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The FT-IR studies of the interactions of CO_2 and polymers having different chain groups

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Abstract

A Fourier transform-infrared spectroscopy (FT-IR) set up has been successfully modified in order to characterize different polymeric materials under sub- and supercritical CO_2 conditions. Polymers used in this study are polyesters (P120 and P130), poly(ethylene glycol) (PEG) and polyphenylene oxide (PPO). Analysis of the corresponding spectra shows evidences of weak interaction (Lewis acid–base) between CO_2 and polymers. In particular, shifts to higher wavelengths of the maximum absorption of chain groups of the polymer and the modification of the absorption band of CO_2 represent a qualitative evidence of such interactions. Analysis of CO_2 absorption bands allowed ranking of the polymeric materials according to interaction strength with CO_2. In general, polymers with ether group display higher interaction strength than polyesters. The effect of the dissolved CO_2 on the depression of the melting point, T_m or the glass transition temperature, T_g can also be studied using the FT-IR depending on the enhancement in the free volume. The shape of the spectrum in PEG, unlike the other polymers, was completely modified above the critical pressure (7.38 MPa).

Keywords: FT-IR; CO_2; Polyesters; Poly(ethylene glycol); Polyphenylene oxide

1. Introduction

Nowadays, CO_2 has become a potential solvent for various polymer applications in polymer processing as well as polymer synthesis [1–3]. An inert nature and a low cost due to its abundance in the atmosphere are the most attractive advantages of CO_2 as a solvent. The dissolved CO_2 in a polymer reduces the viscosity and allows the process or the synthesis to be carried out at a lower temperature. It makes the process or the synthesis less energy consumptive. In the applications, the solubility of CO_2 in a polymer is the vital parameter for its selection as a solvent. The higher the solubility of CO_2 in a polymer, the higher is the reduction in the viscosity. The solubility represents the amount of the CO_2 that can be dissolved at equilibrium conditions. The solubility measurement data of various polymer–CO_2 systems are well described in the literature [3]. The available data have mostly been interpreted thermodynamically in terms of the effect of temperature and pressure on the solubility of CO_2 in a polymer.

Earlier, it was a general notion that the CO_2 solubility in a polymer is a function of pressure and temperature only. In fact, the amount of dissolved CO_2 varies from one polymer to another even at the same conditions. The specific intermolecular interaction between CO_2 and polymer is responsible for the different solubility. The nature of interaction present between CO_2 and a polymer is mostly of a Lewis acid–base kind. Fourier transmission infrared spectroscopy (FT-IR) is a powerful tool to study such interactions [4–11]. Albeit CO_2 lacks a dipole moment, it has a large quadrupole moment and both Lewis acid and base sites. In CO_2, a Lewis acidity results from the electropositivity of the carbon atom due to deficiency of electron density compared to the oxygen atoms. Thus, an electron acceptor–donor interaction is present when CO_2 is contacted with a polymer containing Lewis base sites. Few authors have revealed the specific intermolecular interactions between CO_2 and different polymers by carrying out IR spectroscopy studies.

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The FT-IR spectra of cellulose acetate (CA) and poly(methyl methacrylate) (PMMA) in the presence and the absence of CO_2 were recorded by Fried and Li [4]. In the study, the carbonyl stretching vibrations for CA and PMMA were shifted to higher wavenumbers in the presence of CO_2. Since the observed shifts were rather small, dipole–dipole interactions between the CO_2 and the carbonyl groups were suggested instead of the Lewis acid–base interactions. Later on, Kazarian et al. [6,7] also used FT-IR to study the intermolecular interactions between CO_2 and polymers. They used the bending mode (ν_2, around 660 cm^{-1}) of CO_2 to show the interactions with the polymers. In case of polymers containing carbonyl group, e.g. PMMA, splitting of the ν_2 was observed. The splitting is due to the Lewis acid–base interaction where the carbonyl group act as an electron donor and CO_2 act as an electron acceptor. No such splitting has been reported for the polyethylene (PE) and polystyrene (PS). The reason is the absence of carbonyl group in PS as well as PE. However, some distortion of the ν_2 was observed only in PS. This is due to the interaction between CO_2 and the phenyl ring in PS. Meredith et al. [8] also used FT-IR spectroscopy to test the intermolecular interaction of CO_2 with different Lewis bases: triethylamine (TEA), pyridine (PYR), and tibutyl phosphate (TBP). In case of PYR, a base having phenyl ring, no splitting was observed similar to PS and PE. Recently, both the antisymmetric stretching mode (ν_2) and the ν_2 of CO_2 were used to show the intermolecular interaction between PMMA, PS or polycarbonate (PC) [12]. The recorded spectra for the ν_2 of CO_2 in case of PMMA and PS has shown similar results, as explained earlier. In case of the ν_2 of CO_2 for PMMA and PC, an absorption band having a weak shoulder appeared in the spectra. The width of the absorption band was larger in PC compared to PMMA. Both the carbonyl groups as well as the benzene rings present in PC provide more sites for CO_2 molecules as compared to PMMA. In PS the recorded absorption band was not comparable, in terms of width, to those observed for PMMA and PC. In PS, the interactions are present only between CO_2 and the aromatic rings. These interactions are weaker than the ones present between CO_2 and carbonyl groups in PMMA and PC.

In this study, we have modified a golden gate FT-IR setup, generally used at an ambient pressure, to a high pressure FT-IR setup. The main aim of the study is to reveal the intermolecular interactions between CO_2 and polymers having different chemical groups along the main chain. The chemical groups, which are studied here include ester, ether and aromatic ring. The CO_2 bending mode has been studied for all the polymers to reveal the interactions as significant changes can be expected in it due to Lewis acid–base nature.

2. Experimental

2.1. Materials

Propoxy based (P120) and ethoxy based (P130) polyester (CAS:177834-94-5 and 170831-75-1) resins having molecular weights: Mw-7000 and Mw-20000 were supplied by Akzo Nobel, The Netherlands. Chloroform ($CHCl_3$) and poly(ethylene glycol) (PEG) having Mw-6000 were purchased from Aldrich, The Netherlands. Polyphenylene oxide (PPO) of Mw-20000 was supplied by GE Corporations, The Netherlands. Glass transition temperature or melting points (T_g or T_m) of the polymers are provided in Table 1. High purity CO_2, 99.99%, was used in the FT-IR experiments. The materials were used without any purification treatment.

Table 1
Glass transition temperatures of different polymers

Polymers	T_g or T_m (K)
P120	327.15
P130	330.15
PEG	331.15
PPO	503.15

2.2. Apparatus

2.2.1. A low pressure FT-IR set up

For spectroscopic measurements in the presence of CO_2, the existing FT-IR golden gate apparatus was modified to a high pressure FT-IR set up. The golden gate apparatus is generally used to record spectra of a solid or molten material, which is usually provided in the form of a film or powder. Due to better uniformity a film rather than powder is preferred. The film is kept on the surface of the crystal (Quartz) mounted in the heating plate in conjunction with a temperature controller. The temperature of the material is raised using a heating plate in order to record the spectra of a molten or solid material. The maximum temperature to which crystal can be heated is 473.15 K. For the better contact of the solid film with the crystal, a groove–bolt arrangement is provided to apply a certain force on the film. The CO_2 absorbance becomes too high at higher pressures if the crystal of long path length is selected. Therefore, the ATR (attenuated total reflection) IR spectroscopy with FT-IR transmission was used in the study. The ATR spectroscopy provides the path length of only several micrometers [13].

2.2.2. Modified FT-IR set up

The schematic of the high pressure FT-IR unit is shown in Fig. 1. The high pressure unit consists of a golden gate FT-IR apparatus (Spectrum 2000, Perkin-Elmer, UK), the CO_2 cylinder, a high pressure syringe pump (Isco, USA), a high pressure cell and valves. The high pressure cell, tubes and valves are made of stainless steel. The high pressure cell was built up in the group, University of Groningen (The Netherlands). The same groove–bolt arrangement was used to ensure the good contact of an O-ring with the cell as well as the surface. The O-ring between the cell and the surface of the plate makes the system completely leak-proof. Using the groove–bolt arrangement the force is transferred from the cell to the O-ring by tightening the bolt. The cell can withstand pressures up to 10 MPa. CO_2 inlet and exit lines are