Synthesis and Characterization of High Impact Polystyrene Using a Multifunctional Cyclic Peroxide as the Initiator

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1. Summary

This work deals with the synthesis of HIPS using a novel cyclic multifunctional initiator, the diethyl ketone triperoxide (DEKTP), analyzing its effect on the pre-polymerization step and its influence over the HIPS final properties.

2. Introduction

The incompatibility between polymers was in some cases overcome by the use of interfacial agents that mainly improved the interaction between phases. As an example of materials composed by an interfacial agent that allows combinations of both homopolymers components characteristics is that of a thermoplastic modified with a rubber, as it is the case of High Impact Polystyrene (HIPS) where the interfacial agent, composed by a graft copolymer (rubber-*g*-PS) is formed "*in situ"* during the synthesis [1]. In the case of HIPS, process innovations have been achieved by different polymerization strategies [2], the use of new polymerization techniques [3], mathematical modeling of the process [4], as well as the employ of more efficient initiators, especially of the peroxide type. In this sense, traditional mono-functional initiators have been replaced by linear bi- and multifunctional initiators that lead to a rather complex polymerization kinetics yielding lower pre-polymerization times without diminishing the product final properties. Other reports demonstrate that using bi- and multifunctional initiators it is possible the synthesis of HIPS with excellent mechanical properties in lower polymerization time (lower than 120 minutes) [5] where in the most of the cases the best results were obtained through the use of temperature ramp that allowed a better control in the peroxide labile groups' dissociation.

3. Experimental Conditions

3.1 Materials and synthesis Conditions

The DEKTP initiator used in the HIPS's synthesis was produced and characterized in our laboratories according with a procedure described before [6]. A medium *cis*-polybutadiene from Dynasol Elastómeros S.A de C.V, México was anionically synthesized. Styrene monomer (Poliformas Plásticas) was used as received. HIPS were prepared by mass-suspension polymerization using different DEKTP concentrations in the mass prepolymerization stage and different temperatures (see Table 1) under a heat rate of 2°C/min in the case of using temperature ramp. The PB concentration was kept constant at 8 wt.%

Table 1. HIPS' synthesis conditions and molecular parameters for different reactions

Material	T. in the mass stage T (°C)	$[TPDEC]_0$ (mol/L)	X_{IP} [a]	GD[b] (%)	N_t*[c]	$\overline{M}_{n\,PS_{free}}$ [d]	IS[e] (J/m)
HIPS-1	120	$7.79x10^{-4}$	28.78	99.24	1.01	213000	
HIPS-4	130	$7.79x10^{-4}$	34.93	107.76	1.27	184000	
HIPS-7	120-130	$7.79x10^{-4}$	28.00	102.33	1.05	220000	

[a] X_{IF}:conversion at the IF point; [b]GD: grafting degree; [c] N_t*: grafting density; [d] $\overline{M}_{n\,PS_{free}}$: average molecular weight of $PS_{free,}$ [e]IS: impact strength

3.2 HIPS Characterization.

In all the different HIPS samples free and graft PS produced, conversion, gel content, PS molecular weight, as well as grafting degree (GD), grafting density (Nt*), notched impact strength (IS) and DSC measurements, were analyzed.

4. Results and discussion

In the presence of the trifunctional initiator the molecular weights increase as the polymerization reaction progresses and they are lower at higher temperatures, regardless of the concentration of DEKTP evaluated (See Figure 1, the same behavior is observed for the other DEKTP concentration) and polymers with uniquely high molecular weights (ca. 350,000 g/mol for DEKTP concentration of 7.79×10^{-4} M) can be produced after 2.5 hours of polymerization, at temperatures around 120 °C.

Moreover, regardless of the concentration of initiator used, an increase in temperature from 120 to 130ºC causes an increase in the production of PS, given by the greater concentration of radicals in the reaction medium. However, the kind of PS that increases its production belongs particularly, to the free PS (PS_{total} = PS_{free} + PS_{graft}) because in all the cases the values of PS_{graft} remain without significant changes, close to 7%. This fact is indicative of the low selectivity of the initiator to grafting reactions at any of the concentrations of initiator and temperatures evaluated.

On the other hand, the evaluation of GE and ΔCp (see Figure 2) for different samples taken from the reactor for HIPS-1, evidence a considerable leap in both parameters at conversions close to 30%, which is associated with the point of inversion phase. Until X = 30% the grafting reaction takes place, minimizing the occurrence of this reaction at the point of inversion phase (IP). After the IP, the grafting reaction practically has no place so that the PS_{total} formed substantially corresponds to $PS_{free.}$ The corresponding morphologies (see Figure 3) confirm the fact that the IP takes place at conversion close to 30%. However, when comparing the point of IP for different HIPS, it can be observed that an increase in initiator concentration and/or an increase in temperature, moves the IP point slightly to higher conversion values.

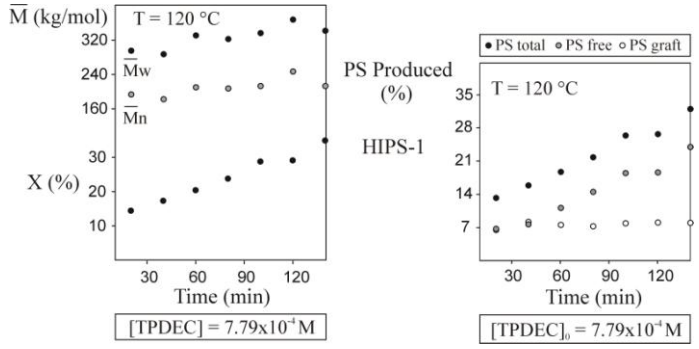

Figure 1

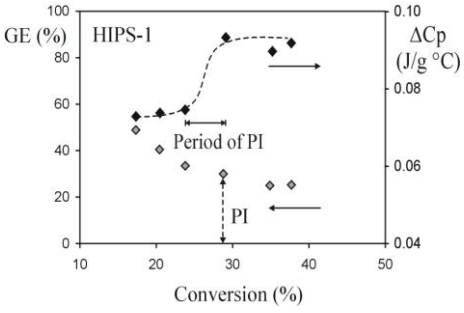

Figure 2

Moreover, an increase in temperature (120 to 130°C) yields larger rubber particles with larger occlusions where the interfacial tension and the viscosity ratio ([ηPB/nSt]/[ηPS/St]) are the responsible for the morphological changes. Taking into account the inability of the initiator to produce the graft reaction, independently the temperature used, and the polymer's lower molecular weight at 130ºC, the size of the rubber particle increases due to an increase in [ηPB/nSt]/[ηPS/St].

In order to control the decomposition rate of the peroxide sites, the reaction temperature was manipulated using temperature ramp. Regardless of the DEKTP concentration, it is noted that the values of X are similar to those obtained under isothermal conditions at 120 ºC however, the molecular weights are, in all the cases lower than those obtained at 120 and 130 ºC, that causes a decrease in the viscosity ratio ([ηPB/nSt]/[ηPS/St]). Under these new experimental conditions, the amount of free PS increases while the amount of graft PS substantially reduces, as the DEKTP concentration increases. The use of temperature ramp also substantially increase the interfacial tension and give rise to an increase in the particle size (See Figure 4) that provokes substantial improvements in the mechanical properties of the synthesized HIPS, mainly on the impact strength (see Table 1).

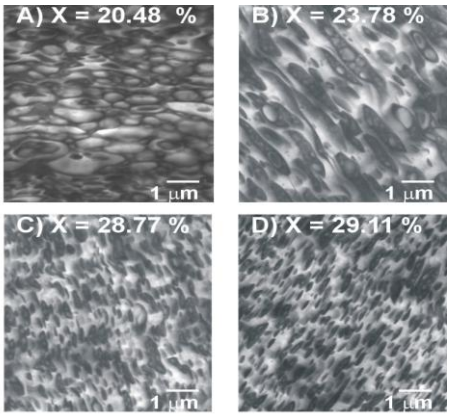

Figure 3

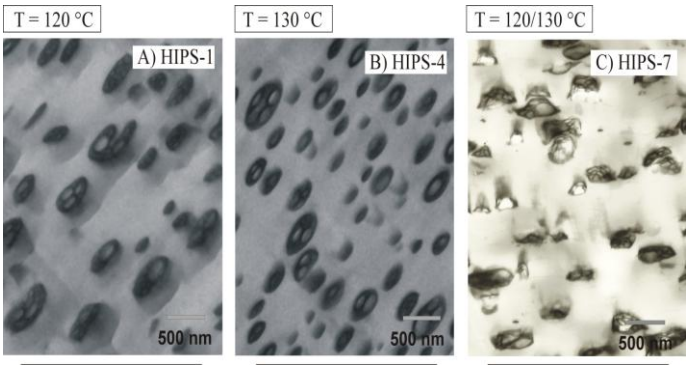

Figure 4

5. Conclusions

With the use of DEKTP as initiator and through temperature ramp (120-130°C) it is possible the synthesis of HIPS with an adequate development of morphology and impact strength.

6. References.

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