Two-Dimensional ATR−FTIR Spectroscopic Investigation on Water Diffusion in Polypropylene Film: Water Bending Vibration

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Received: September 16, 2002; In Final Form: February 12, 2003

Two-dimensional (2D) correlation ATR−FTIR spectroscopy was used to study the dynamic diffusion behavior and state of water in syndiotactic polypropylene (S-PP). The 2D asynchronous spectra of water bending band clearly reveal that there are three separate bands in the $1800-1500$ cm^{-1} region. These three bands at 1676, 1645, and 1592 cm^{-1} are assigned, respectively, to the aggregated water with strong hydrogen bond, the aggregated water with moderate strong hydrogen bond, and the "free water". On the basis of this approach, the following mechanism for the diffusion process of water in S-PP has been proposed: the aggregated water molecules first diffuse into the polymer during the diffusion process. The water molecules with strong hydrogen bond will diffuse slower than water with moderate strong hydrogen bond because of their large size. In the late stage of the diffusion process, some aggregated water molecules in the PP matrix are forced to dissolve into the "free water" form.

1. Introduction

Recent studies have highlighted the process of water diffusion in polymeric materials,[1−5] in large part due to the important role the diffusion behavior in the polymers plays. It is well-known that polymeric materials have been widely used in the ambient environment, and water is probably the most common and important diffusant. For example, polypropylene (PP) may be substituted for glass as primary packaging for various products for clinical use, transport, and waste handling. PP is known to have low water permeability when compared to other plastics such as polystyrene, polycarbonate, low-density polyethylene, etc. However, the diffusion of water through the PP plastic wall will gradually concentrate the constituents in liquids during long-term storage and is often the shelf life limiting parameter for chemically stable aqueous solutions in PP bottles.

Several spectroscopic techniques such as NMR,[6−8] neutron scattering,[9−11] FTIR, and Raman[12,13] are applied to investigate the diffusion process in polymers. Changes of frequency, intensity, and shape have been interpreted in terms of the different species of water molecules in water/polymer systems.[14−16]

Among these spectroscopic techniques, the ATR−FTIR technique is especially widely used to study the various diffusion behaviors. For example, Scholtter and Furan reported the diffusion of additives in polyolefins and attempted to relate the infrared absorbance of the additives to their mass uptake;[17] Barbari and Fieldson have studied the diffusion of water in polyacrylonitrile, acetone in poly(methyl methacrylate), and methanol in polystyrene;[1,18,19] Balik et al. conducted real-time measurements with the ATR technique to measure diffusion of CaCO$_3$ out of paint films exposed to sulfurous acid;[20] and Van Alsten et al. used ATR to study the polymer−polymer interdiffusion.[21] The wide application of the ATR−FTIR technique is because the spectra are measured in situ so the data are accurate and reproducible data of high quality can be obtained.

In the present contribution, ATR−FTIR is used to study the water diffusion process in a syndiotactic polypropylene (S−PP) film. As Marechal has pointed out,[12] the spectra obtained using ATR−FTIR are free from artifacts, a major problem when studying water by IR spectroscopy. Therefore, ATR−FTIR spectroscopy is an excellent tool for probing the dynamic diffusion behavior of water through the films.

Another technique used in this work is a recently developed spectroscopic technique based on two-dimensional (2D) correlation analysis. The 2D-IR technique, originally proposed by Noda,[22−25] has received great attention in many areas, such as biological sciences,[26−28] materials science,[29,30] and especially in polymer science.[31−34]

Owing to the function of 2D-IR technique to identify the number and peak position of underlying bands in an original band shape, it is usually viewed as a useful tool to aid in the interpretation of complex one-dimensional (1D) spectra, especially spectra with broad, multiply overlapped bands commonly encountered in vibrational spectroscopy.[35,36] Thus, certain spectral features not readily observable in conventional 1D spectra can be easily obtained from 2D spectra. It can also probe the specific order of certain events taking place with the development of a controlling physical variable. The usefulness of 2D-IR technique in this work is that it gives a new possibility to analyze the molecular interactions formed between the penetrant and the polymer matrix, as well as structural changes of the water-related hydrogen bond during the diffusion process.

A typical spectrum during the water diffusion process in a PP film is illustrated in Figure 1. Information about the change of the hydrogen bond of water during the diffusion process is expected from the analysis of the spectral regions characteristic of the O−H bands. The O−H vibrational modes of water lead to a very complicated vibrational spectrum, complicated by both intermolecular and intramolecular hydrogen bonding. The fundamental stretching mode and in-plane bending mode occur within the $3900-2800$ cm^{-1} region and at around 1640 cm^{-1}, respectively. In most of the published papers, the discussion was focused on the $3900-2800$ cm^{-1} spectral region, where

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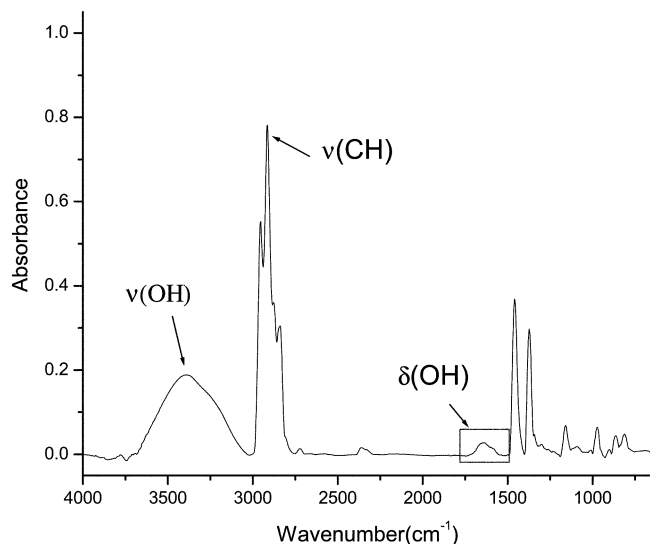
Figure 1. ATR−FTIR spectrum of sorbed water in S-PP in the range 4000−650 cm^{-1}.
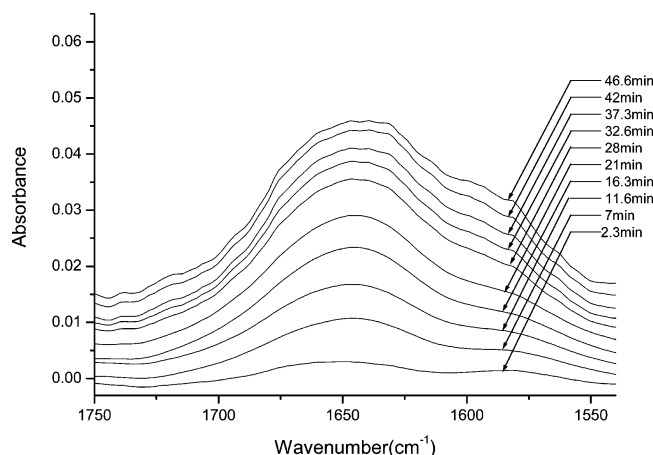

Figure 2. ATR−FTIR spectra of O−H bending band in the range 1750−1540 cm^{-1}.

the peaks are considerably more intense and free of overlapping. In contrast, the bending mode of water (δ(OH)) is usually less intense and often overlapped with the bands assigned to the polymer. However, the O−H stretching modes of water are complicated by symmetric and antisymmetric coupling,[37] which sometimes makes the results of 2D-IR spectroscopy difficult to interpret.

One δ(OH) band is assigned strictly to one distinct species of water molecules present in the investigated water/polymer system.[38] And in the PP/water system, S-PP has no absorption bands in the region of the bending band of water so that the IR spectra in the bending band region are available. (Figure 2) Thus, the water bending mode is an even better alternative (compared to the relatively complicated stretching mode) to differentiate the species of water molecules in this mixed system.

2. Experimental Section

2.1 Materials and Film Preparation. Syndiotactic polypropylene (S-PP) particles are commercial products. The S-PP particles were dissolved in xylene at 100 °C at a concentration of 2% (m/v). Then the solution was cast onto a 75 mm × 25 mm microscope slide. Immediately after casting, the slide was transferred to a vacuum oven. The slide was kept in the vacuum oven at room temperature for about 24 h to remove the residual solvent. The film was then scored around the edges and floated
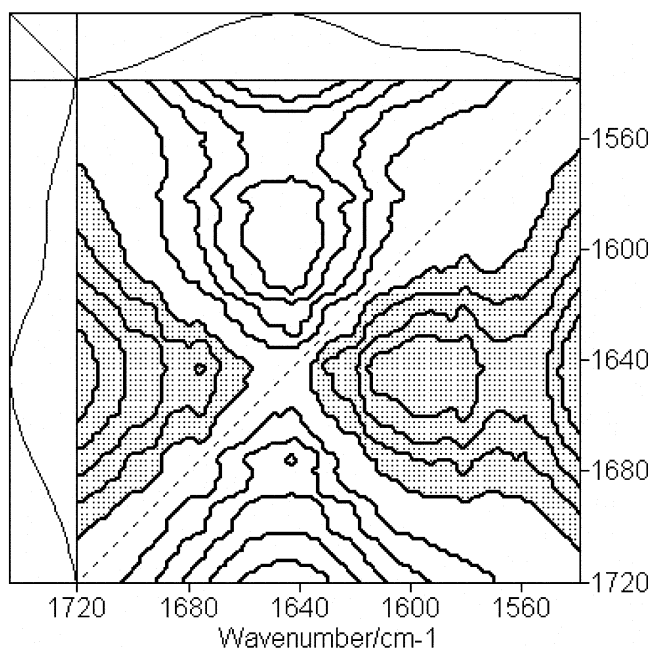

Figure 3. Asynchronous 2D correlation spectra of water bending band in the range 1720−1540 cm^{-1}.

on the surface of double distilled water, from which it was picked up, blotted with filter paper, dried at 70 °C in a clean oven for 24 h to remove the sorbed moisture, and stored over desiccant until required.

2.2 Diffusion Measurements by Time-Resolved ATR−FTIR. All time-resolved ATR−FTIR measurements were carried at 26 °C using a Nicolet Nexus Smart ARK FTIR spectrometer equipped with a DTGS detector, solid cell accessories, and a ZnSe IRE crystal. The IRE crystal covered by the sample film with a filter paper on it was mounted in an ATR cell, and distilled water was then injected into the filter paper while starting the data acquisition using a macro program. The spectra were collected at a resolution of 4 cm^{-1} with 16 scans. The time interval between two successive spectra was about 2.5 min. The original measured wavenumber range was 650−4000 cm^{-1}, however, for the 2D correlation analysis, only the spectral range 1750−1540 cm^{-1} (O−H bending) was used. All the original spectra were baseline corrected under assumption of zero absorbance at 1750 and 1540 cm^{-1} using Omnic 5.1 software.

2.3 Two-Dimensional Correlation Analysis. The first five spectra in Figure 2 at equal time intervals were chosen for 2D correlation analysis. The software for two-dimensional correlation analysis in the present study is 2D Pocha, composed by Daisuke Adachi (Kwansei Gakuin University). The time-averaged 1D reference spectrum is at the side and top of the map. In the 2D correlation maps, unshaded regions are defined as the positive correlation intensities, whereas shaded regions are defined as negative ones.

3. Results and Discussion

Figure 3 shows the 2D asynchronous correlation spectra of the water diffused in S-PP in the spectral range 1500−1800 cm^{-1}. The appearance of an asynchronous cross-peak $\Psi(\nu_1/\nu_2)$ indicates that the bands ν_1 and ν_2 vary out of phase with each other during the diffusion process. So the existence of the two cross-peaks (1676/1645, 1645/1592 cm^{-1}) in the upper left triangle in Figure 3 shows that the water bending band is split into three separate bands located at 1676, 1645, and 1592 cm^{-1}. This result indicates the existence of three different states of

water in the S-PP film during the water diffusion process. In contrast with O−H stretching vibrations, the O−H bending vibrations in water are predicted to exhibit sequential blue shift with the increasing strength of the hydrogen bond.[39−41] Thus, the band at 1676 cm^{-1} indicates that water molecules aggregate together with strong hydrogen bonding (Type I water, hereafter); the band at 1645 cm^{-1} reveals the water molecules cluster with moderately strong hydrogen bonding (Type II water, hereafter); and the band at 1592 cm^{-1} can be attributed to the water molecules approximately without hydrogen bonding, and in this work, it will be called "free water" for simplicity (Type III water, hereafter) (In fact, this kind of water interacts with each other with very weak hydrogen bonding; the hydrogen bond is so weak that this kind of water is just like free water).

According to the rules of Noda,[22] the positive asynchronous bands at 1645/1592 cm^{-1} in the left upper triangle indicate that Type II water (1645 cm^{-1}) varies prior to Type III water (1592 cm^{-1}). The negative asynchronous bands at 1676/1645 cm^{-1} reveal that the change of Type II water occurs earlier than the change of Type I water (1676 cm^{-1}). And in Figure 3, we also can find the band at 1592 cm^{-1} varies later than the band at 1676 cm^{-1}.

From some published papers, in pure water almost all of the water molecules are proposed to exist in the state of hydrogen-bonding water.[42,43] In this system, aggregated water molecules will first diffuse into the S-PP film gradually, but Type I water has significantly lower diffusivity than Type II water because of its larger size. Because of the deeply hydrophobic characteristic of S-PP, with the increasing content of water molecules diffusing into the polymeric matrix more and more water is confined in the S-PP network and the motion of water molecules is more restricted than before. To continue the diffusion process in the film, some water molecules may be isolated and the interactions between them weaken. Thus, in the late stage of water diffusion, some hydrogen bonds may be weakened or broken and part of the hydrogen-bonded water will be forced to dissolve into Type III water. The free water is assumed to be in dynamic equilibrium with the aggregated water. That is, the increase of the free water population occurs only after the hydrogen bonded water permeated into the polymer bulk. In conclusion, Type II water diffused prior to Type I and Type III water, and the Type III water was the last one diffusing to the polymer side contacted with the ATR element.

4. Conclusion

The results presented here demonstrate that the diffusion of water molecules in polymeric materials can be successfully studied by ATR−FTIR spectroscopy. The dynamic information and the state of water molecules during the water diffusion process can be well explained from the analysis of 2D-IR spectra in the water bending mode.

In 2D correlation spectra, the original wide water bending band is found to split into three separate bands, elucidating that there are three states of water in S-PP during the diffusion process. One state is called "free water", which locates at 1592 cm^{-1}; another is the aggregated water with moderately strong hydrogen bonding, and it locates at 1645 cm^{-1}; and the last state is the aggregated water with strong hydrogen bonding and it is located at 1676 cm^{-1}. Furthermore, in the water diffusion process, the hydrogen-bonding water diffused into the polymer first. The water with strong hydrogen bonding diffused slower than the water with moderately strong hydrogen bonding. And the "free water" was formed after some of the aggregated water dissolved into the isolated water molecules in the S-PP film. Therefore, the sequence of three states of water molecules

diffusing to the polymer surface contacted with the ATR element is as follows: aggregated water with moderately strong hydrogen bond → aggregated water with strong hydrogen bond → "free water".

References and Notes

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