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Thierry Vivier

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Grafting: kinetics and distribution influenced by the plastification process

M. Mercier¹, S. Hoppe¹, G.-H. Hu¹, F. Pla¹

B. Jacques², T. Vivier²

- (1) Laboratoire des Sciences du Génie Chimique
1 rue Grandville BP 451-54001 Nancy Cedex France
- (2) CERDATO, Atofina 27470 Serquigny, France

Summary

Grafted polymers are often used in reactive compatibilization [1]. The compatibilizing capacity should depend on the control of the grafting process in terms of yield and grafting distribution [2]. This paper deals with the study of the influence of plastification on the grafting of a monomer onto a polymer backbone. The final objective of this work is to elaborate a predictive model taking into account chemistry and physics, i.e. the plastification phenomena, the grafting efficiency and distribution. This model could be adapted to whatever grafting reaction in a chemical extrusion process.

1. Introduction

In reactive extrusion, the grafting process occurs mainly in the plastification (melting zone) of the extruder [2]. It has been shown that changes in the geometry of the screw profile or in the process variables that affect the plastification rate of the polymer have an impact on the grafting rate and should have one on the grafting distribution. Generally, chemical process models suffer from the absence of description of the plastification. Our purpose is to prove the influence of plastification on grafting efficiency and distribution and to quantify it.

2. Materials and methods

2.1 Chemical system

Polystyrene (PS, Lacqrene Atofina) has been chosen as the polymer to be grafted for its easy characterization and solubility in different solvents. The monomer, *m*-isopropenyl- α,α -dimethylbenzyl isocyanate (*m*-TMI, Aldrich) was grafted onto the polymer chain in the presence of a peroxide, 2,5 bis(*t*-butylperoxy)-2,5-dimethylhexane (DHBP or Trigonox 101, Akzo Nobel), as shown in the figure 1. A mixture of *m*-TMI (6.5% wt) and peroxide (1% wt) was added at different times of PS plastification into an internal mixer (Rheomix Haake 540 p) referring to the grafting of maleic anhydride onto polypropylene [3]. For some reactions, styrene (Aldrich) was added (0.5 mol/mol *m*-TMI) to enhance the grafting yield as shown in the literature [4].

2.2 Analysis techniques

The reaction presented in the figure 2 enables to follow *m*-TMI-grafted function by an UV or fluorescent technique [5]. Differential scanning calorimetry (DSC, Perkin Elmer Pyris 1) measures have been realized to study the reaction between *m*-TMI and modified anthracene (ANT). Moreover, the infra-red spectroscopy can be used to quantify the isocyanate groups during this reaction. The grafting efficiency will then be analyzed by FTIR (Bruker IFS 25) and fluorescence techniques (Spex, Fluorolog-2) and the grafting distribution by Size Exclusion Chromatography (SEC, Waters) coupled with RI and UV detectors. Finally, DSC measurements are used to kinetics studies.

3. Operating conditions

Two different operating conditions of plastification during grafting have been chosen to study its influence on the grafting distribution. Radical grafting of polystyrene initiated by a peroxide was carried out in the internal mixer. The *m*-TMI grafting yield being low (less than 8% wt) under these conditions, the reaction was then carried out in the presence of styrene. The time of introduction of the mixture of peroxide and *m*-TMI into the mixer chamber (during or after the plastification of polystyrene) and the rotors speed were chosen as operating parameters. Table 1 summarizes the experimental conditions.

Experiments	Peroxide + m-TMI +styrene (g)	PS (g)	Presence of styrene	Time of mixing of PS before reaction (min)	Reaction time (min)
Case 1 n1, n2	3,6	42	no	9	10
Case 1 n3	5,6	40	yes	9	10
Case 2 n4	5,6	40	yes	0	10
Case 2 n5, n6	3,6	42	no	0	10

Table 1: Operating conditions

Case 1 represents the following conditions: plastification of PS before the beginning of grafting, N= 70 rpm as rotors speed and a reaction temperature T= 180 °C. Case 2 corresponds to a rotors speed of 20 rpm and a simultaneous introduction of all reactants at T= 180°C.

4. Results and discussion

The DSC results concerning the reaction between m-TMI and anthracene show that this reaction is quantitative and takes only 90 minutes using trichlorobenzene as solvent, at room temperature. Indeed, isothermal tests were made at three temperatures (80, 120 and 180 °C) and at four molar ratios ($n_{\text{ANT}}/n_{\text{m-TMI}} = 0.5, 0.85, 1$ and 1.8). The analysis of the DSC curves leads to the conversion curves versus time and the kinetic parameters. The rate constant is equal to 1.4 l/mol/min at 20 °C. So, each grafted m-TMI will be linked to a fluorescent group.

The grafting rates were found between 8 and 18% depending on the plastification conditions. The optimal conditions are obtained when all reactants are introduced together in the mixer. The higher grafting yield is obtained in the presence of styrene as shown in the table 2. The SEC measurements reveal a decrease of the molecular weight with grafting which proves that degradation occurs. The weight average molecular weight of the PS are 310 000 g/ mol and 220 000 g/mol respectively before and after grafting.

Experiments	Grafting (mol _{ANT} / mol _{PS})
Case 1 n1, n2	0.9
Case 1 n3	2.8
Case 2 n4	4
Case 2 n5, n6	1.3

Table 2: Grafting efficiency

The grafting distribution results present a constant molecular weight distribution curve for all grafted PS but different grafting distribution curves as shown in the figure 3. These curves are bimodal distributions whatever the plastification conditions. The first peak around 1000 g/mol must be due to the existence of polymerization and copolymerization of styrene and m-TMI. The second peak around 100 000 g/mol confirms the influence of plastification on the grafting distribution and underlines the improvement of grafting in the presence of styrene (cf experiment n4).

5. A global model

A global model is being developed now coupling the kinetic and plastification models. The different competitive reactions occurring during grafting reaction are: styrene and TMI polymerizations, copolymerization, styrene and TMI graftings, styrene depropagation and PS degradation. The DSC study of each individual reaction and a kinetic scheme will enable to reach the kinetic parameters. The plastification kinetics will be determined by rheological measurements under different shear rates and high temperatures conditions related to the internal mixer parameters and grafting experiments. An experimental design has been realized in the internal mixer to validate the model.

6. Conclusions and Perspectives

This article reveals the influence of the plastification rate on the chemical results during a grafting process -i.e. grafting efficiency and distribution- and underlines that styrene improves grafting. The global model is being developed to quantify plastification during a grafting

process. Finally, the study will be extended to industrial grafting reactions such as maleic anhydride grafting onto polypropylene.

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