



## Spray process to styrene grafting onto polyethylene film surface for paintability enhancement



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### ARTICLE INFO

#### Keywords:

Film surface modification method  
Styrene grafting  
Spraying  
Polyethylene paintability

### ABSTRACT

A direct and fast post-processing method to modify polyethylene (PE) film surface is proposed in order to improve its paintability performance without changing its bulk properties. This goal is achieved by grafting styrene onto the PE film surface using a macrocarbocationic copolymerization reaction where both catalysts and reagents are sprayed directly on softened film respectively. Pure styrene as grafting molecule and aluminium chloride suspended in n-heptane as catalyst are used. Grafting reaction occurrence was assessed by analyzing the reacted film surface before and after extraction of non-grafted reaction products. The results confirmed by three independent analytical techniques evidence reaction occurrence. A graft-copolymer layer remains onto the PE film surface even when physically adhered reaction products were extracted. This layer enhances PE film water-affinity and paintability either with water or acrylics paints because of the grafted aromatic group and roughness increase. Besides, this modification increments PE thermal degradation temperature giving another beneficial effect for future film applications. The proposed modification film methodology has potential application in continuous film production as reagents spraying onto softened films could be applicable in a cast film extrusion line.

### 1. Introduction

Polyethylene (PE) is the most used polyolefin for both industrial and consumer products because it presents a good cost/performance/sustainability relationship. It is chemically inert, non-polar and hydrophobic in nature and in general, it presents low surface energy. These characteristics limit PE compatibility with polar substrates; e.g., paints, inks and colorants which are really important in one of the main PE applications such as flexible packaging [1]. Indeed, polymer-ink affinity is determined by the polymer surface characteristics where the interaction between them takes place. Thus, compatibility problems are solved by modifying PE surface energy improving paintability, dyeability, and printability, while still retaining its bulk properties; i.e., the desired mechanical, durability, and recyclability ones [2].

Usual methods for surface modification include physics treatments like ultraviolet radiation, corona discharge, flame treatment, plasma, ozonation and chemical treatments such as acid oxidation [3–10]. Up to now, such physical treatments have been automatized in order to enhance their use in industrial production lines, but they are complex, need special expensive equipment and increment final product costs. In addition, a serious problem in surface modification by plasma or corona

treatments is the wetting instability and the hydrophobic recovery that cause the loss of modification effect after certain period of time [11–13]. In this work, a surface modification method with potential to be extended to industrial film production lines is proposed based on surface modification by grafting molecules using spraying technology.

Grafting specific molecules onto film surface is a versatile alternative way to modify film surface characteristics. It allows obtaining tailor functionalization depending on used reagent [14]. On the other hand, spraying techniques are a useful method to introduce reagents on the material surface. In this sense, it is possible to introduce reagents by two or more immediately successive steps performing a modification reaction during calendaring film process, as another stage previous to film complete solidification.

In order to enhance PE surface polarity and consequently film paintability, styrene molecules were selected based on their reactivity and intrinsic polarity to be grafted onto PE softened film. A well-known PS/styrene grafting reaction onto PE is the alkylation via macrocarbocation using a strong Lewis acid as catalyst [15]. In this reaction, a hydrocarbon chain like PE is chemically bonded to the styrene-benzene ring through an aromatic electrophilic substitution. Carrick carried out the reaction in low density PE cyclohexane solution and polystyrene

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(PS) with anhydrous aluminium chloride [16]. He demonstrated that reaction is fast and their product is a PE-g-PS graft copolymer. This reaction was also performed in molten state, mainly for in-situ compatibilization of polyolefins with PS [17–22]. In all of these cases, a graft copolymer is formed at the interfaces of the incompatible PE/PS or polypropylene/PS blends during melt blending using  $\text{AlCl}_3$  as catalyst and styrene as co-catalyst. Copolymer formation was assessed either by enhancement of interfacial adhesion or by chemical evidences. Copolymerization of PE with styrene monomer using macrocarbocation alkylation reaction was also achieved with n-heptane as solvent under near critical conditions [23]. Reaction occurrence was assessed by different analytical techniques. Authors proposed a copolymer architecture where styrene molecules are grafted onto PE chain, forming a PS-g-PE with short PS molecules onto side linear low density polyethylene chains.

Based on previous grafting reaction described above, this work proposes the use of this grafting reaction by reagent and catalysts spraying onto soften PE, thus circumscribing the reaction only to film surface. The main hypothesis that the reaction will occur only on the surface comes from the knowledge that major amount of PE short molecules are on the film surface and they are the most reactive due to their high mobility in soften state [24]. Also, reagents and solvent penetrability could be controlled varying either time or spray drops impact intensity.

In order to assess whether the proposed methodology is appropriate to modify PE film surface and to improve their paintability, a systematic study was performed. Initially, preliminary experiments were carried out to determine reaction conditions, then grafting reaction experiments were performed. Reaction occurrence was determined by comparative analysis using different and independent analytical techniques on PE and reacted films before and after extraction of non-grafted reaction products. The grafting reaction effectiveness and efficacy on paintability with two kinds of paints were evaluated and compared with plasma treatments.

## 2. Experimental

### 2.1. Materials

Films of about 80  $\mu\text{m}$  from Low Density Polyethylene from Dow-Polisor, LDPE 203 (Mw: 229300 g/mol, Mn: 22500 g/mol) were used. Styrene ( $\geq 99\%$  purity) and sublimed anhydrous  $\text{AlCl}_3$  ( $\geq 98\%$  purity) from Riedel-de-Haën were used as graft molecule and catalyst, respectively. N-heptane ( $\geq 99.5\%$  purity) from Cicarelli, and tetrahydrofuran THF ( $\geq 99\%$  purity) from Anedra were used as solvents.

### 2.2. Preliminary studies

Several experiments were performed to analyze different aspects that influence either reaction occurrence or modification method design. Initially, film surface modification temperature was assessed from a fusion behavior study performed in a Perkin-Elmer Pyris I differential scanning calorimeter (DSC). Samples were heated to 180  $^\circ\text{C}$  and kept 3 min at this temperature to remove all prior history. Subsequently, they were quenched to 30  $^\circ\text{C}$  and then reheated to 180  $^\circ\text{C}$ , both steps at a rate of 10  $^\circ\text{C}/\text{min}$ .

On the other hand, experiments summarized in Table 1 were performed to analyze interactions of reagents themselves and with desired final products as well as to determine optimal reaction conditions. Experiments 1–5 were carried out in a heated stirred beaker under atmospheric pressure at 95  $^\circ\text{C}$  during one hour. Experiment 6 was performed in order to analyze the effect of catalyst on PE under the same grafting reaction conditions; a softened PE film surface at around 95  $^\circ\text{C}$  was sprayed with an  $\text{AlCl}_3$ -n-heptane suspension. This sample was sonicated under THF during 2 h (Experiment 7). The last preliminary experiments involve direct styrene onto PE film spraying under the

same conditions of grafting reaction described below (Experiment 8). The goal of this experiment is to study styrene reactions themselves and their interaction with soft PE. This sample was also sonicated under THF in order to extract all PS not chemically bonded to PE (Experiment 9).

### 2.3. Grafting reaction procedure

PE film squares (225  $\text{cm}^2$ ) were surfaced-softened by heating at circa 95  $^\circ\text{C}$ , then sprayed twice. A spray suspension of  $\text{AlCl}_3$  155 mg in 25 ml of n-heptane and 25 ml of pure styrene were consecutively sprayed. A conventional 120° fan nozzle spray equipment connected to a dry air stream at 3 bars was placed 15 cm away from the film surface. Experiments were done at room temperature with a flow rate of 6 ml/min. It is important to note that solvent is evaporated during spraying.

A comparative study and characterization of samples before and after THF extraction (St-g-PE and St-g-PE<sub>THF</sub>) were performed to analyze reaction products. Thus, taking into account that PS could be a reaction byproduct not chemically bonded to PE, the modified films were sonicated for 2 h. in THF to extract not grafted specimens.

### 2.4. Characterization

Interactions between singles reagents as well as reaction products were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Spectra were obtained directly on samples taking 100 accumulated scans in a Nicolet 520-FTIR spectrometer with Attenuated Total Reflection (ATR) mode at 4  $\text{cm}^{-1}$  resolution. All films were also evaluated by FTIR in transmission mode.

Films elemental composition was assessed by Energy Disperse X-ray Microanalysis (EDX) in a JEOL-35CF electron scanning microscope equipped with EDAX DX4 microanalyzer which detects elements from B to U with a surface penetration of 1  $\mu\text{m}$ .

Film surface morphology was analyzed by direct observation with optical microscopy (OM) in a Zeiss Phomi III POL optical microscope (transmission mode) and by scanning electron microscopy (SEM) in a Scanning Electron Microscope Leo EVO-40XVP. In the latter case, samples were previously coated with Au in a sputter coater PELCO 91000. Morphology studies were completed with accurate cross section observations with the same microscopy techniques. For OM observations, samples were cut approx. 90 nm thick in a Leica Ultra-cryomicrotome under liquid nitrogen. For SEM analysis, samples were prepared by direct cryofracture under liquid nitrogen in order to minimize changes in cross section characteristics of modified film.

Film modification effect on overall thermal properties was studied by thermogravimetric analysis (TGA) in a temperature range of 30–800  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were recorded simultaneously using a Discovery TGA equipment from TA Instruments.

Surface affinity to polar substances were evaluated by measuring water contact angle following the drop dimensions method [25–27]. Contact angle is estimated by measuring the water drop radius of known volume laying on film surface using the following equation:

$$\frac{3V}{\pi r^3} = \frac{2 - 3\cos\theta + \cos^3\theta}{\sin^3\theta}$$

where  $V$  and  $r$  are the volume and radius of the drop, and  $\theta$  the contact angle. More than 50 drops of 0.2  $\mu\text{l}$  of doubly distilled water were measured immediately after contact with the surface on each sample with OM. Contact angles values were calculated from the average of three radius per drop and then, averaged again.

A qualitative test of paintability was carried out by painting pure PE, modified PE films and a plasma treated film (oxygen, 150 W, 5 min, 0,001 bar). Two different paints with two different colors were used: a red water based and a blue acrylic one. Paint coverage was naked-eyed

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