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Polypropylene Grafting in Supercritical Carbon Dioxide

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ABSTRACT

Polypropylene (PP), one of the most widely low-cost commodity polymers, has a hydrophobic nature which prevents its use from a large variety of applications. Functionalisation, through free radical grafting of polar vinyl monomers offers an effective route towards higher added value applications especially for environmental remediation, wastewater treatment, and hydrometallurgy.

Classic processes for the modification of polypropylene by polar monomers includes reactive extrusion in the molten state and chemical reaction in the solid-state as well as in liquid solvents. Recently, the use of supercritical carbon dioxide (sc-CO₂) has appeared as an innovative and interesting medium because of its environmentally friendly characteristics and its properties of sorption, swelling and foaming of polymers.

In this study, PP was put in an autoclave in different forms: pellets, fibres or powders. Vinylbenzyl chloride (VBC) was added along with benzoyl peroxide as initiator of the polymerisation. The autoclave was filled with CO₂, pressurised and let for a certain amount of time under controlled pressure and temperature. After opening, the swollen polymer was washed with acetone, analysed by infra-red spectroscopy and the chlorine content was determined. When there is sufficient chlorine the samples were used for further modification with a phosphate ligand in order to perform metal ions complexation from water solutions.

Microphotographs as well as infra-red spectra show clearly that effective grafting with covalent binding is obtained under sc-CO₂ conditions not only at the surface but also into the pellets. It also appears that the reaction is more complete when polypropylene has previously been pulverised. This may come from a larger surface area on one hand and a different crystalline ratio on the other hand.

A two-step process, one aimed at the polymer swelling and the second aimed at the grafting has been successfully compared to the single step process. The influence of several operating parameters was tested: duration of the experiments, pressure and temperature, peroxide content and VBC/PP ratio.

After reflux treatment with triethyl phosphite, the best result achieved was a phosphorus elemental analysis of 1.25 mmol/g. This value shows that a high degree of polymerization has been reached and that the polyVBC is grafted on the PP chains, rather than coated on the surface.

The next study will deal with the capacity of such grafted PP samples to remove heavy metal ions from wastewater.

INTRODUCTION

Water is the one commodity on which life on Earth most depends yet it is one that has been taken for granted and used as a waste repository throughout our history. With the advent of the Industrial Revolution, pollution of our waterways has quickened to the extent that it is difficult to find any body of water that has not been impacted by human activity. This now includes the aquifers, rivers, and lakes on which much of humanity relies upon for its drinking water. Purification of water in the environment is thus one of the most pressing problems facing all countries today. The conventional techniques for removing contaminants from water are insufficiently selective for removing the lethal yet low amounts of contaminants such as lead, mercury, and cadmium metal ions. There is thus a need to develop methods to remove contaminants from water and to do so in a cost-effective manner.

This paper describes a preliminary study aimed at producing a low-cost and accessible process for producing a plastic filter to be used in the removal of toxic metal ions from water in the environment. The filter will be a modified polypropylene (PP) membrane. Polypropylene is one of the most widely low-cost commodity polymer. However, its hydrophobic nature prevents its use from a large variety of applications. To overcome

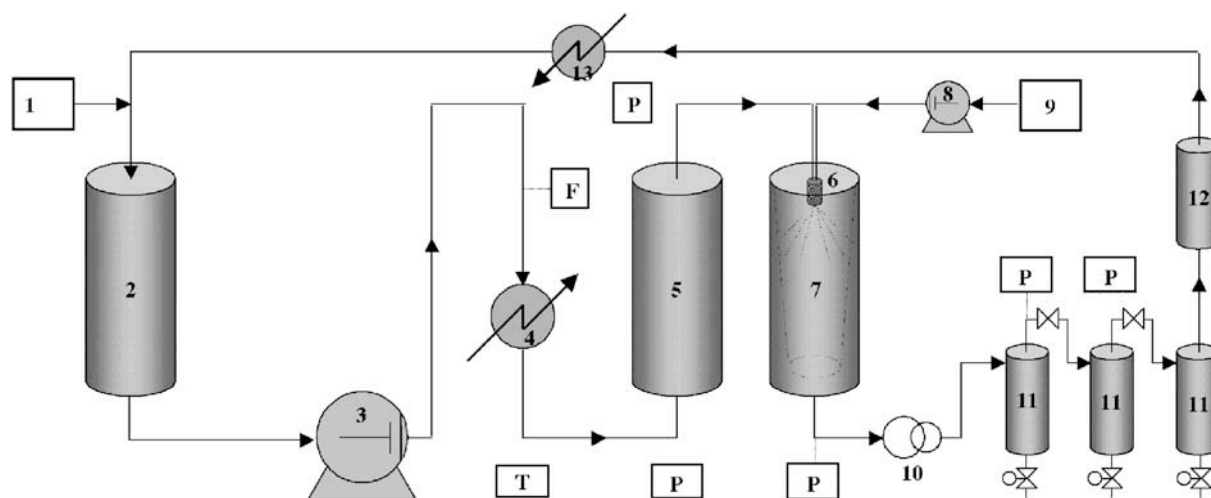
these limitations free radical grafting of polar vinyl monomers offers an effective route towards higher added value applications. This functionalisation, opens a larger compatibility spectrum of the polyolefin with hydrophilic systems.

The modification of PP with polar ligands will permit a new level of applicability to environmental remediation, wastewater treatment, and hydrometallurgy. In these applications, polymers are often applied as beads (ion-exchange or chelating resins) requiring a flow of the aqueous stream through a column. The modification of PP will now permit the preparation of a wide range of ion-selective membranes for applications in which flow through membranes is preferred over flow through a column of beads.

Classic processes for the modification of polypropylene by polar monomers includes reactive extrusion in the molten state and chemical reaction in the solid-state as well as in liquid solvents. Recently, the use of supercritical carbon dioxide (Sc-CO₂) has appeared as an innovative and interesting medium because of its environmentally friendly characteristics and its properties of sorption, swelling and foaming of polymers. This paper describes a method which utilizes supercritical CO₂ in the modification of polypropylene and then further modify this polymer with ion-selective ligands for application to environmental remediation.

MATERIALS AND METHODS

The experiments were carried out in a multifunctional high-pressure pilot plant (Separex Champigneulle, France). A flowsheet of the apparatus is shown on figure 1. Carbon dioxide is cooled and stored in a liquid CO₂ storage tank (2). It is put in motion and pressurized by a membrane pump (Lewa, Germany) (3). In this study, PP was put in a 500 mL autoclave (5) in different forms: pellets, fibres or powders. Vinylbenzyl chloride (VBC) was added along with benzoyl peroxide as initiator of the VBC polymerisation. The autoclave was then filled with CO₂, which was previously heated by passing through a heat exchanger (4) to become supercritical until the desired pressure was reached. The pressurised autoclave was let for a certain amount of time under controlled pressure and temperature.



- | | | |
|---|--------------------------------|-----------------|
| 1 : CO ₂ feed | 7 : Particule formation vessel | 13 : Condenser |
| 2 : Liquid CO ₂ storage tank | 8 : Liquid pump (SAS) | F : Flowmeter |
| 3 : Membrane pump | 9 : Solution (SAS) | P : Manometer |
| 4 : Heater | 10 : Back pressure regulator | T : Thermometer |
| 5 : Extractor | 11 : Cyclonic separators | |
| 6 : Nozzle | 12 : Adsorption bed | |

Figure 1 – Experimental set-up for the polymer grafting experiments under supercritical carbon dioxide

After opening, the swollen polymer was washed with acetone, analysed by FTIR spectroscopy and the chlorine content was determined. When there is sufficient chlorine the samples were used for further modification with a phosphate ligand (triethyl phosphite) in order to perform metal ions complexation from water solutions. Scanning Electron Microscopy (SEM) was also used to visualise the processed polymer.

RESULTS

SEM microphotographs as well as FTIR spectra show clearly that effective grafting with covalent binding is obtained under sc-CO₂ conditions not only at the surface of PP pellets but also into the pellets.

A two-step process, one aimed at the PP swelling and the second aimed at the grafting has been successfully compared to the single step process. In a typical experiment using this approach, polypropylene (PP) pellets (2 mm diameter) were added into a reactor with a volume of 500 mL along with vinylbenzyl chloride (VBC, 10 mL per 2 g PP) and benzoyl peroxide (BPO, 1% based on monomer weight), supercritical CO₂ (scCO₂) was introduced at an initial pressure of 12 MPa and contacted with the reactants in two steps:

- 2 h at 35°C followed by
- 18 h at 80°C.

The reactor was then cooled, the pellets washed extensively with acetone, and dried. The extent of grafting was followed by ATR (the band at 1265 cm⁻¹ is due to C-Cl).

Figure 2 shows the spectrum obtained.

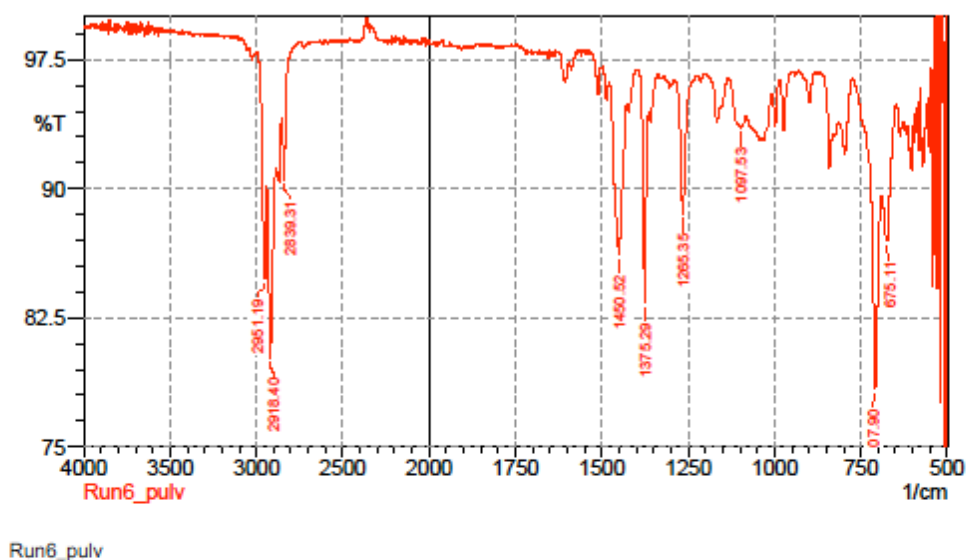


Figure 2. Polypropylene fiber processed with sc-CO₂

The influence of several operating parameters was tested: duration of the experiments, pressure and temperature, peroxide content and VBC/PP ratio. This series of experiments with varying conditions proved the feasibility of the modification.

Most importantly, the polyVBC was permanently bound as shown by converting the -CH₂Cl moieties into phosphonic acid -CH₂P(O)(OH)₂ by reflux treatment with triethyl phosphite. On figure 3 below, the ATR spectrum shows the broad region around 1103 cm⁻¹ which is representative of the phosphonic acid moiety. The phosphorus capacity of 1.25 mmol/g is indicative of a high level of grafting. This value is quite significant,

indicating that the degree of polymerization is high, the polyVBC is grafted on the PP chains, rather than coated on the surface.

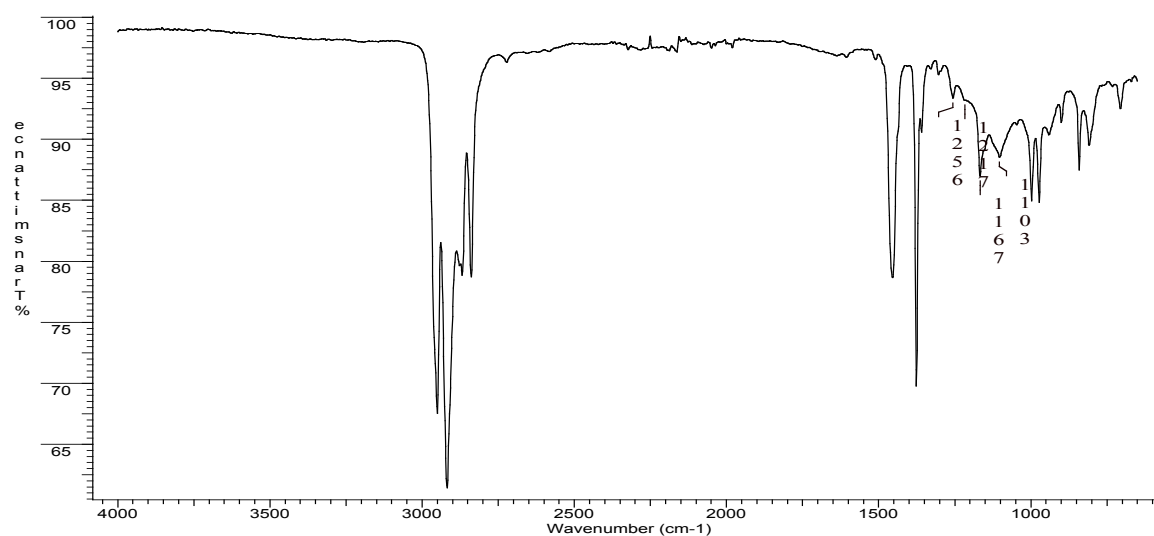


Figure 3. Polypropylene fiber modified with phosphonic acid ligands: phosphorus capacity of 1.25 mmol/g

It also appeared that the reaction is more complete when the PP has previously been pulverised. This may come from a larger surface area on one hand and a different crystallinity ratio on the other hand.

CONCLUSION AND PERSPECTIVES

These first promising results led us to define what could be the next experiments to achieve.

Our specific objective is now to determine the conditions that permit a high degree of modification of polypropylene (PP) with vinylbenzyl chloride (VBC) using supercritical CO₂ as the solvent and benzoyl peroxide (BPO) as the initiator. A unique feature of this research will be the preparation of membranes with higher degrees of modification than previously achieved with BPO by focusing on the swelling time with scCO₂, its initial pressure, and the ratio of VBC to scCO₂. The most novel aspect of this research is that, once polypropylene is successfully grafted with polyVBC, the polymer chains will be modified with ion-selective ligands using chemistry that we have established from research on polymer beads, and then the membranes utilized for the detoxification of environmentally critical bodies of water such as sources of drinking water.

The general objective of this study is to prepare ion-selective polypropylene membranes in a cost-effective manner that can be used for the removal of toxic metal ions from rivers, groundwater, and other sources of drinking water.

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