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ATACTIC POLYPROPYLE. FROM INDUSTRIAL BY-PRODUCT TO HIGH ADDED VALUE MATERIAL FOR ADVANCED APPLICATIONS THROUGH CHEMICAL MODIFICATION PROCESSES

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Abstract

This work is related to the conversion of an industrial by product (or waste) coming from polymerization reactors, as the atactic polypropylene is considered, into materials to be used as interfacial modifiers in heterogeneous materials based on polymers. In fact, this work concerns with the obtain of interfacial modifiers by chemical modification of the polymer by grafting of polar monomers either by one step processes to graft succinic anhydride (SA) or p-phenylen-bis-maleamic acid (pPBM) onto the polymer backbone, or by a two step process to yield succinil-fluoresceine grafted atactic polymers from the modified with SA. The comparison of these chemical processes both in solution and in the melt has allow to us to establish a reaction mechanism, and as a consequence, to obtain interfacial agents with very different functionalities and molecular architectures providing the researcher the ability to design taylor-made advanced materials such as micro- and nano-structured blends, alloys and composites, becoming the interfacial modifiers as the key for their advanced ultimate properties

Keywords: *Polymer wastes, atactic polypropylene, Polymerization by-product, interfacial agent, advanced materials.*

INTRODUCTION

It is well known that isotactic polypropylene (iPP) is a very interesting polymer due to its high versatility that makes it to cover a wide range of applications (either as neat PP or combined in hetero-phase materials). These applications, mainly due to its stereo-specificity, make it suitable for applications from the commodities polymer uses to the engineering materials niche. However, in the

industrial processes for obtaining iPP, a significant fraction of atactic polypropylene (aPP) is produced. The latter, in opposite to iPP, has a lack of stereo-specific regularity that confers it a set of totally different properties in comparison to iPP. Therefore, aPP results in a sticky material, mainly amorphous that exhibit a low glass transition temperature ($T_g = -22.4^\circ\text{C}$) compared to iPP (nearby 0°C), and with non structural consistence to be considered useful as a material itself. So, applications for aPP are mainly constricted to marginal uses. It is noteworthy to mention that the amount of it produced is strongly dependent of both the type of process used to obtain the stereo-specific polymers and of the catalyst system employed [1]. Nevertheless, it can be said that, in dependence to the former, the generation of these wastes are in the range between 2% and 15% of the overall production of polypropylene.

In such scenario, the modification of this waste to provide it of better properties appears as a very attractive choice. This option was early suggested by Prof. Natta (discover of stereo-specific polymerization of propylene) in late fifties [2]. However, although the chemical modification of this polymer indeed enhances its properties, it is their use as interfacial modifiers in hetero-phase materials based on polymer what has demonstrated to be highly effective. The latter that has been dismissed till the authors work has its explanation in a proper interpretation of what is really happening at the inter-phase in such heterogeneous materials. Once this has been ascertained, the tremendous efficiency of some of the modified atactic polypropylenes has proven to overpass even those of the leader interfacial agents in the market [3].

Following the above considerations present communication shows, at a glance, the real possibilities of modification of this waste. So, the chemical modification of aPP with grafting of a series

of polar monomers such as maleic anhydride (MAH), succinic anhydride (SF) and p-phenylene-bis-maleamic acid (p-PBM) performed in solution and/or in the molten state has been reported [3-6]. The employ of such a different reaction media has allowed authors to define a chemical reaction path that explains the differences in architecture, structural properties and ultimate behavior of the modified polymers [3-8] and the heterogeneous materials based on them, including micro- and nano-structured blends, alloys and composites which are in the vanguard of the so called advanced materials based on polymers [9-14].

EXPERIMENTAL

Materials

An atactic polypropylene waste supplied by Repsol-YPF was used. For obtaining the grafted aPP with succinic anhydride moieties (aPP-SA) and pPBM moieties (aPP-pPBM), a maleic anhydride (Panreac) and a p-phenylene-bis-maleamic acid (synthesized in our laboratories)[6] were employed. In both cases, a dicumyl peroxide, POx, (Perkadox BC; Akzo) was used as initiator. Besides, to prevent thermo-oxidative degradation of the polypropylene (mainly β -scission) during the process, a mixture of Irganox 1010 and Irganox B225 stabilizers (Ciba-Geigy) was incorporated into the reaction media. The aPP with grafted SF groups was obtained from aPP-SA by a condensation reaction between SA groups and resorcinol (1:2 stoichiometric) in the presence of $ZnCl_2$. The solvents used for both the process in solution and the washing operation of the modified polymers were xylene (Panreac) while a dimethyl-formamide (Scharlau/FEROSA) was also used for aPP-pPBM.

Procedures and Characterization

The chemical modification in solution was conducted in a conventional reflux glass flask. First, the polymer was dissolved in boiling xylene (1/30 and 1/5 w/w polymer/solvent ratios) incorporating thermal stabilizers (0.1%). The pre-heated xylene-dissolved MAH or pPBM was then incorporated into the reactor and then the peroxide. Additional experiments were performed with MAH to the further reaction step with resorcinol to yield aPP-SF. Once the set reaction

times elapsed, the solution was precipitated into cool methanol, filtered, and the polymer recovered and dried for further characterization. The reactions in the molten state were performed in the same way (and absence of solvent) in a mixing chamber (Rheomix600 by Haake) working at different gear rates [3 to 8]. Experiments were done by using POx in the 0.7 to 4.1% range and the polar monomer in the 0.5 to 17.5% interval. Operation temperature was fixed in 140°C in all cases [3 to 8].

Grafting levels were determined by an improved hot titration method [3, 5, 6]. Infrared spectra were recorded using a Spectrum One FT-IR spectrophotometer and the presence of grafted SA, SF or pPBM groups was concluded. Heterogeneity of grafts was determined by n-heptane selective extraction. Further characterization was done by X-R, thermal analysis and optical microscopy.

RESULTS AND DISCUSSION

Although grafting processes have been widely studied, the real chemical pathways involved in their obtaining are far to be understood. However, it is generally accepted that there are competitive reactions in the polymer bulk that give rise mainly to in-chain scission or the degradation of polypropylenes. Nevertheless, the un-steady process proposed by authors agrees with the fact that short reaction times are not only sufficient but necessary for the greatest graft yields to be attained, while preventing degradative processes. It confirms the real possibility of obtaining them in continuous processes such as reactive extrusion. It is well worth to notice that the reaction media is conditioning the architecture of the modified polymer due, mainly, to the radical activity transfer and possibilities of termination reactions. In such circumstances, it is expected that reactions in the melt would exhibit higher grafts, as it exactly occurs. Note that for similar experimental conditions the grafting degrees obtained are in the 0.5 upto 2.5% interval for the modified in solution, and in the 0.5 upto 4.2% for those aPP-SA obtained in the melt. Similar values are found for aPP-SF and aPP-pPBM if grafting expressed in SA equivalent. As expected, it is noteworthy to mention that the presence of grafts increase the glass transition temperature of the modified aPP to values close to that of iPP.

Further, the reaction media are conditioning the architecture of the grafted polymers according to the consecutive reaction scheme proposed [7, 8]. Indeed, in the melt the termination processes evolve to chain scission yielding the grafted group as an end group. However, in solution a great part of the termination processes does by recombination yielding SA groups grafted side to side to PP chains. The latter implies that, in solution, the condensation reaction leads to grafted polymers with both SA and SF due to the SA forming an anhydride bridge is unable to be reacted by resorcinol. Even more, this waste (aPP) has allowed to conclude about the role of other effects in the reaction yielding (stereoregularity, temperature, kind of solvents, and so on).

Hence, the interfacial agents obtained have to be a very different behaviour in composites and polyblends as described elsewhere [9-14].

CONCLUSION

The certainty of obtaining proper interfacial modifiers (or agents) from an industrial waste have been properly proven. The choice of obtaining modified polymers with a wide range of functionalities (as desired) jointly to the real possibility to allocate preferentially the grafts, allow us to use them as interfacial materials for whatever performance required under the only limitations imposed by the matrix nature in the heterogeneous material.

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