Properties of Composite Films Comprising Surface Modified Fine Collagen Particles Dispersed in Polyurethane Matrix

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ABSTRACT: Collagen-rich natural leather powders (PPd) with average particle size of 12 μm were modified and dispersed in a polyurethane (PU) matrix. Three kinds of surface modification techniques were employed; surface polyaddition of PU, copolymerization with acrylamide (AAm), and grinding of the PPd with PU powder in a planetary ball mill. Surface modification was confirmed mainly by FTIR signals from the modifier. The DTA exothermic peak shifted toward a higher temperature by 260 K when copolymerized with AAm. On the copolymerized sample, the IR peak due to C=O stretching appeared between those of the original AAm and PPd, indicating the mutual chemical interaction. The tensile yield stress and critical strain of the composite films increased by surface modification with PU, while the latter decreased for the film containing the PPd powders copolymerized with AAm. Judging from the micrographs of the expanded films, the increase in the adhesive strength between the powder surface and the matrix after modification by AAm was larger than those by PU. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1693–1700, 1997

Key words: composite films; collagen particles; polyurethane matrix

INTRODUCTION

Natural leather has many advantages over artificial materials, but it is less robust against mechanical scratches or weathering. Higher flexibility is often required as well. Many attempts were made to combine the advantages of natural leather and synthetic polymers. One of the methods was to disperse powdered natural leather into a matrix comprising synthetic polymers. In such a case, affinity at the powder/matrix interface is a matter of primary importance. There have been a series of studies to improve and examine the strength of matrix/filler interaction.[1–3] Polymer alloys based on interpenetrating polymer networks were also devised for similar purposes.[4,5]

When a composite material with powdered species dispersed in a matrix is explored, it is essential to find a matrix with a high affinity for the dispersing species. Because the main ingredient of natural leather is collagen, synthetic polymers with amido groups seem to be promising. As a matter of fact, we preliminarily tried to disperse natural leather powders into polyurethane (PU) matrix in our laboratory. It turned out, however, that the adhesion at the leather/PU interface was not strong enough. Because the matrix PU is nevertheless attractive for its intrinsic mechanical properties, we tried to explore the methods of modification of the powder surface to increase the affinity with PU.

Thus, the purpose of the present study was to find an appropriate method to improve the surface of the natural leather powder in order to increase the adhesion strength with the PU matrix and to improve the mechanical properties of the composite films. Emphasis was on examining whether

and to what extent chemical interaction at the powder/matrix interface changes after surface modification of the natural leather powders.

EXPERIMENTAL

Starting Materials

The initial collagen-rich natural leather powders (PPd) were supplied by Idemitsu Petrochemical Co. Ltd. (Protein Powder®, fine). These were obtained by grinding thermally pretreated natural cowhide with a jet mill. PU as a dispersing matrix was a single liquid type commercial product (Dainich Chemical, Lethamine® ME-3612LP).

Polyaddition of PU

Ten grams of PPd powder was put into a 300-mL Erlenmeyer flask together with 0.4 g NaOH and 200 mL deionized water. After gentle mixing at room temperature for 1 h, the temperature was elevated to 55°C. After immersing for 5 min, 4 g PPd powder was dispersed into 16 g buthanediol and mixed in a ball mill with 100 6-mm glass balls. After drying at 50°C for 1 h, the powders were put into 100 mL chlorobenzene in a small reactor, equipped with a drop funnel and a reflux condenser. After 30 min of nitrogen flow to substitute the atmosphere with nitrogen, 2.8 g hexamethylene diisocyanate dissolved in 26 mL benzene was added quickly. Another 2.8 g diisocyanate was added dropwise from the same benzene solution during the following 3 h and was subsequently heated for 1 h at the same temperature. The resulting powders are denoted as PB-PU.

Grinding with PU

After synthesizing PU by the method given above without PPd powder, 0.72 g PU and 4.0 g PPd powders were mixed and ground in a laboratory-sized water-cooled planetary mill. These composite powders are denoted as P/PU.

Copolymerization with Acrylamide (AAm)

Copolymerization was carried out in an aqueous condition under nitrogen flow. Two hundred milliliters H_2O, 10 g PPd powder, 3 g NaOH, 0.038 g $NaHSO_4$ and 0.1 g potassium persulfate were mixed with a predetermined amount of AAm monomer with the weight ratio AAm/PPd = 3/1

and 1/9. The polymerization reaction was carried out in all cases at 55°C for 2.5 h. The copolymerized particles were named A/P(3/1) and A/P(1/9), respectively.

Preparation of Composite Films

Six and a half grams of PPd powders with and without various modifications were mixed with 32.5 g dimethyl formamide (DMF). A paste for a composite film was then prepared after admixing with 65 g liquid PU. An automatic film applicator (Yasuda, Automatic Film Applicator 542-AB) was used at a sweeping rate of the coating bar of 3.2 cm/min to obtain composite films on the nonadhesive paper substrate. Vacuum suction was made during coating in an attempt to obtain films as quickly and as uniform as possible. The thickness of the wet paste sheet was controlled by utilizing vinyl adhesive tape ca. 0.35 mm thick on both sides of the substrate. A film was obtained after drying at 80°C for 15 min, and it was peeled off the substrate.

Characterization of Modified Powders and Composite Films

Powders and films were characterized by various methods: X-ray powder diffractometry (XRD) was done by a diffractometer (Rigaku, CN2013). Infrared spectroscopy (FTIR) was carried out by a spectrometer (Dig-Lab FTS-65) with the KBr disk method. Thermal analyses (TG-DTA) were made by a commercial apparatus (Mac Science 2020) in a dry air stream (200 mL/min) at a constant rate of heating of 10 K/min. Mechanical properties of the composite films were determined by a tensile tester (Shimadzu Autograph IS-500). Abrasive tests were also carried out by a rotary abrasion tester (Toyo Instruments).

RESULTS AND DISCUSSION

Particle Size and Morphology

PPd powder particles are jagged as shown in Figure 1. While no appreciable comminution is observed even after mixed grinding, severe agglomeration takes place after copolymerization with a large amount of A/P(3/1). Apparent particle size remained almost unchanged from 12 μm before any treatments to 17 μm at most after surface
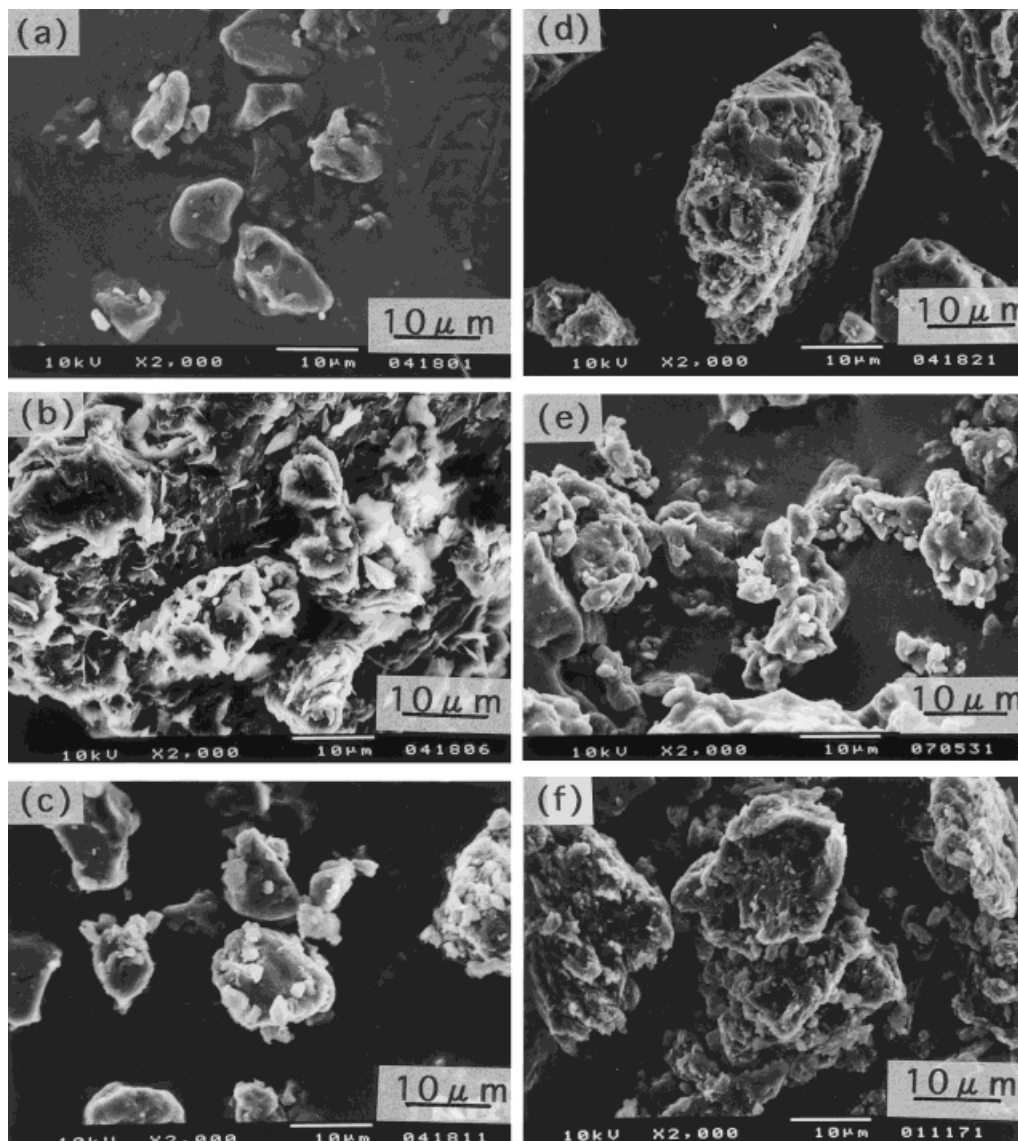
Figure 1 Scanning electron micrographs of representative powders with and without surface modification. (a) PPd, (b) PB-PU, (c) P/PU-D, (d) A/P(3/1), (e) A/P (1/9), and (f) PA/P(1/9) [for abbreviation of sample names, see Table I, except PA/P(1/9) is the product of copolymerization of poly(acryl amide):PPd = 1:9].

pretreatment, except for the sample A/P(3/1) that was as large as 70 μm.

Change in Crystalline States

As shown in Figure 2, PPd was almost noncrystalline without showing any sign of a secondary structure of an α-helix, which might have appeared by the diffraction with CuKα at $2\theta = 30.8°$ (0.29 nm) and 20.2° (0.44 nm) for the latitude and longitude periodicities of the α helix, respectively.[6] In contrast, the synthesized PUs were crystalline, showing several X-ray diffraction peaks at $2\theta = 21°$ and 23° as shown in Figure 2, curves PB-PU and P/PU. While simple grinding of PU did not bring about amorphization (not shown), grinding a mixture of PPd and PU made their structure rapidly noncrystalline (Fig. 2, curve P/PU). Copolymerization with AAm also diminished the crystallinity of AAm as shown in Figure 2, curve A/P(3/1). These amorphizations indicate interaction between PPd and the modifier, PU or AAm, with mechanical as well as chemical treatments, because the structural deg-
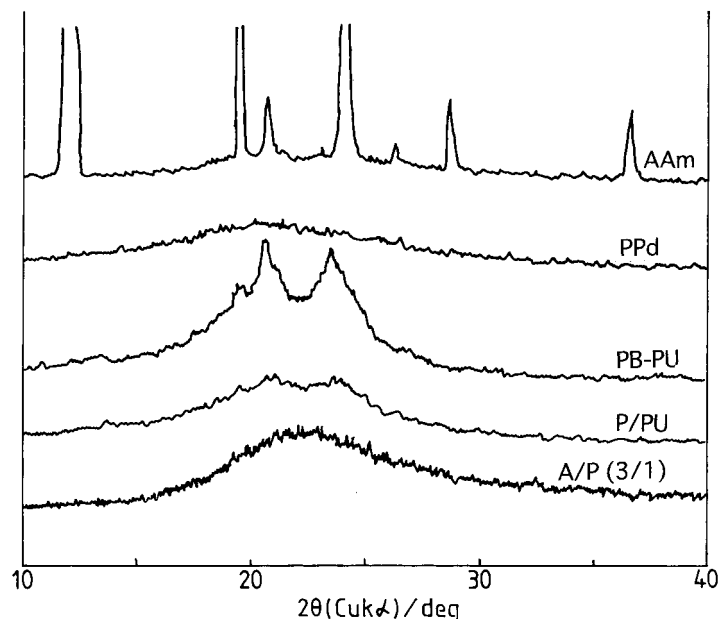
Figure 2   X-ray diffraction profiles of representative powders.

radation of the crystalline additives occurred only in the presence of PPd powder.

Thermal Properties

As shown in Figure 3, the weight loss began immediately after heating, followed by a steep decrease of the weight above 200°C. The latter weight loss was accompanied by a sharp DTA exothermic peak (Figure 4) and corresponded to the decomposition of collagen. Thermal decomposition of intact PPd powders takes place at 320–340°C, being slightly above the reported decomposition temperature of amino acids, for example, glycine with its decomposition temperature of 262°C.[7] This suggests the existence of internal crosslinking of the amino acids in a short-range ordering, being ineffective for X-ray diffraction.

As mentioned above, all the surface treatments retarded thermal decomposition. In the case of polyaddition with PU (sample PB-PU), the temperature shift was by about 90 K, with some DTA subpeaks before the main exothermic one. The most striking change in the thermal decomposition was the film with PPd copolymerized with AAm, which brought about the temperature increase by 260 K in the A/P(3/1) sample. Note that the decomposition temperature of AAm itself, ca. 170°C, is even lower than that of the PPd powder.

The shift of DTA peaks strongly depended on the amount of AAm added. Simple addition of AAm by the same amount brought about a sig-

nificant temperature shift, but to a much smaller extent; 120 K. Therefore, we concluded that copolymerization changed the structure of PPd and AAm simultaneously.
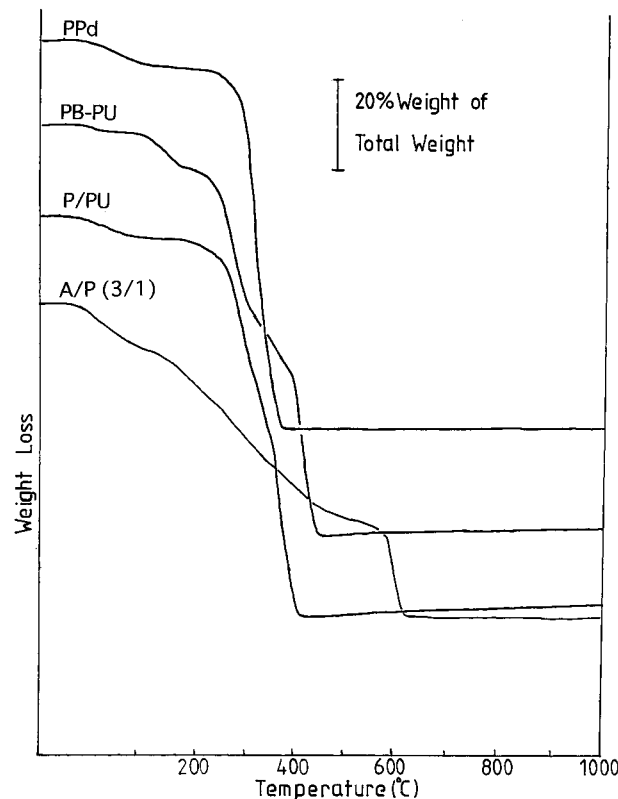

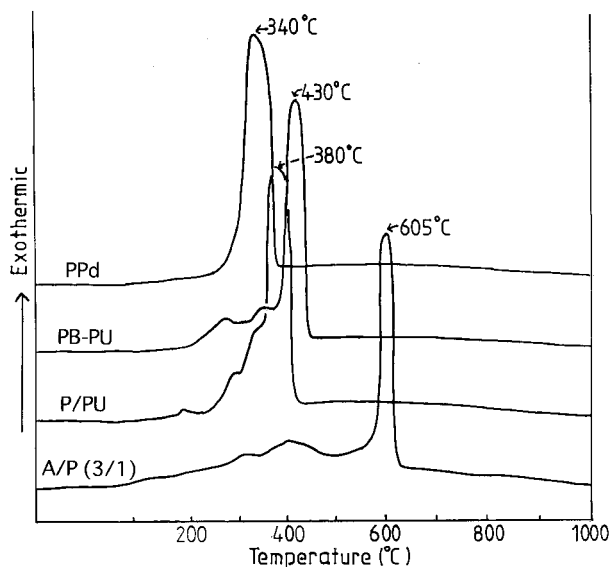**Figure 3**   Thermogravimetric curves of representative powders.

Figure 4 DTA profiles of representative powders.

The profile of the thermogravimetry with A/P(3/1) was unique with its sluggish weight loss in a wide temperature range, that is, a gradual weight loss immediately after the start of heating and just before the final rapid weight loss at ca. 600°C. If we assume that only the final rapid weight loss corresponds to the decomposition of PPd, the amount observed on the curve of A/P(3/1) is slightly less than the amount of PPd initially contained. We can therefore assume that a part of the PPd powder decomposed together with AAm in a wide temperature range, beginning at temperatures much lower than the intrinsic decomposition temperature of PPd.

Chemical State of Surfaces

In the foregoing, the structural changes due to copolymerization with and without polyaddition to the PPd powder were suggested. To examine the content of the chemical change, IR spectroscopy was carried out. As shown in Figure 5, IR absorption bands typical for amido groups (—CONH—), notably those of N—H stretching (3420 cm^{-1}), C=O stretching (amido I, 1650 cm^{-1}), C—N stretching (amido III, 1280 cm^{-1}), and as N—H stretching (amido II, 1540 cm^{-1}), are observed on the intact PPd powder.[8,9] Absorption bands typical for PU, some of which are close to those of collagen, are N—H stretching (3320 cm^{-1}), —CH$_2$—vibration (2960 cm^{-1}), amido I (1680 cm^{-1}), and C—N stretching (1280 cm^{-1}).

The appearance of those peaks after polyaddi-

tion of PU on the PPd powder indicated a successful surface modification by PU. Stronger signals from PU were recognized on the polyaddition sample (PB-PU) than on the ground mixture (P/PU). The spectrogram of PB-PU was more similar to PU, particularly with respect to the peaks near 2960 cm^{-1} for —CH$_2$— and —CH$_3$. Conversely, PB/PU, the ground mixture, showed closer resemblance of its spectra to that of PPd. These indicate that better surface affinity of PPd to PU was attained by surface polyaddition than simple grinding, although such mechanical grinding of a mixture often brings about mechanochemical interactions at the interface.[10,11] An explicit statement with respect to the bonding between PU and PPd is not possible from IR spectra alone. However, the results of XRD, TG-DTA, and FTIR consistently indicated that the chemical interaction between PPd and PU was stronger by polyaddition than by mechanical grinding of the mixture.

Crosslinking of PPd with AAm

FTIR spectroscopy produced more informative data with respect to the chemical changes of PPd due to copolymerization with acryl amide. As shown in Table I, the band from amido I shifted
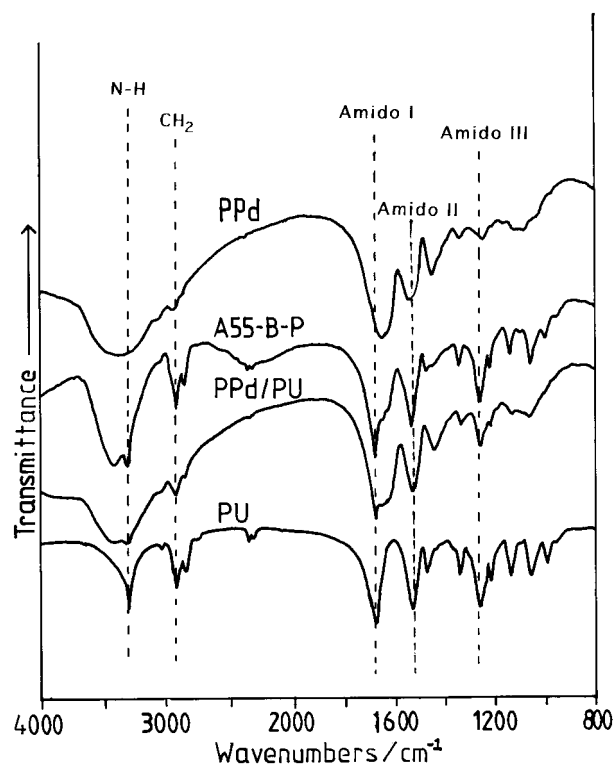

Figure 5 FTIR patterns of representative powders.

Table I IR Peak Shift of Amido I and II for Copolymerized Samples

Sample Name	Wave Number Amido I (cm⁻¹)	Wave Number Amido II (cm⁻¹)
PPd	1651	1538
A/P (3/1)	1655, 1667	1544, 1558
A/P (1/9)	1653	1542, 1558
AAm	1674	1613

toward a higher wave number after copolymerization. The extent of the shift was larger with a larger amount of AAm. Furthermore, shoulders were observed on the amido I peak at 1655 cm⁻¹ for compolymerized samples and at 1542 (1544) cm⁻¹ on the amido II peaks, with the main peak at 1558 cm⁻¹ also observed for copolymerized samples. It is known that by changing the structure from α helix to random coil and β sheet, the amido I peak shifts toward a higher wave number and those of amido II in the opposite direction.[12] These amido I and II peaks for the copolymerized sample were observed just between those from intact PPd and AAm. Therefore, we concluded that the secondary structure of the collagen changed as a result of copolymerization of PPd with AAm. It is also possible that a part of the original collagen structure (α helix and random coil) turned into random coil and β sheets during copolymerization, although none of these structural units exhibited long-range ordering detectable by XRD.

Morphology and Structure of Composite Films

Composite films under expansion demonstrate various pores at the powder/matrix interface, as shown in Figure 6. A smaller amount of pores generally indicates better adhesion between the powder particles and the matrix.[3] The amount of pores decreased by the polyaddition of PU. After copolymerization with AAm almost no pores were observed, indicating particularly good adhesion to the PU matrix.

An alternative observation was carried out on the surface of the composite films after wear abrasion tests. As shown in Figure 7, craters after
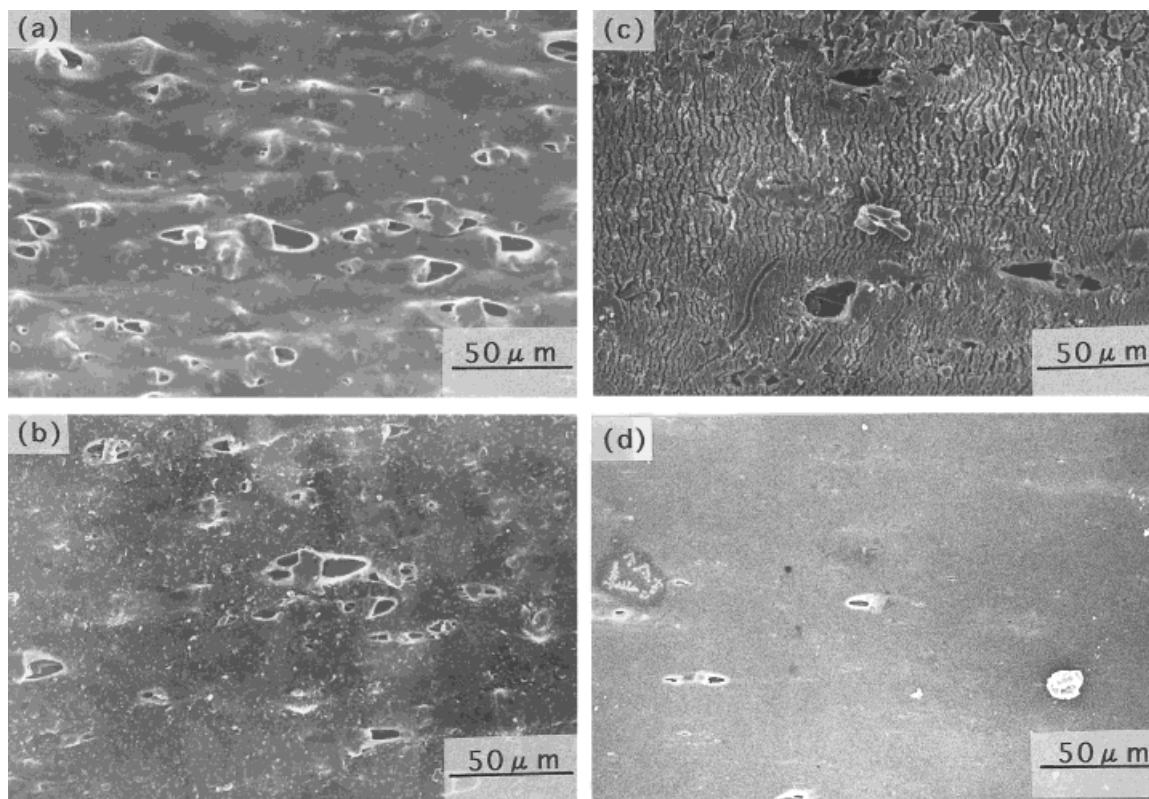

Figure 6 Scanning electron micrographs of representative composite films observed under 250% expansion. Films were prepared by dispersing powders (a) PPd, (b) P/PU, (c) PB-PU, and (d) A/P in polyurethane.
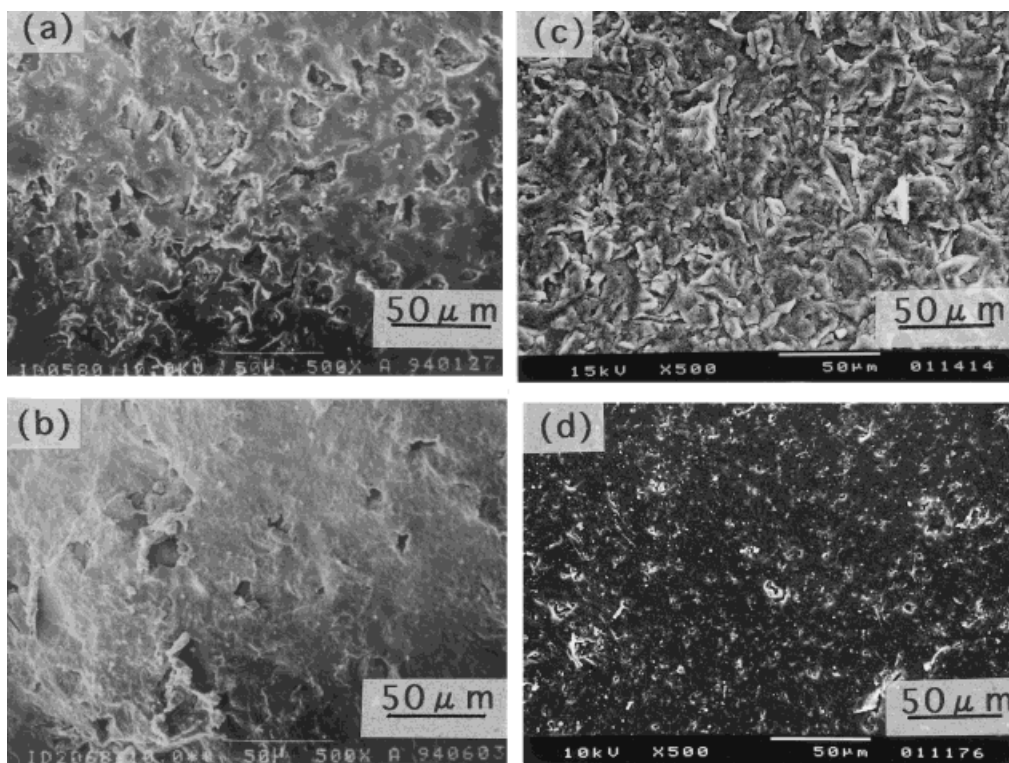
Figure 7   Scanning electron micrographs of representative composite films after abrasion tests. Films were prepared by dispersing powders (a) PPd, (b) PB-PU, (c) A/P(1/3), and (d) A/P(1/9) in polyurethane.

abrasion became less apparent after surface modification. Some large pores on the abraded A/P(3/1) sample were attributed to the large agglomerates, as already mentioned.

Mechanical Properties of Composite Films

The stress–strain curves obtained from the tensile tests are shown in Figure 8. As summarized in Table II, the tensile yield stress and critical strain of the composite films increased by surface modification with PU, while the former decreased for the film containing the PPd powders copolymerized with AAm. Critical strain of the film with PPd copolymerized by AAm was similar to that with surface polyaddition of PU.

Polyaddition of PU on the surface of the PPd powder produced little change in the yield stress while remarkably increasing the critical stress to rupture. This was attributed to the improved adhesion strength at the interface between dispersing PPd and the matrix, PU. This was obvious from the comparison of the micrographs under tensile stress shown in Figure 6(a,c) without and with the surface polyaddition, respectively, of PU.

Note that simple grinding of a mixture of PPd and PU did not bring about such a remarkable increase in the critical stress. This was attributed to the weaker adhesion of PU to PPd and to the lower crystallinity of PU in the case of the ground mixture as compared to the surface modification by polyaddition.
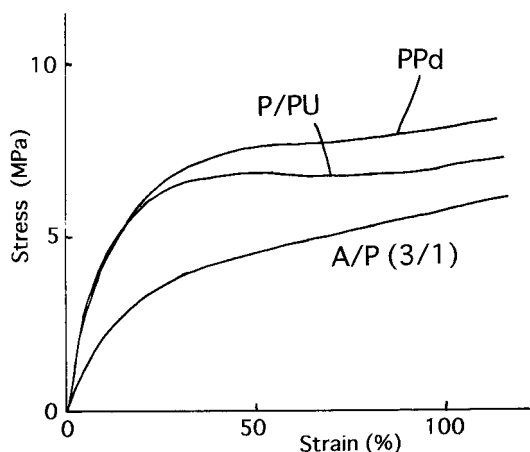

Figure 8   Stress–strain curves for representative composite films.

Table II Mechanical Properties of Composite Films Containing Respective Powders

Dispersed Powder	Yield Stress (MPa)	Yield Strain (%)	Critical Stress (MPa)	Critical Strain (%)
PPd	8.12	11.1	26.1	380
PB-PU	8.40	7.8	41.0	432
P/PU-D	7.61	8.1	22.6	369
A/P (3/1)	5.79	9.5	25.4	439
A/P (1/9)	5.89	9.5	22.1	431

The decrease of the yield stress, and accordingly the increase in the flexibility of the film by copolymerization of AAm, could be explained by the crosslinking[13] at the interface between AAm on the surface of the PPd and PU in the matrix as confirmed by the FTIR measurements. These results imply that the film tended to become more rigid with the surface polyaddition of PU, while it was more flexible after copolymerization of AAm on the PPd powder.

CONCLUSION

The DTA peak temperature of collagen powder was increased by 260 K by copolymerization with AAm. At the same time, the IR peak due to $C=O$ stretching was observed at wave numbers between those of original AAm and intact collagen powders. The tensile yield stress of the composite films decreased and critical strain increased by surface copolymerization with AAm. All these results indicated chemical interaction between PPd and AAm and crosslinking of AAm with PU matrix as a result of surface polyaddition. It was also found that the adhesion to the PU matrix was increased by surface polyaddition of PU to PPd, and even to a larger extent by copolymerization with AAm.

We conclude that methods of surface modification can be chosen for the desired mechanical properties of the films with dispersed natural protein powders: by surface polyaddition of PU for stronger and more rigid films, or by copolymerization of AAm for more flexible and temperature resistant films.

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