

Infrared and SFG Studies on Hydrogen Bonding Interaction between Poly(acrylate) and Bisphenol A

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The miscibility of polymer blends strongly depends on the physical and chemical interactions between the polymers.^{1,2} Hydrogen bonding is one of the important chemical interactions in the polymers with electron acceptor and donor groups. In the present study, the hydrogen bonding in the blends of poly(2-methoxyethyl acrylate) (PMEA), which is promising biomaterial with excellent blood compatibility,³⁻⁵ and bisphenol A (BPA) have been investigated by infrared reflection absorption spectroscopy (IRRAS).^{6,7} These results have been discussed in comparison with the hydrogen bonding behavior on the PMEA surface observed by sum frequency generation (SFG),⁷⁻⁹ which is an intrinsically interface-sensitive vibration spectroscopy technique,^{10,11} after immersion in a BPA solution.

PMEA ($M_w \sim 8.5 \times 10^4$) was synthesized by the radical polymerization.³ PMEA and BPA were blended in methanol with different ratios. The polymer blends were deposited on the solid substrates by casting. IRRAS spectra were recorded by coadding 32 interferograms with a grazing angle reflection kit using a Bio-Rad FTS 575C FT-IR spectrometer. The SFG system using a tunable broadband infrared pulse ($3700 \sim 1000 \text{ cm}^{-1}$, 200 cm^{-1} fwhm) and a narrow-band visible pulse (800 nm , $< 10 \text{ cm}^{-1}$ fwhm) has been described elsewhere.¹²

Figure 1 shows IRRAS spectra of the polymer blends on Au surface, in the frequency region of (A) O-H stretching ($3700 \sim 3100 \text{ cm}^{-1}$) and (B) C=O stretching ($1800 \sim 1650 \text{ cm}^{-1}$). IRRAS spectra of deuterated polystyrene (dPS) blended with BPA (9 %) were also given for comparison (Fig. 1b). A strong peak was observed at 1740 cm^{-1} for pure PMEA (Fig. 1B(a)) and can be assigned to C=O stretching of the carbonyl group in PMEA film. In the BPA/dPS blend, this peak was not observed while two broad bands were identified around 3340 and 3530 cm^{-1} (Fig. 1b). As extensively investigated in previous work, these two peaks can be assigned to the OH stretching of multimers and dimers of hydroxyl group in BPA, respectively.^{1,2}

As BPA was blended into PMEA, a new peak was clearly observed at 1715 cm^{-1} . This peak can be attributed to the C=O stretching of the carbonyl group in PMEA hydrogen bonded to the hydroxyl group in BPA. This peak increased with BPA contents in the blends. Detailed analysis shows a new component at 3430 cm^{-1} in the OH region. The relative intensity of this band demonstrates a similar BPA content dependence with that of the peak at 1715 cm^{-1} , suggesting that the band at 3430 cm^{-1} is due to the OH stretching of hydroxyl group in BPA coupled with carbonyl group in PMEA.

Quantitative analyses for Fig. 1 show that the hydrogen bonded OH multimers of BPA dominate IRRAS spectra when the molar ratio of BPA in the blends are higher than 36 % (Fig. 1A(d)). As previously proposed by Coleman

et al.,^{1,2} the inter-association and self-association types of hydrogen bonding are employed to characterize the interaction between PMEA and BPA molecules. The calculation results showed that equilibrium constant of self-association ($K_B=66.8$) is much larger than that of inter-association ($K_A=2.0$), indicating that BPA molecules readily associated with themselves, i.e., a phase separation occurred in the bulk of PMEA/BPA blends.

Furthermore, SFG results on the BPA/PMEA blend surfaces will also be provided for direct comparison between hydrogen bonding states in bulk and on the surface of polymers.

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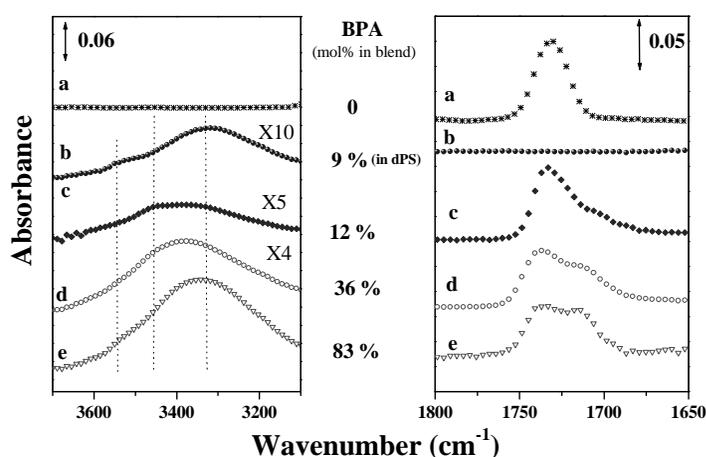


Figure 1 IRRAS spectra of the polymer blends on Au surface, in the frequency region of (A) O-H stretching and (B) C=O stretching, for different molar ratio of BPA in the blends between PMEA and BPA. See text for details.