Note

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BOUNDARY PHASE STRUCTURE BETWEEN POLY(HYDROXYPROPYL ETHER OF BISPHENOL A)/POLY(METHYL METHACRYLATE) BLEND AND POLYAMIDE SUBSTRATE*By Minekazu Kodama and Kazuo Kuramoto*

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ABSTRACT

Study of X-ray photoelectron spectroscopy (XPS) has been made on the film of poly(hydroxypropyl ether of bisphenol A) (P)/Poly(methyl methacrylate) (M) blend formed on nylon-6 substrate to elucidate the boundary phase structure between the substrate and the polymer blend. It can be found by analysing the C_{1s} spectrum that the boundary phase is almost composed of M alone. This result can be useful for fundamental information to understand the reinforcing mechanism of the Kevlar®-fiber reinforced composite made with P/M blend as matrix.

1. INTRODUCTION

It was reported in the previous paper that the fiber efficiency factor for strength K_a increased with the fraction of polar components in the matrices for the Kevlar®-fiber reinforced composites made with the blends of poly(methyl methacrylate) (M)/polystyrene (S) and poly(hydroxypropyl ether of bisphenol A) (P)/S¹⁾. This means that the interaction between the reinforcement and matrix increases with the fraction of polar components in the matrix.

On the contrary, K_a of the Kevlar-fiber reinforced composite made with the blend of polar components (P/M) was larger than that anticipated from the additivity of the strength of the polar components¹⁾. That is, a synergistic effect appears in the matrix-reinforcement interaction for the composite.

The boundary phase structure can be formed in the vicinity of reinforcement as a consequence of reinforcement-matrix interaction. In this work, the film of P/M blend formed on nylon-6 substrate (N) is probed by X-ray photoelectron spectroscopy (XPS) in order to explain the reinforcing mechanism of the Kevlar-fiber reinforced composite

made with P/M blend. N is used as a model compound for Kevlar-fiber^{2),3)}. It is known from XPS study that the carboxylic group and hydroxyl group or ether linkage preferentially concentrate on the N surface for the films of M and P formed on N, respectively^{2),3)}.

2. EXPERIMENTAL

The N plate of ca. 1mm thick was obtained by compression molding of Novamide 1010 (nylon-6 produced by Mitsubishi Chemical Industries Co.). The cleaned N plate was repeatedly dipped in a 2% blend polymer solution of tetrahydrofuran. Thickness of the coated sample was ca. 0.5mm. The blend ratio of P/M was selected as 1/1 by weight, as the synergistic effect mentioned above appeared significantly in the vicinity of this blend ratio¹⁾. After removing the solvent, the polymer film formed on the N substrate was carefully separated from the substrate so as not to damage the film surface. By leaving the coated specimen for a week in air, the film was easily separated from the substrate. XPS spectra were measured for the separated film on the surface exposed to air (air-facing side) and N substrate (N-facing side).

XPS spectra were obtained with a VG HB 50A

scanning electron microscope. An aluminum anode X-ray source producing $Al/K\alpha$ X-ray at 1486.6 eV was used by operating at 12 KV and 20 mA. The instrument was maintained at 1×10^{-8} mbar or less for all measurements. The data were analyzed on the high resolution spectra of the C_{1s} region. The overlapping peaks in the C_{1s} spectra were resolved into their individual components after background subtraction, assuming a Gaussian type symmetric function²⁾. Charge correction in the binding energy scale was made by setting the peak for hydrocarbon component at 285.0 eV in binding energy. Angular dependence of XPS was measured by tilting the surface of the sample. The effective sampling depth would decrease with decreasing take-off angle of photoelectron (θ), which is the angle between the surface of the sample and electron analyser axis.

3. RESULTS AND DISCUSSION

In Figure 1, the observed C_{1s} spectra (dotted curve) and resolved components (broken curves) are shown for both the air-facing and the N-facing sides at various take-off angles. The resolved components C_1 , C_2 and C_3 can be assigned to CH_x , $C-O$ and $O-C=O$, respectively.

The component C_3 cannot be observed for P, and the relative peak area of component C_2 is nearly equal to that of C_3 in the spectrum at the largest sampling depth for the air-facing side of atactic poly(methyl methacrylate) (M) as reported in the previous works^{2),4),5)} (the materials and experimental condition were the same as those in this work). From these facts it can be said that the component C_3 comes from M alone. Therefore, C_3 can be used as a measure of the behavior of M in the blend.

The boundary phase structure was probed by comparing the XPS spectra between the N-facing and air-facing sides.

The relative peak areas of C_1 , C_2 and C_3 components were obtained and plotted against the take-off angle ($\sin \theta$) in Figure 2. The relative peak area of C_1 is somewhat larger than the value anticipated from the chemical structure and composition (66.1%), and increases with decreasing $\sin \theta$ (decreasing sampling depth), in both the air-facing and N-facing sides. This is probably due to the increase in relative peak area of C_1

Fig. 1. XPS spectra for poly(hydroxypropyl ether of bisphenol A)/poly(methyl methacrylate) blend polymers.

Fig. 2. Relative peak area vs. electron take-off angle relations for observed values (C_1 : ●, C_2 : ▲, C_3 : ■), re-estimated values (C_1 : ○, C_2 : △, C_3 : □), anticipated values from chemical structure and composition for P/M blend (-----) and anticipated values from chemical structure for M (— —), for air-facing side (a) and N-facing side (b).

component on account of the hydrocarbon contamination layer deposited on the sample during measurement⁶).

By assuming simply the relative peak area of C_1 , which is free from the hydrocarbon contamination, to be 66.1% in the range of $\sin \theta$ measured at the air-facing side, the relative peak areas of C_2 and C_3 were re-estimated from the observed values. The results are also shown in Figure 2. The re-estimated values of C_2 and C_3 become close to those anticipated from the chemical structure and composition. At the N-facing side, the relative peak areas of C_2 and C_3 were re-estimated from the observed values by assuming the relative peak area of C_1 to be 60%, which is free from the hydrocarbon contamination. The re-estimated values of C_2 and C_3 become close to the relative peak areas of C_2 and C_3 for M homopolymer anticipated from the chemical structure. This means that the boundary phase is composed of almost M alone.

The carbonyl-containing polymer poly(ethylene adipate) (A) also concentrates at the N-facing side for the case of P/A blend film formed on N as reported in the previous paper²). N and P are known to self-associate through strong hydrogen bonding^{7),8}). Therefore, M or A, which is not hydrogen bonded by itself, tends to concentrate on the self-associated substrate when the blend

of hydrogen bonded polymer with M or A (P/M or P/A) contacts with the substrate. This is probably because of the easier occurrence of interaction between N and M or A compared with the case of N and P. The carbonyl-containing polymers, M and A, can also destroy the self-association of P and interact with the dissociated P^{2),8}). If, such a boundary phase structure is formed in the Kevlar-fiber reinforced composite made with P/M blend, the synergistic effect as mentioned above may arise in the composite.

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フェノキシ樹脂 / ポリメタクリル酸メチル ブレンドとポリアミド基材間境界相の構造

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ナイロン-6 基材上に形成したフェノキシ樹脂(P) / ポリメタクリル酸メチル(M)ブレンド物のフィルムについて、基材とブレンド高分子間境界相の構造を調べるために、X線光電子分光スペクトルを測定した。C_{1s}ス

クトルの解析結果から、境界相はほとんどMだけで構成されていることがわかった。これは、P/Mブレンド物をマトリックスとするケブラー繊維強化複合体の強化機構を理解する上での基本的な知見となる。