FROM POLYMERIZATION WASTES TO INTERFACIAL AGENTS: ATACTIC POLYPROPYLENE BASED ADDITIVES AS INTERFACIAL MODIFIERS IN MULTIPHASE MATERIALS BASED ON POLYPROPYLENE.

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Abstract
This work is related to the use of a series of new interfacial agents consisting in atactic polypropylene (from polymerization wastes) with grafted moieties as a highly efficient interfacial modifier in polymer composites and polymer blends and their characterization (mainly) by Dynamic Mechanical Analysis (DMA) by using sDOE . The use of sDOE models (such as Box-Wilson methodology) has allowed modeling the systems in order to obtain tailor-made product with a previously known performance. Finally, present communication shows, at a glance, as mere examples, a series of study cases evidencing the efficient role of these kind of interfacial agents in heterogeneous materials based on polypropylene and mineral reinforcement (PP/mica), and polypropylene/polyamide systems.

1 Introduction

It is well known that a very efficient way to improve the interactions between components in heterogeneous materials based on polymers is the presence of polymer based interfacial agents containing grafted groups as interfacial modifiers in the material bulk. So, polymer composites and/or polymer blends and alloys would be good examples about [1-6]. The interfacial agents must resemble chemically the polymer matrix jointly of exhibiting affinity with the dispersed phase (reinforcement or polymer). It must be mentioned here that the silicate particles which constitutes mica are aggregates of smaller primary platelets consisting of thin lamellae of ultra thin dimensions (a few nanometres) just in the scale wherein the interfacial phenomena occurs [2, 3]. The real possibility to obtain a grafted polymer with a desired grafting degree has allowed us to design polypropylene based heterogeneous materials on the basis of changing not only the additive content but also the grafting level jointly to the type of interaction by the action of chemically different polar monomers. The use of new interfacial agents appears as a promised way to understand and to control the performance of such kind of advanced materials and more when these are obtained from industrial by-products. Further, the better the interfacial agent (in terms of type and critical amount) the better ultimate properties of the composite material can be reached [5, 6]. Most works in literature concerning the use of interfacial agents in polypropylene based materials are mainly referred to grafted polymers containing maleic anhydride moieties [5]. However, this paper is devoted to the interfacial modifications caused by a family of novel interfacial agents synthesized in our laboratories from polymerization wastes [7] on heterogeneous materials

with a rigid interphase (being the case study a PP/mica system) and with a mobile interphase (PP/PA systems) [1,8]. The interfacial agents used here have been atactic polypropylenes with succinic anhydride (aPP-SA), succinil-fluoresceine (aPP-SFSA) and *p*-phenilen-bis-maleamic grafted moieties (aPP-*p*PBM) in the polypropylene backbone. These interfacial agents were obtained by authors either in solution or in the melt aided by sDOE resulting in a wide variety of tailor-made additives with maleic anhydride (MA), succinil-fluoresceine (SF), both of them (SF/SA) or p-phenylen-bis-maleamic acid (pPBM) onto the polymer backbone with grafting degrees as desired and in the 0.01 up to 6% interval (and more under forced conditions) [1,7,8,11,12]. Finally, only to mention that the goal of these kinds of studies would be to find the correlations between the experimental results from the different instrumental techniques, looking for the macro-micro-meso-nano structuring of the materials. For such purpose a series sDOE worksheets have been used to obtain algorithms predicting the final values of the measured property. In our cases and for the purposes of this work these models have been mainly applied to dynamic mechanical analysis parameters.

2 Materials and testing methods
2.1 Materials

As starting materials an isotactic polypropylene, ISPLEN 050 (Repsol), a polyamide 6, Ultramid B3 (BASF) and mica (potassium aluminium silicate platelets, by Alsibronz®) were used. Table 1 lists some physical properties of the starting materials as received. Mica (density = 2.85 g/cm^3; specific surface BET = 1.5 m^2/g; and Average particle size = 79.8 µm) was chosen on the basis of absence of changes in the mean size and particle size distribution all along the processing steps [1,9,10].

Trade Name	Molecular Weight			Density (g/cm^3)	T$_m$ (ºC)	T$_g$ (ºC)	H$_2$O (%)
	M$_w$	M$_n$	HI				
Isplen 050	334400	59000	5.62	0.90	165	-13	0
Ultramid B3	25000	13000	1.92	1.13	221	65	10

Table 1. Physical Properties of the industrial polymers used.

The interfacial agents used (Figure 1) were an atactic polypropylene succinic anhydride grafted groups (aPP-SA) with 3% w/w (3 x 10^{-4} mol/g $_{polymer}$); with both succinic anhydride and succinil-fluoresceine grafted groups with 2.5% and 3.7% w/w of SA and SF respectively (6.2 x 10^{-4} mol/g $_{polymer}$); and *p*-phenylen-bis-maleamic acid grafted units (aPP-*p*PBM) with 15% w/w (5 x 10^{-4} mol/g $_{polymer}$) obtained in our laboratories from polymerization wastes as described elsewhere [1,9-12]. Figure 1 shows the chemical structure of these interfacial agents.
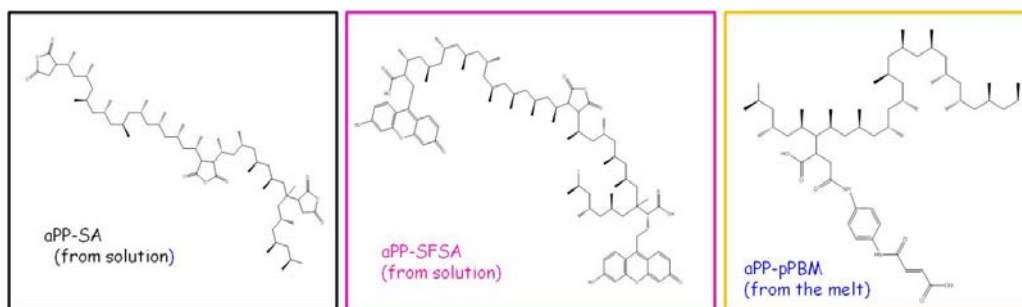

Figure 1. Chemical structure of the interfacial agents used in this work.

2.2 Processing

All the samples as indicated in Table 2 were compounded in a Rheomix 600 chamber (attached to a Rheocord 90 by Haake). The working temperature was set up at 190 ºC and 240ºC in the cases of the PP/Mica and PP/PA respectively. The neat PP and PA were also processed in the same way in order to obtain them under the same processing conditions than the compounds for further comparison at each case. So, the interfacial agent was incorporated by replacing the corresponding amount of the polypropylene (PP) in the compounds. In the case of the PP/Mica composites the compound obtained from the internal mixer, once cooled, was milled to pellets and then injection molded (dog-bone type 1BA EN 527-2) in a Babyplast 6/6 micro-injection machine working at 200ºC. Afterwards a series of rectangular specimens with the following dimensions (length=19.5mm, width=4mm, and thickness=2mm) were cut off for DMA measurements. The PP/PA based compounds were compression molded into approximately 100 µm thick films (Dr. Collin Press). So, specimens with the following dimensions (length=19.5mm, width=5mm, and thickness=0.1mm) were shaped for the dynamic mechanical study.

Experiment	(PP/PA) iPP/additive (%)	(PP/Mica) iPP/additive (%)
1	15/3	85.6/1.46
2	85/3	65.4/1.46
3	85/15	85.6/8.53
4	15/15	65.4/8.53
5	0.5/9	90/5.00
6	99.5/9	60/5.00
7	50/0.51	75/0.001
8	50/17.49	75/9.999
9-13	50/9	75/5.00

Table 2. Box-Wilson worksheets used to perform the experiments and model the final behavior of the indicated PP/PA blends and the PP/mica composites.

2.3 Characterization Procedures

The quality of the particle distribution in the PP/Mica composites was ascertained by means of ESEM microscopy (Philips XL30) over samples previously gold coated after being impact fractured and an homogeneous distribution of the particles concentrically distributed following the typical flow pattern of the injection molding process. The morphology of the PP/PA samples was studied by means of FESEM microscopy (Jeol JSM-6305F) over tensile tested samples. Additional studies by tensile, flexural and impact properties, thermal (DSC), thermo-mechanical (DMA), thermo-optical (OM), optical (OM, ESEM, FESEM), FT-IR and so on were performed elsewhere [1,8-15].

Being the main (but not the only) subject of this work the study of how the presence of these kind of interfacial agents affect the mechanical behavior of these materials under thermal dynamic conditions, a series of measurements were conducted using a METTLER DMA861 in the tension mode over the injection molded samples (PP/mica) and compression molded specimens (PP/PA systems) once shaped at the adequate dimensions defined in the previous section. Dynamic mechanical properties were measured within the range of linear viscoelastic behavior of the material. Consequently, a dynamic force of 12N oscillating at a fixed frequency (1 Hz) and amplitude of 3µm was used at a heating rate of 2ºC/min in the case of the PP/Mica composites. Meanwhile, in the case study of the PP/PA based blends the

conditions in order to ensure the linear viscoelastic behavior of the material were a dynamic force of 0.2N oscillating at a fixed frequency (1 hz) and amplitude of 4μm was used at a heating rate of 2ºC/min. The temperature was varied in the range from -30ºC to 140ºC in both series.

3 Discussion

The whole discussion of present work is based in the role of interfacial agents obtained from industrial by-products either in heterogeneous materials with a rigid interphase (composites) or in those with a deformable interphase (polyblends). For such purpose, for this presentation we have chosen, as mere examples, a PP/mica composite system and a PP/PA system both compounded in a wide composition range (Table 2) and incorporating these kind of interfacial agents. The interfacial agents obtained have to show a very different behaviour in composites and polyblends as described elsewhere [1,8,10,15]. Due to the very good results obtained in these preliminary stages the following step has been to undertake the modelling of the behaviour in terms of sDOE approaches (such as Box-Wilson) by considering this kind of systems as Agents Based like models where each one of the components are said as to be the "agents" interacting each other. As mentioned before, a selection of the interfacial agents obtained from the aPP by-product has been evaluated here. In both Figures 2 and 3 they can be appreciated that the presence of the interfacial agents cause changes in the behaviour of the composites and of PP/PA blends as to change enough the behaviour of the material not only in terms of stiffness but also in terms of damping behaviour, what is strongly related to impact properties. Figure 2 is showing the storage modulus and the damping factor evolution with temperature for all the PP/Mica samples in Table 2 and all the above mentioned can be clearly appreciated.
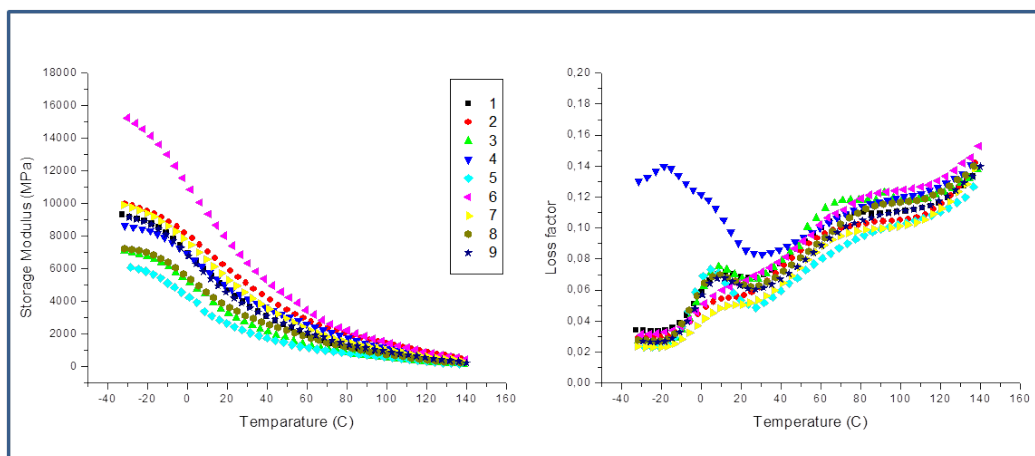

Figure 2. Evolution of the Storage Modulus and the Damp factor with temperature for all the samples corresponding to the sDOE worksheet for the PP/Mica system.

It is well known that the key of the functionalised polypropylenes as efficient interfacial modifiers can be associated to the increase of the second order interactions between the matrix and the dispersed phase as well as to the higher mobility of polar groups bonded at the chain ends, jointly to their ability to be hosted at the interphase between the reinforcement and the matrix, especially useful to reduce the interfacial tension between the components of the heterogeneous system. It can be seen that the compounds with higher mica content exhibit higher stiffness. The presence of mica as odd solid particles embedded into a polypropylene matrix usually induces a nucleation effect evidenced by a significant increase in the crystalline content of the polymer if compared with the neat polymer when processed at the

same setup conditions. This may explain, as a first approach the increase in storage modulus with mineral content. Besides, it results necessary to differentiate the amorphous/crystal polymer interface and the amorphous polymer/mineral interface where the interfacial agent trend to be embedded [1,8,10,15]. The aspects related to the finite dimensions of the interfacial area at the polymer/mineral interphase when trying to modify it by replacing a part of the polypropylene matrix by the interfacial agent must be considered in the interpretation of the relaxation phenomena taking place in all the temperature space scanned. Not only the changes observed in the so called α and β transitions, but also the relaxation mechanism in between and beyond these points and how they are affected by the presence of interfacial agents. These considerations are out of the scope of this presentation and will be object of a further study in future publications. The use of Box-Wilson methodology let us to obtain algorithms that predict the behaviour of the system in the experimental space scanned. In this way, and as a mere example, Figure 3 plots the isoline maps showing the evolution of the storage modulus with both the mineral and the interfacial agent content at room ambient temperature (25ºC) and glass transition temperature. So, by fitting data at whichever temperature the researcher choose the forecast of the property can be obtained. Note that in both case the $[r^2]$ was higher than 0.9, excellent for a quadratic model.
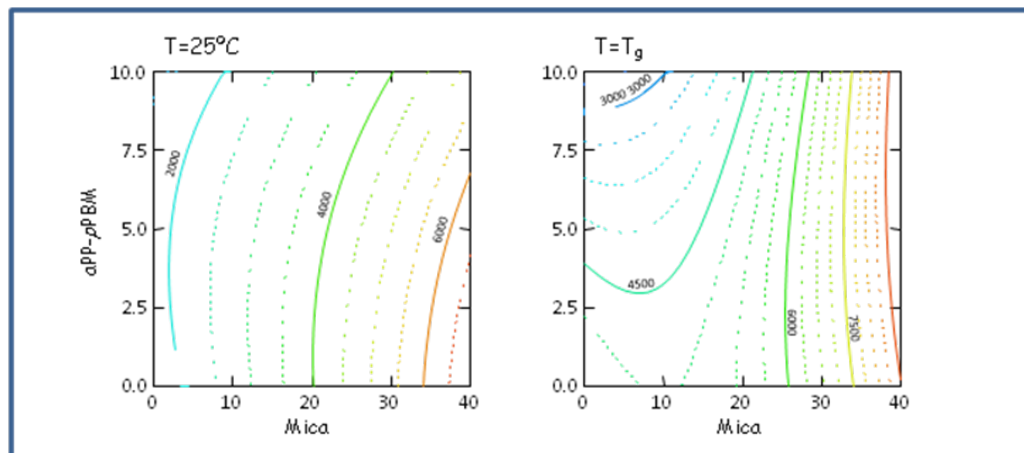

Figure 3. Isoline maps obtained from the sDOE model showing the evolution of the storage modulus as a function of the interfacial agent and the mineral contents at the indicated temperatures for the PP/Mica System.

The latter gives an idea why the interfacial agents derived from aPP works properly in this kind of systems. The possibility to obtain such a broad spectra of properties open the real chance to design materials with previously defined properties and/or performance rather than to design with materials. Of course, the other parameters associated to the DMA technique (and other type of properties also exhibits a similar quadratic evolution. According the Top-Down approach followed by authors in the experimental planning design, once the macroscopic responses of the material have been optimized because of the interfacial modifications induced in the cited polymer composites, they have been also detected for whatever the techniques purchased such as mechanical properties (tensile and flexural conditions), thermal (DSC), dynamic-mechanical (DMA), optical (OM) and thermo-optical (TOM), ESEM, FESEM) and synchrotron FT-IR [1,8,9-15].

In the case of heterogeneous materials (based on organic polymers) with a deformable dispersed phase such us polymer blends and alloys, the interfacial activity of the so called interfacial agents has been evaluated also by checking the compatibilization capability of two immiscible semi-crystalline polymers such as polypropylene (iPP) and polyamide (PA6). From an academic viewpoint, this family of blends are an excellent model for the most

general Polycondensation/Polyolefin polymeric systems, by focussing on the development and control of post-reactive processing stable morphologies able to yield a material with the desired performance as well as a good processability, low water absorption and liquid and vapour permeability, improved dimensional stability, good impact strength and improved chemical resistance to alcohol and glycols [8]. As an example Figure 4 shows the evolution of both the storage modulus (E') and the loss factor (tan δ) with the temperature in the -30ºC up to 140ºC range for a series of modified PP/PA blends jointly with those corresponding to the unmodified blend as well as the neats polymers. So, the effect of the interfacial agent (in this case aPP-SA and aPP-SFSA) by considering the temperature dependant relaxation phenomena can be ascertained. In fact, it can be observed that the presence of a mere 3% of either aPP-SA or aPP-SFSA causes a great effect on the storage modulus of the PP/PA compounds but with very different values. The latter suggest a different compatibilisation mechanism played by both interfacial modifiers. This has been clearly observed by means of FESEM and FTIR techniques. Nevertheless, the presence of whatever additive affect greatly the overall behaviour in terms of stiffness and damping behaviour, and more respecting the neat polymers. The study of this system by means of Box-Wilson experiment designs allowed to propose a micromechanical model based in the possibility of chemical reaction through the interphase in dependence of the type of polar group of the interfacial agent [1,13]. The latter has been checked by FESEM microscopy and will be showed in the ECCM15.
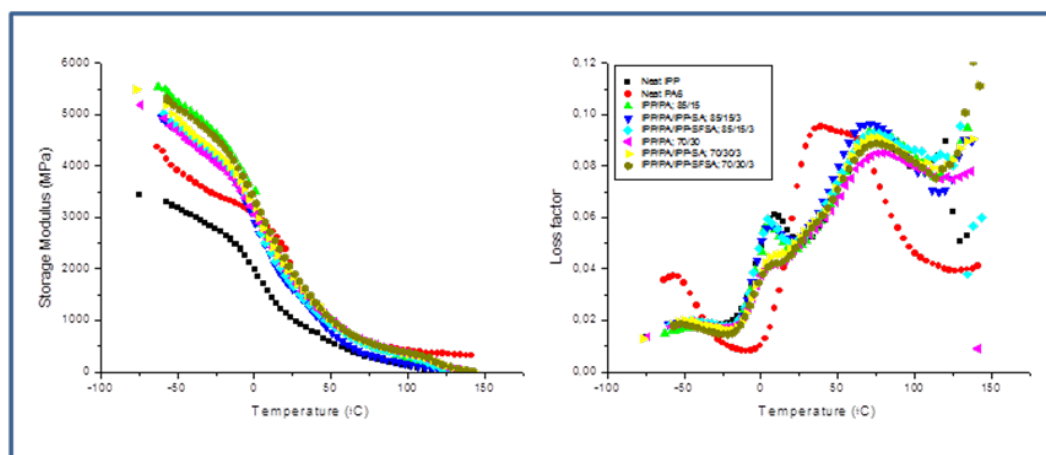

Figure 4. Evolution of the Storage Modulus and the Damp factor with temperature for the indicated samples.

4 Conclusions

The real possibility of handling a series of interfacial agents with very different functionalities and molecular architectures let the researcher plenty of routes (and so freedom) in designing composite materials with improved interfacial activity. Finally, only to mention that the changes in properties has been clearly ascertained by authors by whatever the techniques performed such as mechanical properties (tension, flexural and impact), thermal (DSC), thermo-mechanical (DMA), thermo-optical (OM), optical (OM, ESEM, FESEM), FT-IR and so on. So, models predicting the behavior of the quantitative physical properties of the composites have been implemented being these statistically accurate. So, and to end by now, it can be said that DMA spectroscopy has proven to be very useful in the study of the mechanical properties of a material in dependence with temperature, implying the possibility to follow the type of relaxation phenomena observed. The possibility to discuss separately on the elastic behaviour of the composite (Storage Modulus) and the viscous response of the same (Loss Modulus) offers plenty of possibilities for a fine interpretation of the interfacial

phenomena. The use modified polymers with different functionalities (as desired) allow us to use them as interfacial materials for whatever performance required between the limits imposed by the matrix in the heterogeneous material. The analysis of data aided by sDOE approaches open a wide window in the designing of materials with a desired performance. The grafted atactic polypropylenes used here showed the expected result as very efficient interfacial modifiers. Hence, although serendipity has played a prime role in the ultimate efficiency of these interfacial agents, they will be the markets needs which will define the ultimate function of the target material.

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