

Structure of polyacrylate/nanoparticle interfaces

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The structure of polymer/nanoparticle interfaces was discussed using X-ray diffraction measurements with mixtures of polyacrylates [poly(ethyl acrylate) and poly(*n*-butyl acrylate)] and nanoparticles (Al_2O_3 and SiO_2). The amorphous halo with two peaks present for the bulk polymers changed, both in diffraction angle and intensity, into a peak in the mixtures. A novel polyacrylate structure at the interface (5–10 nm) with nanoparticles was formed with a specific chain conformation that was different from the bulk structure observed using Fourier transfer infrared spectroscopy.

1. Introduction: It is widely known that the physical properties of a polymer at an interface are different from those of the bulk phase. In 1994, Keddlé *et al.* evaluated the dependence of the glass transition temperature on the film thickness using an ellipsometer. They reported that the glass transition temperature of the polystyrene thin film was significantly reduced with the decreasing thickness of the film [1].

Physical properties at the surface and interface of polymer thin films have been actively studied [2, 3]. The glass transition temperature of the interface region changes due to the strong interactions of the polymer and substrate [4]. Furthermore, the glass transition temperature in free-standing films can dramatically decrease with a decrease in its thickness [5]. Zhang and Tasaka [6] performed thermal analyses of samples prepared by mechanically grinding the polystyrene with alumina nanoparticles and observed a surface glass transition temperature (14–17°C) that was significantly lower than the bulk glass transition temperature. Considering these reports, the interactions of polymers and substrates and those of polymers and air are major factors that determine the glass transition temperature.

Even in bulk properties, different amorphous structures under high pressure in isotactic poly(4-methyl-1-pentene) (P4MP1) were found by Chiba [7]. In addition, double glass transitions in poly(ethylene terephthalate) and polycarbonate were reported by Diego [8] and by Arif Masud [9], respectively.

Polar polymers are sensitive to the influence of other substances at the interface and surface. Due to the strong electric interactions among the polar groups, it is believed that ferroelectric polymers form long-range specific structures, namely, polar structures [10–12]. Polar groups are aligned if the polar polymers adapt certain conformations at the interface. Polar polymers are liable to show more significant interphase properties than non-polar polymers since the electrical interactions between polar groups occur at longer distances.

Polyacrylates are generally known to have excellent tacky, heat-resistance and transparency properties, which enable their use as adhesives or a pressure sensitive adhesives to metals. Specifically, T_g -like thermal changes at temperatures higher than the bulk T_g have been observed in the case of thin film samples sandwiching ‘poly(ethyl acrylate) (PEA)’ or ‘poly(*n*-butyl acrylate) (PnBA)’ in silver thin films. The sub T_g was not observed in the case of PnBMA, which had rigid main chains, and the sub T_g did not depend on the molecular weight or metal substrate [13].

In this Letter, we discuss the interphase structures of mixed samples with large numbers of alumina nanoparticles in polyacrylates. The interfacial structure of amorphous polymers was

characterised by X-ray diffraction (XRD) and Fourier transfer infrared spectroscopy (FTIR). It has hardly been reported so far that the amorphous structure of the polymer changes at the nanoparticle interface. Revealing the structure of the amorphous polymer at the nanoparticle interface contributes to further development in the nanocomposite and adhesion fields.

2. Experimental: PEA and PnBA were purchased from Aldrich. The M_w of PEA was 95,000, its T_g was -23°C , and its ρ was 1.21 g/cm^3 . The M_w of PnBA was 99,000, its T_g was -54°C , and its ρ was 1.09 g/cm^3 . The metal oxide particles mixed with PEA or PnBA were γ -alumina (Al_2O_3) or silica (SiO_2). The average particle diameter of Al_2O_3 was 41.4 nm, and its density was 3.6 g/cm^3 . The average particle diameter of SiO_2 was 33.9 nm, and its density was 2.1 g/cm^3 . These metal oxide nanoparticles (nanoparticles) were spherical and were purchased from Kanto Chemical.

Mixed samples of the polymers and nanoparticles were prepared as follows. These nanoparticles were heated for 2 h at 700°C to remove residual water and hydroxide in nanoparticles using a muffle furnace, FO100 (Yamato Scientific), before mixing. PEA or PnBA was dissolved in tetrahydrofuran and added to the nanoparticles. These samples were mixed ~ 20 min in a mortar and cast on an aluminium substrate at 150°C .

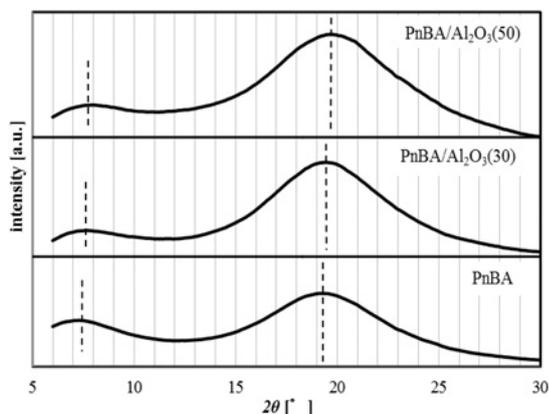
XRD was performed using a MiniFlex 300 (Rigaku). The measurement was performed using $\text{CuK}\alpha$ radiation as an X-ray source, a tube voltage of 30 kV, tube current of 30 mA, scan range of $5\text{--}40^\circ$, and a scanning speed of $2^\circ/\text{min}$. The XRD intensity from the alumina or silica particles was subtracted from the intensities of the mixture samples to eliminate the structural information of the polyacrylates. IR spectra were obtained using an FT/IR-4100 (JASCO) with a diamond cell (Type DX2010, Sumitomo Electric Hard Metal). The resolution, scan number and measured wavenumbers were 2 cm^{-1} , 500 and $500\text{--}4000\text{ cm}^{-1}$.

Table 1 shows the abbreviation and composition of each sample used in this Letter.

3. Result and discussion: Fig. 1 shows the XRD patterns of the PnBA, PnBA/ Al_2O_3 (30) and PnBA/ Al_2O_3 (50). The numbers in parentheses indicate the weight percentages of the nanoparticles in the samples. The curves in the figure were calculated by subtracting the pattern of the nanoparticles from those of the mixed samples [14]. Two main peaks that are characteristic of the XRD pattern of polyacrylates were observed. One peak occurred at a lower angle due to its side chain, and the other occurred due to main chain packing [15]. The PnBA had two peaks at $2\theta = 7$

Table 1 Abbreviation in this Letter and composition of mixed sample

Abbreviation	PnBA, wt%	Nanoparticle, wt%
PnBA	100	0
PnBA/Al ₂ O ₃ (30)	70	30
PnBA/Al ₂ O ₃ (50)	50	50

**Fig. 1** XRD patterns of PnBA, PnBA/Al₂O₃ (30) and PnBA/Al₂O₃ (50) represent the pattern resulting from subtraction of Al₂O₃ pattern

and 19°. From the results of each sample, the peak intensity at $\sim 2\theta = 7^\circ$ greatly decreased and, the peak at $\sim 2\theta = 19^\circ$ shifted to a higher angle with an increase in the amount of Al₂O₃ nanoparticles.

The decrease in the peak intensity at $2\theta = 7^\circ$ is thought to be due to the conformation change of the side chain at the interface from the IR measurement results that will be shown later. The shift in the peak at $2\theta = 19^\circ$ to a higher angle suggests that the polymer chains may have formed a denser structure at the interface. In addition, the peak change increased as the number of added alumina nanoparticles increased.

Therefore, it was found that PnBA formed a novel structure at the interface with alumina nanoparticles.

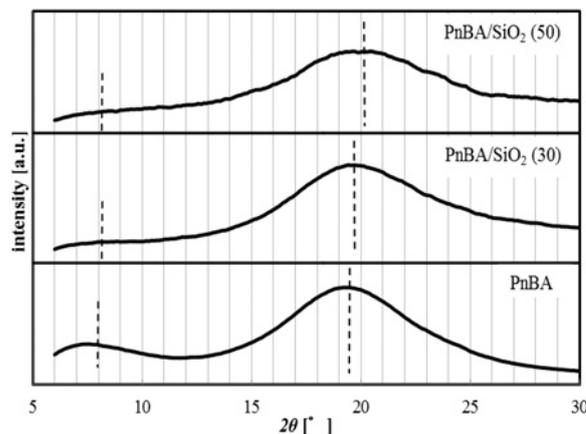
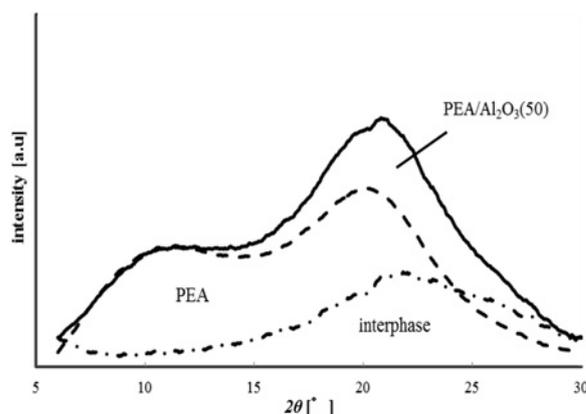
The peak of PEA changed similarly after the addition of alumina nanoparticles. However, the change was smaller than in the case of PnBA. The data of PnBA/nanoparticles with remarkable changes will be shown in this Letter. The thickness of PEA/Al₂O₃ was ~ 5 nm and that of PnBA/Al₂O₃ was ~ 10 nm, as a result of estimating the thickness of the polyacrylate in which the structure was changed by adding nanoparticles by the method described later. This is thought to be related to the strength of the interactions between the polyacrylate and the nanoparticles.

Fig. 2 shows the XRD patterns of the PnBA, PnBA/SiO₂ (30) and PnBA/SiO₂ (50). The peak changes of the mixtures after adding nanoparticles were more clearly observed in the mixture with SiO₂. The interface of PnBA/SiO₂ may have been wider than that of PnBA/Al₂O₃ and had strong interactions at the polymer/nanoparticle interface to form a different packing structure.

Therefore, polyacrylates formed a different structure at the interface in the presence of nanoparticles.

The diffraction peaks of PEA or PnBA at lower angles were due to sidechain packing [16], and the peak intensity was reduced after adding alumina. The XRD patterns of the mixed samples consisted of the sum of the bulk and interphase diffraction patterns. Therefore, the thickness of the interphase could be estimated from XRD pattern separation.

Fig. 3 shows the separations of the PEA diffraction patterns of PEA/Al₂O₃(50) from the peaks of PEA in the bulk and interphases.

**Fig. 2** XRD patterns of PnBA, PnBA/SiO₂ (30) and PnBA/SiO₂ (50) represent the pattern resulting from subtraction of SiO₂ pattern**Fig. 3** Deconvoluted patterns of PEA/Al₂O₃ (50), PEA and interphase

Here, the results of the PEA sample with small peak intensity changes on the low angle side are shown for ease of viewing. ‘Interphase’ refers to a polyacrylate with a different structure at the nanoparticle interface. We assumed that the peak intensity, $\sim 11^\circ$, was attributed only to the diffraction of the bulk PEA, and the intensity of the bulk PEA was subtracted from the intensity of the mixture sample to remove the intensity at $\sim 11^\circ$. The residual intensity was assumed to be attributed only to the diffraction of the interfacial PEA.

Here, we assumed that the Al₂O₃ nanoparticles had a uniform size and an ideal spherical shape and uniformly dispersed in the sample and that the densities of the PEA in the bulk state and the interface had no significant difference. The ratio of the peak area of the interphase to the peak area of PEA corresponded to the weight ratio of PEA and the interphase. As a result, the thickness of the interphase of PEA/Al₂O₃ was estimated to be ~ 5 nm. Additionally, the thickness of the interphase of PnBA/Al₂O₃ was estimated to be ~ 10 nm. The interphase thickened by ~ 2 – 3 nm in the case of SiO₂. These values were larger than the radius of gyration in the polymer in the solid phase and were smaller than the polymer chain length. Additionally, the interphase became thicker as the amount of Al₂O₃ increased. This indicated the existence of restricted chains at the surface of Al₂O₃.

In fact, there was a high probability that the nanoparticles were aggregated in the sample. Therefore, it was expected that interface structure was not formed around all the nanoparticles. Therefore, the thickness of the interface was at least ~ 10 nm, so detailed calculation results were not described here. In addition, the interphase

was thicker in the case of using PnBA as the polyacrylate or SiO₂ as the nanoparticles.

The conformations of polar polymer chains generally maintain a polar position at interfaces [12]. Previous results support the fact that polyacrylates have different conformations and structures at interfaces. To estimate the conformations of PnBA in the interphase, IR spectra at 1200–1300 cm⁻¹ were measured. The peaks of the high-frequency region (~1265 cm⁻¹) corresponded to the trans-trans conformation, and the peaks of the low-frequency region (~1240 cm⁻¹) corresponded to the trans-gauche conformation [17].

The trans-trans conformation fractions of the PEA and PEA/Al₂O₃(70) samples in the region of the conformational band were compared. The trans-trans conformation fraction of PEA was 56% and that of PEA/Al₂O₃ (70) was 66%. The trans-trans conformation fraction increased with the increase of the added number of Al₂O₃ nanoparticles. From this, the polyacrylates were suggested to form a structure different from that of the bulk structure at the interface with alumina nanoparticles.

4. Conclusion: The structures of PEA and PnBA at the interface with nanoparticles were examined from XRD measurements and IR measurements. The polyacrylates had special structures at the interface with nanoparticles, and the thickness of the interface layer was 5–10 nm. This structural change was due to the interactions between the polyacrylate and nanoparticles.

5 References

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