosity of the filled polymers increases with increasing the amount of fillers, this behaviour is evident in Fig. 1 where the flow curves of the three virgin materials are reported. The presence of calcium carbonate strongly increases the viscosity of the polypropylene and the filled polymers do not show the Newtonian plateau at very low shear rate. The decrease of the viscosity – and in particular of the Newtonian viscosity – is larger with increasing the content of calcium carbonate. The more pronounced non-Newtonian behaviour of the filled PP systems tends to approach the curves at high shear rates.

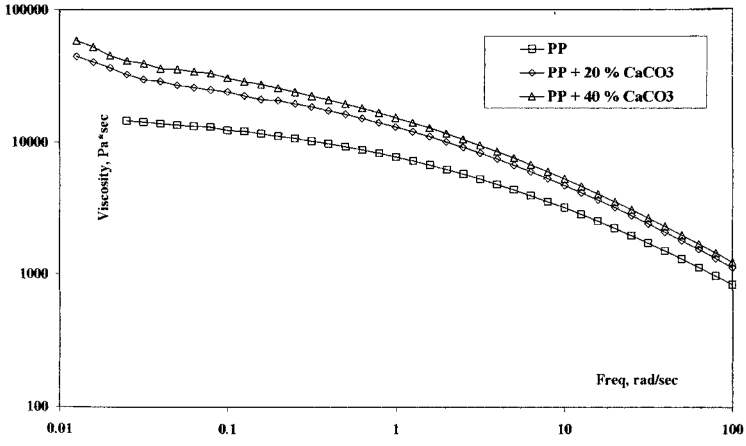

Figure 1. Flow curves of the unfilled and filled polypropylene processed 5 min.

Figs. 2-4 report the flow curves of the three investigated systems for different times of processing. As said previously, the material processed 5 min. is considered the virgin, undegraded material. With increasing the processing time, the flow curves lower and the decrease of viscosity is larger with increasing the amount of filler content. This phenomenon is due to the thermomechanical degradation of the molten polymer. Indeed, the degradation of PP during processing is mainly due to the temperature, but the presence of a mechanical stress applied on the melt increases the degradation kinetic. The stress acts as a catalyst of the thermal degradation.

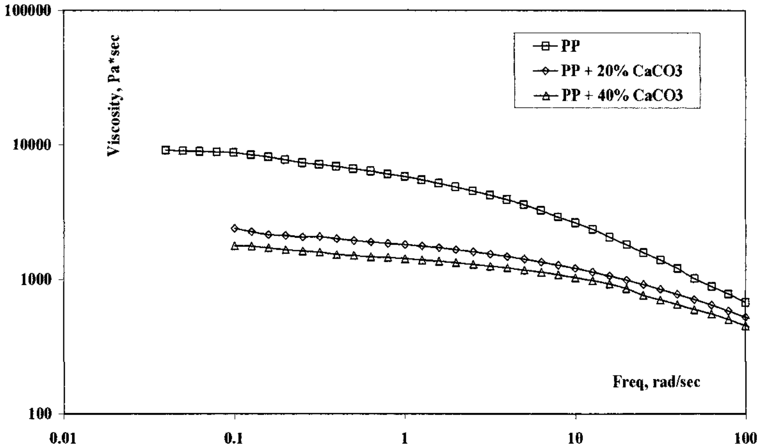

Figure 2. Flow curves of the unfilled and filled polypropylene processed 10 min.

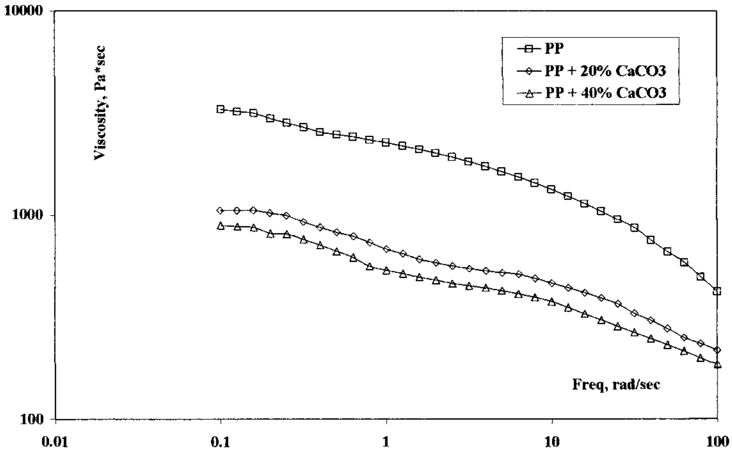

Figure 3. Flow curves of the unfilled and filled polypropylene processed 20 min.

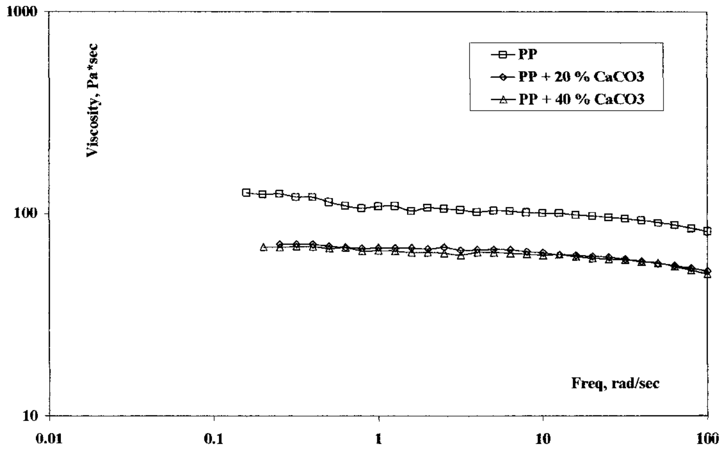

Figure 4. Flow curves of the unfilled and filled polypropylene processed 40 min.

The increased viscosity of the filled material, increasing the mechanical stress, has a negative effect on the thermomechanical degradation of the filled samples. After a long processing in the mixer, the viscosity of the filled materials turns to be lower that of the unfilled polymer. Because content, shape and dimension of the calcium carbonate particles do not vary, the reduction of the viscosity is only due to the decrease of molecular weight of the polymer matrix as a consequence of the cleavage of the macromolecular chains.

The influence of the filler content on the degradation kinetic of the calcium carbonate filled PP sample is better put in evidence in Fig. 5 where the viscosity at 100 s^{-1} has been plotted against the processing time for the three samples. This shear rate has been chosen considering that the shear rate during mixing is in this range. The same qualitative behaviour is, however, observed for all the shear rates. After about 8 min. the viscosity of the filled samples become lower than that of the pure polypropylene. The presence of the filler, then, changes the degradation kinetic of the polypropylene that increases with increasing the viscosity of the samples and then with increasing the filler content.

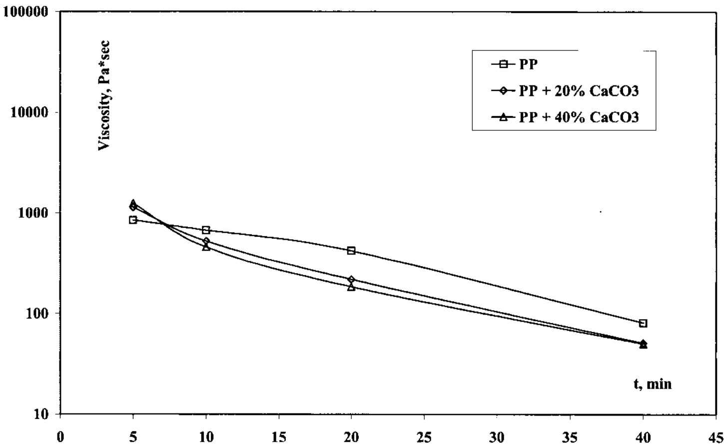

Figure 5. Viscosity at a shear rate at 100 s^{-1} as a function of the processing time.

The kinetic constant of the PP degradation can be evaluated as the slope of the viscosity-time curve for the three materials. In Fig. 6 these values are plotted against the viscosity of the sample. The values of the slope have been calculated at 5, 10, 20 and 40 min. The values of the viscosity have been taken at 100 s^{-1}. Once again, however, it is to notice that similar behaviours have been observed in all the shear rate range investigated. All the points lie, within the experimental scattering, on the same curve. This fact clearly indicates that the larger the viscosity of the molten polymer systems, in the processing conditions, the larger is the degradation kinetic of the filled samples. As the viscosity is a function of the type and content of the filler, then, the degradation kinetic of the filled polymers depends on the content of inert fillers. Of course, this conclusion holds only when the shape and the average dimension of the filler particles do not vary because of the melt processing. If the dimension and the aspect ratio change, like for the fibres, the viscosity changes as well and the strict correlation between viscosity and degradation kinetic could not be valid.

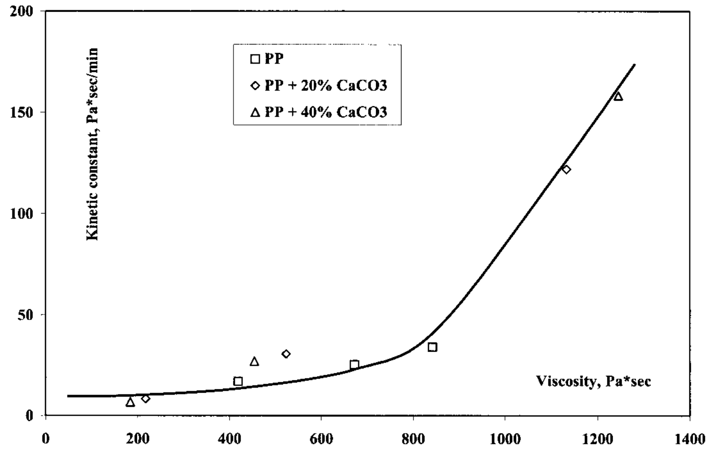

Figure 6. Kinetic constant of unfilled and filled polypropylene as a function of the viscosity at 100 s^{-1}.

The mechanical properties, elastic modulus, E, tensile strength, TS, and elongation at break, EB, are reported in the Figs. 7-9 as a function of the processing time. The presence of the filler increases the modulus of the polypropylene while the tensile strength is slightly decreasing and the ductility is strongly decreasing.

The slight increase of the modulus with increasing the processing time can be interpreted considered two different mechanisms occurring during the reprocessing: reduction of the molecular weight and rise of the crystallinity. Indeed, the decrease of the molecular weight gives rise, in semicrystalline polymers, to an increase of crystallinity due to the enhanced mobility of the shorter chains.

This behaviour – rise of modulus and crystallinity - has been observed in the recycling of some semicrystalline polymers [7,8] while no increase of the modulus has been observed for amorphous polymers [9].

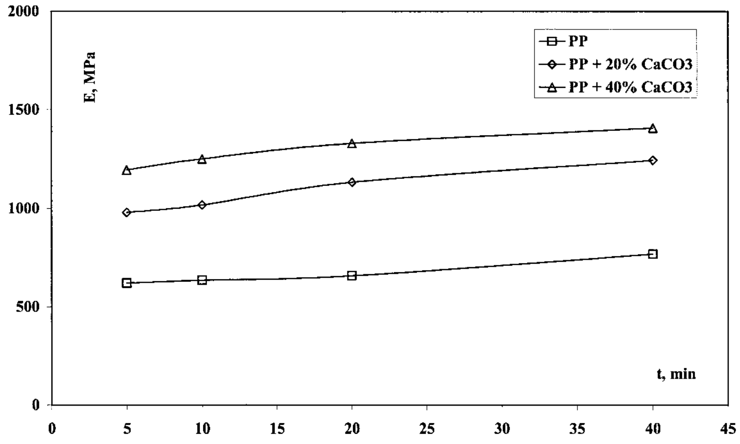

Figure 7. Elastic modulus of unfilled and filled polypropylene as a function of the processing time.

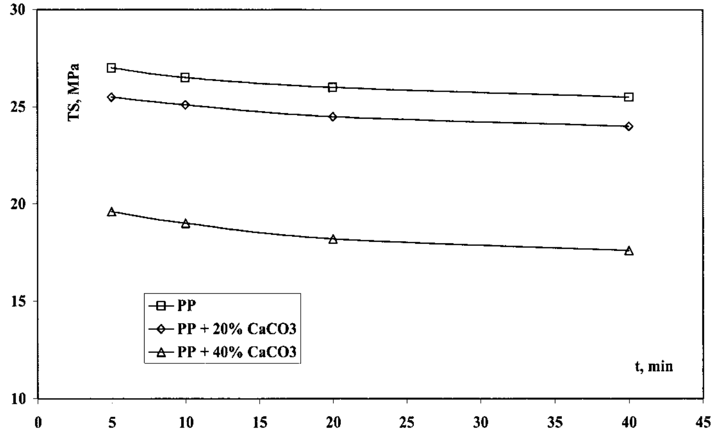

Figure 8. Tensile strength of unfilled and filled polypropylene as a function of the processing time.

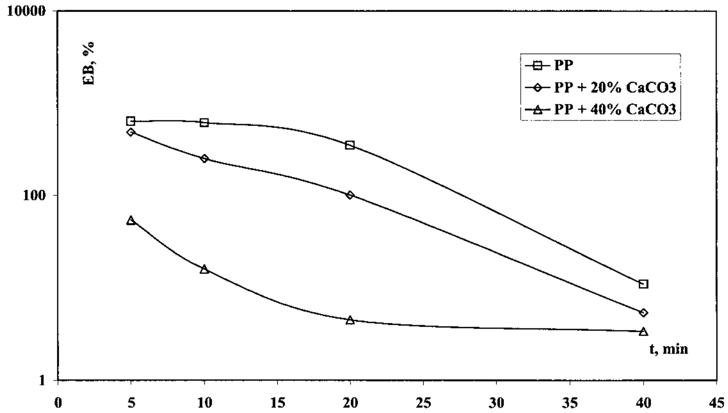

Figure 9. Elongation at break of unfilled and filled polypropylene as a function of the processing time.

The reduction of the molecular weight depresses the modulus that, on the contrary, is strongly enhanced by the increased crystallinity. These two cocurrent mechanisms can explain the sligth rise of the modulus – processing time curves.

The scarce effect of the processing time on tensile stress can be explained considering that dependence of the tensile stress on moleculare weight is very low and partially contrasted by the rised crystallinity.

The decrease of the molecular weight and the rise of the crystallinity are also responsibles for the decrease of the elongation at break. In this case, however, both parameters act in the same negative direction. For this reason the loss of ductility is remarkable and with incresing the processing time a ductile-brittle transition is observed. The larger reduction shown by the filled polymers is directly correlated to the larger change of molecular weight. It is, indeed, well known that the elongation at break of polypropylene is a sharp function of the molecular weight in a short molecular weight range [7].

Conclusion

Filled polymers present a thermomechanical degradation kinetic faster than that of the same unfilled polymer. The degradation kinetic rises with the content of filler due to the increase of the melt viscosity and then of the thermomechanical stress acting on the molten polymer.

The properties of recycled post-consumer filled polymers are then lower than that of the same unfilled material.

The mechanical properties worsen with increasing the processing time and a brittle-ductile transition can observed. This transition occurs at lower processing time for the filled polymers because of the faster decrease of the molecular weight.

[1] J. I. Eguiazábal, J. Nazábal, in *"Handbook of Plastic Recycling"*, F.P. La Mantia, ed, RAPRA, to be published.

[2] D. L. Reinhard, *SPE Antec Technical Papers* **1992**, 38, 1545.

[3] G. Guerrica-Echevarría, J. I. Eguiazábal, J. Nazábal, *Polym. Deg. Stab.* **1996**, 53, 1.

[4] D. Maldas, B. V. Kokta, *J. Thermoplastic Comp. Mat.* **1995**, 8, 420.

[5] C. A. Bernardo, A. M. Cunha, M. J. Oliveira, *Polym. Eng. Sci.* **1996**, 36, 511.

[6] J. J. Balatinecz, M. M. Sain, *Macromolecular Symposia* **1998**, 135, 167.

[7] M. Marrone, F.P.La Mantia, *Polymer Recycling* **1996, 2**, 17.

[8] M. Kostadinova Loultcheva, M. Proietto, N. Jilov, F.P. La Mantia, *Polym. Deg. Stab.* **1997**, 57, 77.

[9] F.P. La Mantia, F. Conte, *Macplas International* **1997**, November, p.31.