

POLYETHYLENE FINAL PROPERTIES IMPROVEMENT BY GRAFTING OF STYRENE IN SUPERCRITICAL MEDIA

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The use of near and supercritical fluids, as solvent aid in polymer processing, has been incremented from the last decade. They can have gas-like diffusivities, which have important implications for reaction kinetics, as well as liquid-like densities, allowing solvation of many compounds. On the other hand, macromonomer cationic copolymerization is a growing field of synthetic polymer chemistry. Friedel-Crafts alkylation involves the alkylation of an aromatic ring and an alkyl halide using a strong Lewis acid catalyst. It can be applied to obtain a copolymer from an aromatic monomer and polyethylene (PE) chains as a macromonomer. In the present work a novel method of copolymerization is proposed. Near critical n-heptane is used as reaction medium and swelling agent for the copolymerization of PE with styrene monomer using $AlCl_3$ as catalyst. The reaction was performed in a stirred batch reactor at 140 °C and 150 bar. It was determined that PE is completely solubilized in the n-heptane at high pressure-high temperature conditions. In this way, it is expected that using near critical n-heptane as reaction medium, PE chains and the catalyst will be more available to react each other. The copolymerization reaction was corroborated analyzing the reaction products after a careful pure polystyrene separation by selective Soxhlet extraction using tetrahydrofuran. The copolymer obtained was characterized and polystyrene grafted quantified by Fourier transform infrared spectroscopy (FTIR), and Differential scanning calorimetry (DSC).

The oxygen barrier of grafted PE films was improved in a 30% respect to pure PE, when around of 7% of styrene was grafted. Tensile mechanical properties of the same samples show that although the rigidity lightly increases, the grafted PE could be processed as films because the elongation at break remains around of 260%.

INTRODUCTION

In the last years, the most significant trends in the field of plastics are changing focusing in the final material use. The compromise between economy and technique requirement is frequently reached, by development of materials with predetermined properties, based in commodity plastics [1]. In this sense, the introduction of a new functional group into a polymer molecule can modify its properties. Thus, copolymers are molecules generated by chemical reactions of two or more homopolymers combining synergistically their properties. They have found applications in diverse fields like adhesives, paints, coatings, emulsifiers, and biomedical materials [2].

There are some promising reactions that begin from macromers or macromonomers. In this sense, cationic copolymerization is an exciting, growing field of synthetic polymer chemistry, which provides a variety of avenues toward a large number of unique materials with unusual combinations properties [3]. Friedel-Crafts alkylation reaction is an attractive reaction to

obtain a copolymer from an aromatic monomer. This reaction involves the alkylation of an aromatic ring and an alkyl halide using a strong Lewis acid catalyst. In this way, a hydrocarbon chain, like polyethylene (PE) can be chemically bonded to the styrene benzene ring through an aromatic electrophilic substitution. Aluminum chloride (AlCl_3) is probably the most commonly used Lewis acid and also one of the most powerful [4-6].

On the other hand, the use of near and supercritical fluids as an inert or active reactive medium for synthesis, extraction and/or processing of polymers is even more frequently [7]. PE polymerization in supercritical ethylene [8, 9], supercritical extraction of plasticizers from PVC [10, 11] and polymer plasticization using supercritical CO_2 [12, 13], are typical examples.

In a previous work [14] it was determined that the PE is completely soluble in n-heptane at high pressure-high temperature conditions. In the present work, a novel process to copolymerize styrene with PE is proposed. Near critical n-heptane is used as reaction medium and AlCl_3 as catalyst. The copolymerization reactions were carried out at these conditions and varying the catalyst content.

In the present work, results from reaction quantification and final properties of reaction products are presented and discussed. The quantification was performed by combined infrared and thermal techniques. The final properties analyzed were oxygen permeability and mechanical properties on films.

MATERIALS AND METHODS

Materials: Styrene (analytical grade) and linear low-density polyethylene from Dow-Polisur, LLDPE 6200 (Mw: 52000 g/mol, Mn: 17000 g/mol) were used as reactants. The alkylation reaction was catalyzed by anhydrous AlCl_3 (>98% purity) from Merk. N-heptane (Tc: 267.2 °C, Pc: 27 bar), with purity higher than 99 wt% was used as reaction medium.

Equipment: The experimental system consists in a high-pressure stirred Parr reactor with a temperature controller and a manual pressure generator. The reactor vessel is made of stainless steel with a capacity of 600 ml. It has a maximum working pressure of 200 bar.

Catalyst release system: In order to assure that the AlCl_3 acts when the PE is entirely solubilized, a catalyst release method was designed. The catalyst is placed into a PE capsule, thus when the capsule is solubilized, the catalyst is released and the reaction takes place with both reactants in the solution. The PE of the capsule is similar to the LLDPE 6200, but not exactly the same, then the polymer for the reaction is a blend of different LLDPE and from here is called "PEmix".

Reaction procedure: The reaction conditions were selected based on theoretical and experimental previous studies [14, 15]. It was determined that PE can be entirely solubilized at 145 °C and 150 bar, and this conditions were selected to perform the reaction. Initially, the reactor is charged with 10 g of PE films, 20 ml of styrene and the capsule with AlCl_3 . After this, it is filled with n-heptane and heated, stirred and pressurized to the final conditions. The catalyst content added varied from 1 to 4 wt%. After 1 hour, the reactor was cooled to room temperature and finally the vessel was opened and the product was filtered to eliminate the solvent and remaining styrene. The collected sample was dried under vacuum to remove the residual solvent and/or styrene. The reaction product will be named with "R" follow the catalyst content. Thus, R1 is the reaction product prepared with 1 wt% of AlCl_3 .

For a complete characterization, the products were subject to a selective Soxhlet extraction with tetrahydrofuran (THF), to remove polystyrene homopolymer (PS) formed during the reaction. The extraction was performed for 15 h. Theoretically, the no copolymerized PS is extracted and the soluble fraction (SF) should be contain only PS. The insoluble fraction (IF),

formed by a mixture of copolymer and homopolymer, was dried in a vacuum oven to remove any residual solvent. Both fractions were characterized by FTIR in order to analyze the chemical composition and quantify the styrene in each fraction.

Characterization techniques: Different techniques were applied to characterize raw materials and reaction products before and after THF extraction. These techniques are:

Fourier Transformer Infrared Spectrometry (FTIR): Qualitative identification of reaction products at atmospheric and high pressure, and quantitative measures of PS copolymerized were carried out in Nicolet 520 FTIR equipment. The PS concentration was estimated by comparing the ratio of typical infrared absorption peaks on films samples (peak at 700 cm^{-1} for PS and at 719 cm^{-1} for PE). Previously, a calibration curve was performed with PE/PS blends of known concentrations.

Differential Scanning Calorimetry: The thermograms of samples were obtained in a Perkin Elmer Pyris I equipment. The samples were heated to $180\text{ }^{\circ}\text{C}$ and kept at this temperature for 3 min to remove all prior thermal history. Subsequently, they were quenched to $30\text{ }^{\circ}\text{C}$ and then reheated to $180\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$.

Oxygen permeability measurements: The equipment used was a MOCON OX-TRAN 2/21. The oxygen barrier properties were determined at $23\text{ }^{\circ}\text{C}$ with 0% of relative humidity over films of $10\text{ }\mu\text{m}$ of thickness prepared in a hydraulic press at 180°C . Ten samples were measured for each reaction condition and for pure PE.

Mechanical Properties: The tests were carried out in an INSTRON tester with pneumatic clamps over films of $200\text{ }\mu\text{m}$ of thickness prepared in a hydraulic press at 180°C . The measurements were performed at $25\text{ }^{\circ}\text{C}$, $2\text{ mm}/\text{min}$ using a cell of 1 kN . Ten samples were measured for each reaction condition and pure PE.

RESULTS

The reaction occurrence and quantification of the catalyst content effect on PS grafting amount were assessed by FTIR. The PS content determination was initially determined in the reaction product and the PS percentage is shown in Table 1. The amount of PS increases as the catalyst content increases, as expected. The PS in the reaction product could belong to homopolymer or copolymer molecules. In order to assess the amount of PS in the copolymer molecules, a Soxhlet extraction with THF was performed on reaction products. As THF mainly dissolves PS, during extraction the PS homopolymer is removed. The same extraction was performed on pure polyethylene (PE_{mix}), observing that some short molecules were solubilized (see Table 1). These results were taken as reference, because at least, around of this amount of PE must be solubilized with the PS during the extraction on reaction products. In Table 1 the mass extracted and PS content in soluble and insoluble fractions (SF and IF respectively) are also shown for each reaction product. The amount of mass solubilized could contain three kinds of molecules, PS, PE and copolymer molecules, where PE chains are dragged by PS grafting on it. Because of that, the mass solubilized exceeds the sum of the PS and reference PE_{mix} in all experiments. It was corroborated by Gel Permeation Chromatography that PE does not suffer chain scission then the previous hypothesis is valid. The PS molecules detected in the IF appertain to copolymer, but surely the amount of PS in copolymers molecules is greater than this value because of the above explanation. Also, it can be noted that PS content in the IF, and then, the copolymer formed increases as the catalyst content increases, as expected.

A further analysis that gives evidence of the copolymer presence and the effect of catalyst content were observed by DSC. The thermogram of the different reaction products were

obtained and compared with PEmix one. Reaction products curves shift to lower temperatures, resulting in lower melting temperatures compared with PEmix. Another change observed is the phase transition enthalpy (ΔH) and then the material crystallinity. The area under the curve, and consequently the crystallinity, is lower than the PEmix. Taking into account that not PE scission is observed during the reaction, the incorporation of amorphous PS in PE chains introduces irregularities in the PE structure and consequently in the chain order, producing the diminution in melting temperatures and crystallinity degree. It was demonstrated by other authors for PE/PS blends [16, 17] that neither melt blending nor the incorporation of a compatibilizer change the crystalline morphology of PE. In the last case, only the dispersed phase particle size is reduced but the DSC thermograms remain unaltered. In order to quantify the changes detected, the melting temperatures and enthalpies, as well as, the crystallinity degree, are summarized in Table 2 for each reaction product and PEmix. It can be observed, that both, melting temperature and crystallinity decrease as the catalyst content increases. These changes are consequence of copolymer formation. The amorphous branch of PS impedes the PE main chain crystallization and then, the crystal perfection is altered. This conclusion agrees with the decrement observed in the melting temperatures values. Similar results were observed by other authors when analyze the influence of the copolymer formation in the PE crystallization behavior [18, 19].

Table 1. PS weight percent detected by FTIR in reaction products and in soluble and insoluble fractions of Soxhlet extraction.

Sample	PS in the product (wt%)	Extracted mass (wt%)	Soxhlet Extraction	
			PS in IF (wt%)	PS in SF (wt%)
PEmix	-	21.6	-	-
R1	5	31.3	2	11.7
R2	6.4	36.7	3.2	11.5
R3	10	38	5.5	17.5
R4	11	85	7.6	11.5

Table 2. Temperatures and melting enthalpies of polyethylene and reaction products

Sample	Tm (°C)	ΔH (J/g)	Crystallization degree (%)
PEmix	125.42	137.13	47.5
R1	123.94	132.58	45.9
R2	123.09	122.22	42.3
R3	120.77	113.54	39.3
R4	119.8	101.21	35.0

Furthermore the copolymer quantification, a preliminary study of the final properties of the reaction products was carried out. First, the oxygen barrier properties were analyzed. The data of the measurement of the reaction products oxygen permeability compared with pure PE are presented in Table 3. The influence of the copolymer presence, as well as the PS molecules is evident because the permeability decrease as the amount of catalyst increases. The reaction products with 1% of catalyst content enhance their barrier properties in a 22 %, while when 4% of catalyst is used the barrier to the oxygen increase in a 33%. Usually, the increment in

barrier properties in this kind of polymers could be attributed to a decrement in the free volume and/or to the chain mobility. Crystal presence increases the polymer density, decreasing the free volume and then the “oxygen passage” through the film is more impeded because of the “tortuosity” included by the crystallites [20, 21]. In the reaction products, the crystallization degree decreases as the catalyst content increases (see Table 2) because of copolymer molecules with aromatic rings in the pendant chains. Then, the increment in the barrier properties could be just attributed to the incorporation of these aromatic rings that impede the chain mobility and diminish the free volume of the sample. Regarding the experimental results, the last phenomena seem to be more important than crystallinity in this kind of samples. Similar results were reported by Baer et al. [22]

Also, the tensile behavior was investigated. Results of tensile properties from films of reaction products, comparing with pure PE are shown in Table 4. The rigidity of the films increases as the amount of PS increases, as expect. This increment is not dramatically, in R1 around 15% and in R4 25%. However, the films retain their capability to elongate, in all of the cases the sample form the neck and this neck propagates up to around 200% of elongation prior to break. This is a very interesting feature because samples are complex multiphase material. The high values of elongation at break are another indication of the good compatibility of the phases in the material. This is in agreement with the morphology showed in the above section, where the adhesion between PS/PS-g-PE/PE seems to be very good. The increment in the strength is also expected because the presence of the PS-copolymer and/or copolymer microdomains adhered to the PE matrix [23]. Please note that the values compared are the tensile stress at yield at zero slopes. This value is the maximum one for reaction products but not for pure PE. The maximum value in the last case is 11.2 MPa at 585 % of elongation, near breaking.

Table 3. Oxygen permeability measured at 23 °C and 0% of relative humidity of pure PE and reaction products.

Sample	Permeability (cm ³ mil/m ² día atm)
PEmix	8295
R1	6500
R2	6200
R3	5800
R4	5600

Table 4. Tensile properties measured from films of pure PE and reaction products.

Sample	E (MPa)	Strength (MPa)	Elongation at break (%)
PEmix	247.5 ± 15.5	8.3 ± 1.2	590 ± 71
R1	299.7 ± 12.3	9.91 ± 0.6	243 ± 10.1
R2	305.8 ± 25.2	8.96 ± 0.82	201 ± 12.01
R3	344.1 ± 35.1	8.83 ± 0.9	162 ± 36
R4	329.6 ± 10.5	8.6 ± 1.01	133 ± 42

CONCLUSIONS

In the present work a novel method of copolymerization is proposed. Near critical n-heptane is used as reaction medium for grafting styrene onto PE using AlCl_3 as catalyst. It was demonstrated that the copolymer amount increases as the catalyst content increases. The crystallinity of the reaction product decreases respect to the pure PE, indicating the copolymer formation. Also, the copolymer presence increases the oxygen barrier properties without deteriorate so much the mechanical properties of the films.

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