

ON THE CHANGES IN GLASS TRANSITION TEMPERATURES OF ATACTIC POLYPROPYLENES INDUCED BY GRAFTING OF POLAR GROUPS

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(Received March 10, 1999)

Abstract

A discussion on the influence of grafted polar groups (succinic anhydride and succinil-fluorescein) in glass transition behaviour of atactic polypropylene is shown in this work, on the basis of the reaction conditions used to obtain the modified polymers, kind and amount of grafted groups, and the degradation processes which may take place. The Box-Wilson experimental design methodology for two independent variables (reactant concentration to obtain the modified polymer) has been used to follow variations in glass transition temperatures. The existence of undesired degradation processes is considered as independent of the grafting reactions, and the model predictions seem to agree with this latter.

Keywords: atactic polypropylene, a-PP-SA, a-PP-SF, Box-Wilson, glass transition temperature

Introduction

One way to understand the behavior of solid state in polymers is through their thermal transitions. Otherwise, the structural modifications in the polymer backbone cause changes in the thermal transitions values respecting those of the original polymer.

In fact, thermal transitions in polymers are highly structure dependent, due to both stereospecificity effects and to the existence of inter- and intra-chain interactions. The possibilities to correlate the glass transition temperature of a macromolecular system with the individual contributions of each one of the atomic units conforming the macromolecule are, at present, quite far from the quantitative explanation of the experimental data. However, this latter informs about some qualitative considerations extremely valuable to explain experimental results.

Generally, the substitution of an hydrogen atom in a methylenic sequence by any bigger group leads to a increase in the glass transition temperature of the system. An

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example would be a methyl group as a substituent in one of each two methylenic sequences (polypropylene). When this methyl group is randomly disposed all along the backbone chain, the polymer has an amorphous character and its glass transition temperature is about -20°C [1–4].

From early years, the process of chemical modification of polyolefins, and mainly polypropylene, by polar monomers, by using a peroxide like initiator, has been broadly studied [1–3, 5–20]. Because the semicrystalline character of the commercial grades of polyolefins is usually considered to be modified, and due to the very low number of grafted groups in the polymer backbone, the changes in the thermal transitions – mainly associated to the crystalline fraction of the polymer – are very little too.

Because, by definition, the grafted groups are excluded from the crystalline cell, they would be confined to the amorphous regions of the polymeric system. Hence, the study of the thermal transitions associated to the amorphous phase would exhibit the most significant changes. Glass transition is the most representative transition associated to the amorphous regions in the polymer. As it is well known, based on ethylene polymers (PE) present an added difficulty to be studied under this point of view due to the easy packing of the $-(\text{CH}_2)_n-$ sequences and then a high crystallization capability. This means that the little amount of amorphous phase associated to PE explains the hard controversy existing in literature [4, 21, 22] about the value assigned for T_g (associated to fully amorphous $-(\text{CH}_2)_n-$ sequences). On the contrary, the atactic polypropylene homopolymer is a good option to undertake these investigations due to the presence of the randomly dispersed methyl group all along the polymer backbone, that confers an amorphous nature to this polymer. The purpose of present work is to discuss the influence of the grafting reaction yielding of polar monomers in atactic polypropylene and, therefore, on its glass transition temperature.

Experimental

Modification reactions were carried out in our laboratories and a series of modified atactic polypropylene containing different levels of grafting (up to $4 \cdot 10^{-2}$ polar groups per each 100 g of modified polymer). Succinic anhydride (SA) and succinyl-fluoresceine groups (SF) were the polar groups grafted to the atactic polymer. The modified polymers are named as a-PP-SA and a-PP-SF, respectively.

Those atactic polypropylenes containing SA or SF grafted groups were obtained starting from a by-product of polymerization reactor supplied by Repsol Química. The modification processes were performed in the melt (140°C) in a mixing chamber Rheomix 600 (at 45 rpm) attached to a Rheocord 90 (Haake). Figure 1 shows a reaction scheme of the two step chemical modification process. Details of the chemical modification process, as well as the determination of grafting levels have been broadly described elsewhere [1–3, 15–17, 20].

Thermal measurements were performed in a Mettler TA 4000/DSC 300 Calorimeter. Scans were conducted in a -150 up to 200°C range at a heating rate of $10^{\circ}\text{C min}^{-1}$.

An important question is concerned to the evolution of the thermal transitions on modified samples (taking as reference the T_g value of the original homopolymer), and related to the reaction conditions to modify the polymer. This study has been conducted by using a Box-Wilson experimental design considering two independent variables (maleic anhydride (MAH) and peroxide (POx)). Reaction time was considered ten min for the first step and five min for the second (Fig. 1). Table 1 compiles

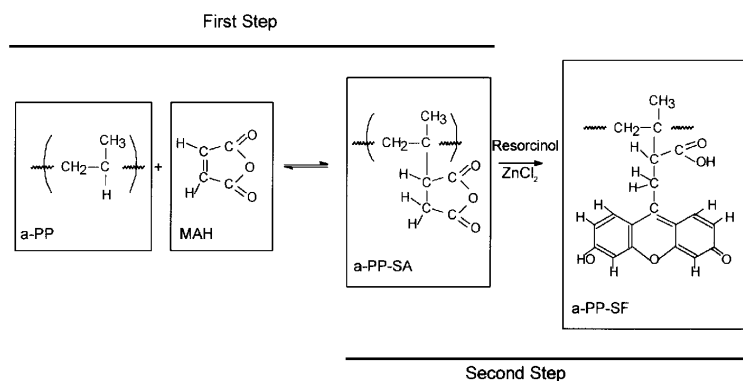


Fig. 1 Reaction scheme of the process of obtention a-PP-SA and a-PP-SF

Table 1 Box-Wilson experimental runs and experimental values of grafting level and variation in glass transition temperatures

Exp. Nr.	POx/	MAH/ %	Grafting/	T_g	
				T_g	ΔT_g^* °C
1	0.70	3.00	1.10	-13.8	8.6
2	3.50	3.00	2.55	-12.7	9.7
3	0.70	15.00	0.78	-13.9	8.5
4	3.50	15.00	2.10	-13.5	8.9
5	0.12	9.00	1.00	-8.3	14.1
6	4.10	9.00	2.70	-11.4	11.0
7	2.10	0.51	0.50	-14.0	8.4
8	2.10	17.49	0.50	-12.4	10.0
9	2.10	9.00	2.50	-14.1	8.3
10	2.10	9.00	2.40	-13.8	8.6
11	2.10	9.00	2.45	-13.9	8.5
12	2.10	9.00	2.10	-14.5	7.9
13	2.10	9.00	2.15	-14.0	8.4

$$^* \Delta T_g = T_g^{\text{a-PP-SF}} - T_g^{\text{a-PP}}; T_g^{\text{a-PP}} = -22.4^\circ\text{C}$$

Box-Wilson worksheet and values for T_g and ΔT_g (defined as $T_g^{\text{a-PP-SF}} - T_g^{\text{aPP}}$), as well as the grafting level of all the samples. As an example, Fig. 2 shows a thermal scan of some modified polymers. Results discussed at present work are corresponding to T_g values calculated from the middle point of the typical sigmoid curve of such transition.

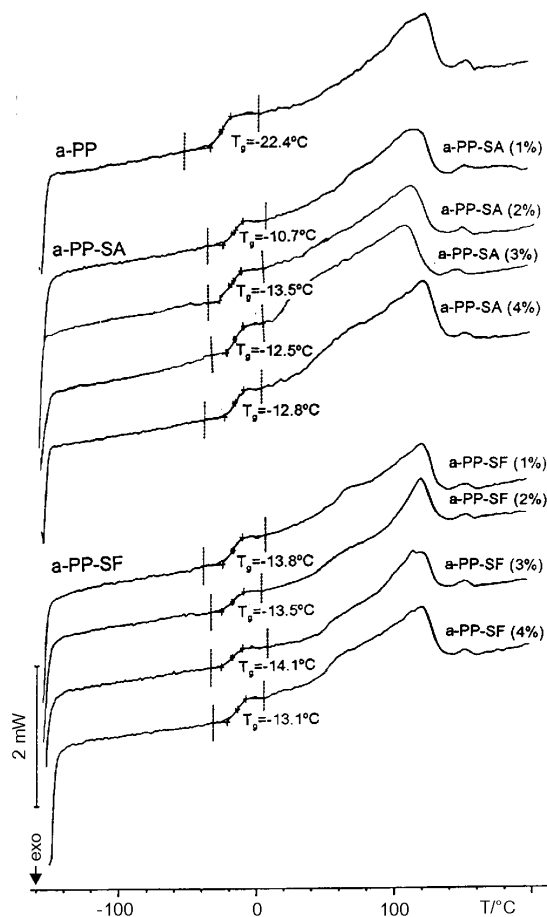


Fig. 2 Thermal scans used for the determination of T_g in the indicated samples

In order to check the degradation reaction extension, intrinsic viscosimetry measurements on selected samples were performed as usual for polypropylenes, in decline at 135°C. The following viscosimetric equation was used to obtain the viscous molecular weight average [23–25]:

$$[\eta] = 1 \cdot 10^{-4} M_v^{0.80}$$

Results and discussion

Effect of reaction conditions to obtain a-PP-SF in its glass transition

A value of -22.4°C was obtained for the original homopolymer (a-PP) used at present work, where the sigmoid that appears at lower temperature has been assigned to the randomly methyl groups sited all along the backbone of the macromolecular chains. Other sigmoids appearing above ambient temperature may be seen in Fig. 2, as well as melting processes for all the samples. These aspects illustrate the complex nature of the system and will be the main goal of next papers. The peroxide ends of the experimental range were selected according the criteria, on the one hand, of throwing the minimum reaction yielding (lower limit), and on the other hand, the minimum value to take under control degradation processes (upper limit). Moreover, the maleic anhydride concentration range was chosen considering the highest values where no segregation between monomer and macromolecular system exists in the reactor where the process is being carried out [1–3].

The values for ΔT_g , defined as mentioned before and compiled in Table 1, were fitted according to the Box-Wilson quadratic model of surface response [26–28]. Then, a polynomial ΔT_g defining as a function of reactant concentrations is obtained. A $\langle r^2 \rangle$ value of 60% (quite good for a quadratic evolution) was obtained. Analysis of variance for this regression leads to a confidence factor of 80% for the polynomial obtained. Each one of the coefficients showed a statistical significance higher than 95% in the case of the independent term, and linear and quadratic terms corresponding to [POx]. The latter means there is a strong dependence between changes in the T_g values of the modified polymer and the fraction of peroxide used as initiator in the radicalar chemical modification process. At this point, and due to the fact that the condensation reaction is fully quantitative, the governing step is the previous radicalar reaction between a-PP and maleic anhydride (MAH) to yield a-PP-SA [1–3] (Fig. 1).

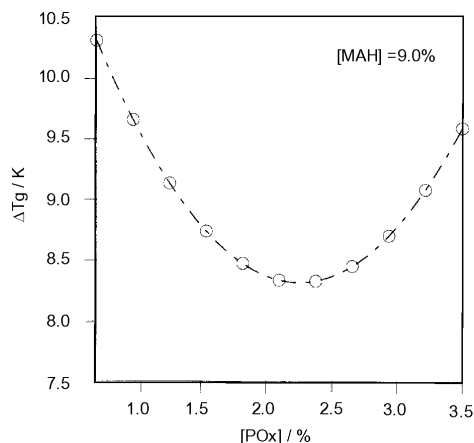


Fig. 3 Evolution of ΔT_g with the level of POx used in the synthesis step (MAH=9.0%)

Figure 3 is showing ΔT_g as a function of peroxide concentration keeping constant the maleic anhydride concentration in its central value inside the experimental plane. The existence of a minimum in the optimum value for $[\text{POx}]$, or what is the same, an increase of 8.5°C in the glass transition temperature respecting the unmodified atactic polymer, would be indicating the minimum perturbation induced on the polymer by the chemical modification reaction conducting to grafting SF groups.

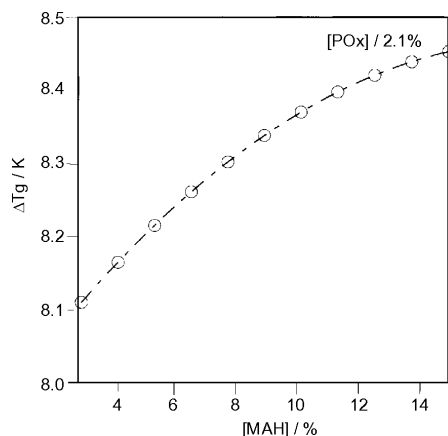


Fig. 4 Evolution of ΔT_g with the level of MAH used in the synthesis step ($\text{POx}=2.1\%$)

In Fig. 4, the ΔT_g evolution when $[\text{MAH}]$ varies while $[\text{POx}]$ remains constant in its central value, has been plotted. Comparing with the previous one, it is important to remark, when it is only $[\text{POx}]$ that varies (Fig. 3), ΔT_g values fluctuate between 8 and 10.5 degrees; and when only varies initial maleic anhydride changes are very little (from 8.1 to 8.5). The latter agrees with the negligible effect of $[\text{MAH}]$ on ΔT_g , displayed in Table 1.

Effect of the amount and type of grafts in glass transition

With the purpose to study the influence of the size of the grafted groups and the number of grafts, a series of samples containing 1, 2, 3 or 4% of grafts were prepared under optimized conditions (Table 2).

The T_g values corresponding to the modified polymers containing either succinic (a-PP-SA) or succinil-fluoresceine (a-PP-SF) grafted groups have been compiled in Table 2, and plotted in Fig. 5. There, an increase of more than eight degrees in T_g can be clearly observed. This latter seems to confirm the influence that grafted groups attached to the backbone of the polymer have on this thermal transition. This may be first assigned to the influence of the size of the groups grafted as well as their conformational possibilities according to the scheme given in Fig. 1.

The way they have been synthesized must be considered to explain the changes induced by them in T_g . It can be assumed that at a molecular scale SF groups would be acting as trazers of the positions were SA groups were previously bonded. At this

Table 2 Glass transition temperatures and viscosimetric parameters of the indicated samples, including their reactive processing history

Exp. Nr.	Sample	Reaction conditions					T_g °C	$^a\Delta T_g$ °C	η / dl g ⁻¹	M_v	$^bM_v^*$
		POx/ %	MAH/ %	Time/ min	Grafting/ %						
1	a-PP	—	—	—	0.0	-22.4	0.0	0.246	17 300	1.00	
2	a-PP-SA	0.12	9.0	10	1.0	-10.7	11.7	0.310	18 700	1.10	
3		3.50	3.0	4	2.0	-13.5	8.9	0.306	23 000	1.33	
4		4.10	9.0	4	3.0	-12.5	9.9	0.264	19 000	1.10	
5		4.10	9.0	6	4.0	-12.8	9.6	0.308	23 000	1.33	
6	a-PP-SF	0.7	3.0	10	1.0	-13.8	8.6	0.298	22 000	1.27	
7		2.1	9.0	8	2.0	-13.5	8.9	0.266	19 000	1.10	
8		2.1	9.0	13	3.0	-14.1	8.3	0.304	23 000	1.33	
9		4.1	9.0	6	4.0	-13.1	9.3	0.298	22 000	1.27	

$$^a\Delta T_g = T_g - T_g^{a-PP}; \quad ^bM_v^* = M_v / M_v^{a-PP} = M_v / 17300$$

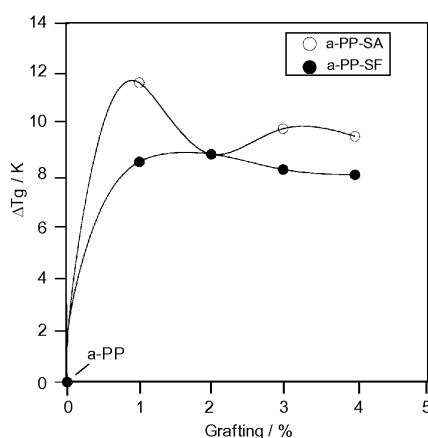


Fig. 5 Variations of T_g with the grafting level present in the modified polymer

point, it must be remembered that SF groups are obtained by a condensation reaction between single grafted SA groups and resorcinol, yielding the same number of groups of SF [1–3, 20, 29, 30]. The effect that the SF groups have on the glass transition is in the way to stabilize T_g values in a limited range being produced little variations with the level of grafting in the polymers. The oscillations respecting the unmodified polymer are smoother than those of the polymers containing SA groups. The differences in molecular size as well as the conformational possibilities of the SF group (plate like – i.e. far from spherical – geometry) respecting SA groups (quasi-spherical geometry, and smaller in size) lead to a lower increase in the T_g than those produced by the SA substituent. According to the classification compiled by Wunderlich [31], both of them would be sharply conditioning the order/disorder characteristics of the polymeric system. Differences between T_g of modified polymers and original homopolymer have been also plotted in Fig. 5, that shows the above mentioned effect. The T_g values for a-PP-SA samples vary from -9 up to nearly -12°C , and from -8 up to -9°C for a-PP-SF samples. Also it is remarkable that the two present the same values when they contain 2% of grafts.

Influence of degradation processes

At the effects of the present study it must be noticed that in the process of chemical modification of polypropylene two reactions are taking place: a grafting reaction that reaches a very little yielding and another degradation reaction (β -scission) occurring in the polymer bulk and leading to the chain breaking of polypropylene. This degradation reaction – although minimized by using thermal stabilizers – leads, at least, to a higher number of end chains and then to lower interchain distances. This is a well known effect that can play a very important role in the decrease of the glass transition temperature in macromolecular systems. Long times of reaction (ten min and higher), as it is the case of the Box-Wilson experimental design considered at present work, make the effect of reaction time to be significant in the system [1, 2].

In an attempt to determine the degree of degradation suffered by the polymer (as a whole) during the chemical modification process, viscosimetric measurements were performed. Results have been compiled in Table 2. From these data it can be concluded that no significant degradation has been produced in the system. In fact, when plotted M_v^* , defined as the ratio between the viscous molecular mass average of each modified sample and of a-PP, vs. the grafting level, it can be noted that all of them present similar values that are even higher than of a-PP (Fig. 6). This would be indicating there is no degradation in the system. Or better, the degradation has a local character that does not reach a macroscopical scale on the modified polymers.

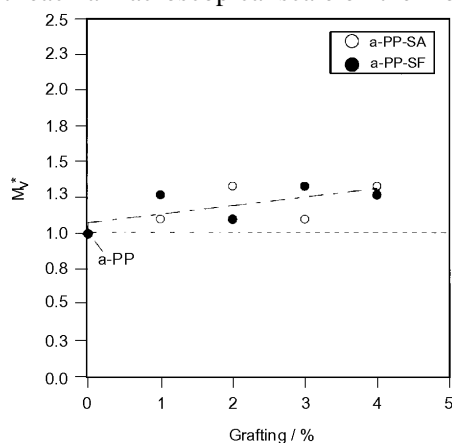


Fig. 6 Evolution of M_v^* with the grafting level of the indicated samples ($M_v^* = M_v / M_v^{a-PP}$)

Although the maxima variations in M_v^* are only about 20%, it would be important to notice the alternance of M_v^* with the grafting level and type of grafted group. This effect, although not so evidenced, was observed also for T_g . *This variation would be explained by the changes in the hydrodynamic volume of the modified polymer due to the grafted group and to other phenomena (segregation of grafts) too. These aspects will be studied in next papers.*

Conclusions

The great importance that the previous reactive processing history plays in the final values of glass transition temperatures of the modified polymers has been demonstrated. Box-Wilson methodology has been proved to be a powerful tool to follow the variation of any property in complex systems (as a macromolecular system is) where a lot of competitive effects take place. The local character of degradation, and so, its no macroscopical dimension before reaching a certain degree, confirms the very important relationship between synthesis step and the final characterization properties of the system. The existence of many factors having influence on the final responses of the system, as the size and the spatial volume of the grafted groups, or their different distribution in the polymer bulk caused by the reaction conditions dur-

ing the synthesis step, makes the responses of the macromolecular system to follow a non-linear evolution.

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A part of this work was supported by Plan Nacional de Materiales under its MAT 95-0189 Project.

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