

Structure and Properties of Flame-Sprayed Poly(Ethylene-Co-Vinyl Alcohol) Copolymer Coatings

Mustafa Öksüz,¹ Hüseyin Yıldırım²

¹Technical Education Faculty, Marmara University, 34722 Goztepe, Istanbul, Turkey

²Department of Chemistry, Yıldız Technical University, 34210 Esenler, Istanbul, Turkey

Received 12 August 2003; accepted 30 March 2004

DOI 10.1002/app.20869

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Powder coatings formed by flame spraying are being used in industrial applications. The resistance of plastics and their composite materials to chemicals, solvents, and atmospheric conditions and their high impact strength even at low service temperatures increase the importance of plastic and plastic-based coatings. In this study, an ethylene vinyl alcohol copolymer powder was coated via flame spraying with gases of oxygen and acetylene. The bond strengths and microstructures of the coatings were determined with tensile testing, scanning electron microscopy, and Fourier transform infrared. The bond strengths of the

coatings were determined according to ASTM C 633. Oxidizing, carburizing, and neutral flames were used. The bond strengths were lower for the oxidizing and carburizing coatings than for the neutral flame coatings. The results indicated that during the flame-spraying process, the composition, gas, spraying distance, and coating thickness were important factors in the coating bond strength. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1357–1364, 2004

Key words: coatings; FT-IR; plastics; strength; structure

INTRODUCTION

Surfaces are increasingly coated with protective layers to improve the surface characteristics of materials or to protect them from environmental factors. Surface coatings are applied on the basis of two principles. The first is coating through the formation of a diffusion bond between the surface of the coating and the coated surface. The second is coating by mechanical adhesion without the formation of a diffusion bond between the surface of the coating and the substrate. In diffusion-bonded coatings, the properties of the bond are directly related to the composition of the coating material. For coatings applied without a diffusion bond, the mechanical adhesion between the coating and the substrate varies according to the coating conditions and the structural qualities of the used coating materials. Coatings applied to surfaces provide some properties, include optical, magnetic, electric–electronic, biological, thermal attack, corrosion, and tribological properties. These coating properties are very important in surface engineering applications. Surface decoration is another goal.^{1–4}

A major problem in surface design and coating performance is that many desired properties, such as adhesion between the coating and substrate interface, strongly depend on the chemical composition, spraying parameters, and substrate surface. For very high

coating bond strengths to be obtained, the processing parameters should be controlled to eliminate excessive stress and shrinkage between the substrate and coating.¹ The substrate must be cleaned by chemicals and sand-blasted to form an anchor pattern, which improves the adhesion of the sprayed powder coating layer.²

Plastic materials are commonly used in all kinds of industries because of their ease, speedy production, corrosion resistance, low density, and high impact resistance even at low service temperatures, and plastic-based materials have increased both the use of and interest in those materials. For this reasons, plastic powders are coated with many methods, even flame and plasma spraying. These methods have only recently begun to be used to coat surfaces with plastic-based powders; these are coated with metallic and ceramic-based powders with flame- and plasma-spraying methods.^{3–7}

Powder coating are used for their strength and durability; they provide protection from corrosion and environmental affects and ensure functionality and long life. Powder coatings provide a wide range of performance properties, offering excellent resistance to corrosion, heat, impact, abrasion, fading from sunlight, and extreme weather. Color selection is virtually unlimited, with high- and low-gloss, metallic, and clear finishes available. Powder coatings are attractive and durable in both thin- and thick-film applications.^{1,4}

Nylon, polypropylene, polyethylene, and poly(tetrafluoroethylene) are among the most commonly used

Correspondence to: M. Öksüz, (moksuz@marmara.edu.tr)

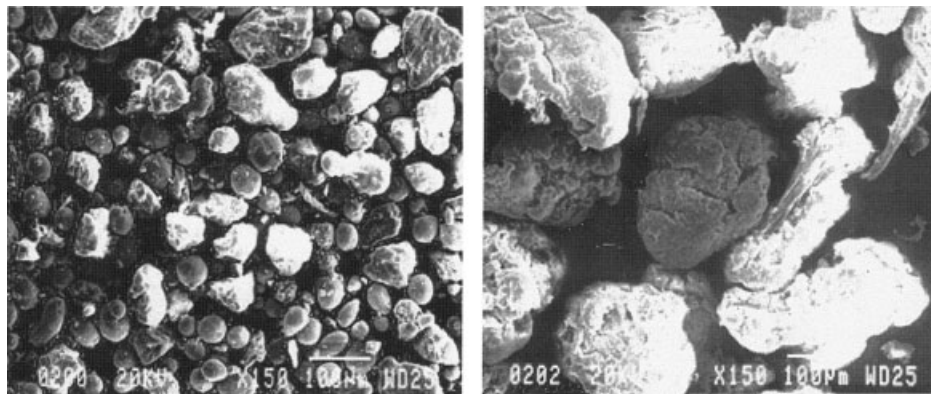


Figure 1 Scanning electron morphology of the EVOH copolymer powder used for coating.

thermoplastic materials used for flame- and plasma-spraying processes.^{4–6} Because ethylene vinyl alcohol copolymer (EVOH) coating powders are oxygen-preventive, they produce good results in coatings. For this reason, they are commonly used in packing and coating production. In recent years, EVOH powders have started to be frequently used for surface coatings. During the coating process, EVOH powders ensure better coating properties, including oxygen-preventive features, which make them a frequent choice for packing and coating surfaces.^{1,5–10}

Using polymeric coatings is an important and effective way of preventing the corrosion of various metallic materials. Because of their obvious advantages with respect to the environment, in many applications the use of powder coatings continues to grow strongly. Because of their excellent resistance against aggressive chemicals and corrosion, they are used for heavy-duty applications such as buildings, structural steel, solvent tanks, transport vehicles, pipes, valves, rail cars, bridges, and sport and leisure equipment. The main properties of plastic powder coatings are ease of processing, safety in handling, and the absence of gas or odor pollution during the coating process. Flame-spraying coating processes can be carried out manually or automatically with a wide range of available equipment.^{1,5,11–14}

As in many spraying techniques, generally the material used during the coating process is in a powder form for a flame-spraying method.^{2,3,9} The most important reason to use plastic in coatings with a flame-spraying technique is the low cost. The filler and fibers in the powder also improve the properties of the coating without affecting the coating process. The disadvantages of plastic flame spraying include the open flame; small and complicated parts that are difficult to coat; the need for experienced and skilled operators; and the melting of the plastic in the flame, which can degrade the plastic coating and possibly give off hazardous gases.^{5,9}

The polymer powder coating market is growing considerably because of the easy processing, ecologi-

cal benefits, excellence of finish, efficiency, economy, and energy savings. These factors are increasing the use of polymer coating. In the surface coating process, not only polymer powders but other powders (metallic and ceramic) can be used. The production costs for metallic and ceramic powder are quite expensive. Metallic and ceramic powder can wear the machine parts during the application process.^{1,7}

This study examines, in more detail, properties of EVOH coating powders. The mechanical and morphological properties have been studied as a function of the flame type and coating thickness. Because of its properties, EVOH is suggested for surface coating applications.

EXPERIMENTAL

Materials

EVOH powder was used as a coating material with a flame-spraying technique. The powder material (80–150 μm) was supplied by Messer Griesheim. The EVOH powder particles had a complex morphology, and the morphology had an important role during the coating process, specifying the homogeneity of the coating. The surface morphology of the powder material and the coated surface was researched with scanning electron microscopy (SEM), and some of these morphologies are shown in Figures 1 and Figures 6 and 7 (shown later). Those with complex grain sizes formed characteristic wavy patterns.

Gases

During the coating of metal substrates with the EVOH powder via flame spraying, oxygen was used as the burner gas, and acetylene was used as the combustion gas. The flame types were based on the oxygen/acetylene gas ratios. Oxidizing, carburizing, and neutral flames were used during the coating process. The oxygen/acetylene ratios were 1.30–2.50 for the oxidizing flame, less than 1.0 for the carburizing flame, and

TABLE I
Flame-Spraying Gases¹

Gas mixture	Flame temperature (°C)	Heat value (kJ/m ³)	Ignition rate (cm/s)	Flame yield (kJ/cm)
Oxygen/acetylene	3200	56,430	1350	45

¹ please supply data

1 for the neutral flame. The properties of the gases are listed in Table I.

Equipment

The coatings were carried out with a Messer Griesheim model 06 00243 flame-spraying system. The samples prepared for coating were coated with different parameters (Table II). The coated samples were bonded with Devcon double-component epoxy-based adhesives and oven-dried at 75°C. The bond strengths of the coatings were determined according to ASTM C 633-79¹⁵ with a Hounsfield universal tensile testing machine. The crosshead speed for the bond strength test was set at 1 mm/min. The bond strengths were performed at room temperature. At least five measurements were taken, and the average values are reported. The measurement setup for the bond strength is schematically presented in Figure 2. The powder morphology and microstructures of the EVOH coating were examined with a JEOL JSM-840 scanning electron microscope. Figures 1 and Figures 5 and 6 (shown later) show the SEM morphology of the powder and coating surfaces, respectively. Before the SEM investigation was conducted, the samples were coated with gold. The SEM investigations were performed at 20 kV after coating the samples were coated with gold for conductivity. The changes in the structural characteristics of the coatings were examined with a Mattson 1000 Fourier transform infrared spectrometer.

TABLE II
Flame-Spraying Parameters

Type of spraying gun	Duromet 560
Type of spraying nozzle	MG-C 26
Spraying distances (mm)	150, 300, and 450
Coating thicknesses (mm)	0.5, 1, 1.5, and 2
Spraying angle (°)	70–80
Oxygen pressure (bar)	2
Acetylene pressure (bar)	1
Air pressure (bar)	5
Oxygen flow ratio (m ³ /s)	1.7
Acetylene flow ratio (m ³ /s)	1
Spraying ratio (kg/s)	0.7
Spraying powder	EVOH
Substrate	SAE 1035 steel
Flame types	Oxidizing, carburizing, and neutral
Spraying rate (kg/s)	0.7–0.9

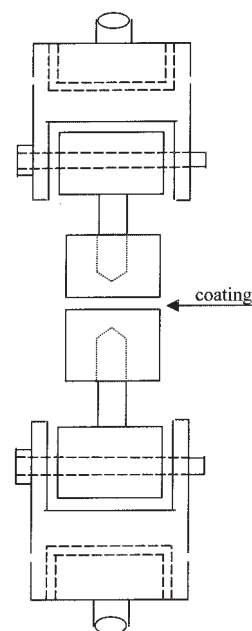


Figure 2 Test setup used to determine the bond strength.¹⁵

Coating of the EVOH powder

Before the deposition of the EVOH powder, the substrate material was cleaned with the solvent trichloroethylene (Merck) for grease removal. The substrate/coating interface quality was highly dependent on surface cleaning. After the solvent cleaning process, the metal substrate was roughened with 30- μ m alumina powder to remove oxides for better bond strength between the substrate and EVOH coating layer. As for the bond strength of coatings on substrates, surface cleanliness is believed to be very important. The roughened surfaces were preheated ($\approx 100^\circ\text{C}$) to eliminate the harmful effect of any residual moisture before the coating application. After this process, the coating operation was carried out on the prepared substrates with an angle to the substrate surface of approximately 70–80°. Figure 3 shows the formation, flow, and constitution of the coating process in the flame-spraying method. The process parameters used during the EVOH powder coating are listed in Table II. The surfaces coated with EVOH powder were air-cooled at room temperature after the coating process was completed.

The varied spraying distances were obtained with the vertical motion of the nozzle. The coating spraying distances in this study were 150 (short), 300 (medium), and 450 mm (long), respectively.

RESULTS AND DISCUSSION

The results, including those of the bond strength tests, showed that the properties of the EVOH coatings were highly dependent on the spraying parameters and flame types. The strength of the bond strength be-

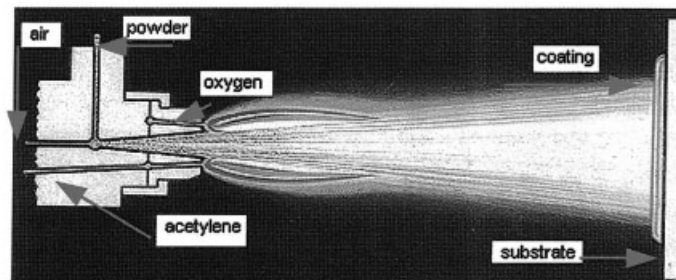
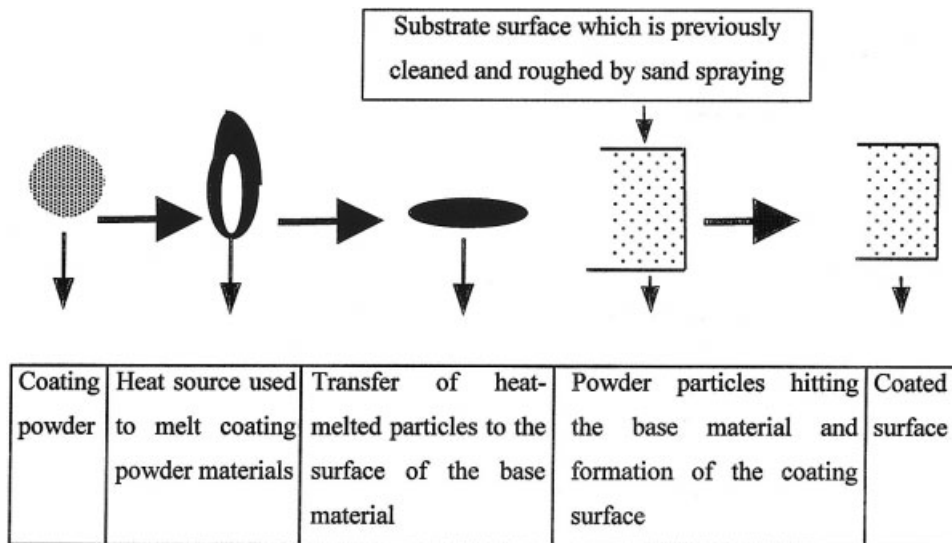


Figure 3 Flow and formation diagram for the coating process used in flame spraying.¹

tween the flame-sprayed surface and substrate was extremely important for the coatings.¹ The bond strength values were measured with an adhesion test¹⁵ of the EVOH coatings (Fig. 4). The basis of the bond strength mechanism was mechanical adhesion in this type of coating. The strength of the adhesion between the flame-sprayed surface and substrate was extremely important for the coatings.⁹ The bond strengths were assessed on the basis of the spraying distance, coating thickness, and flame type. It was very important to control the spraying parameters, which corresponded to the bond strength and performance of the coatings. Good adhesion played an important role in the mechanical properties that affected the life performance of the coatings.¹ According to the results, the bond strengths measured with the adhesion test¹⁴ of the coatings depended on the spraying distance, thickness, and flame type. The bond strength values for 150-, 300-, and 450-mm coatings performed with oxidizing flame were lower than those performed with carburizing and neutral flames [Fig. 4(a-c)]. The spraying distance, flame type, and thickness were important parameters that could influence the

porosity and porosity level of the coating material.¹ The ideal coating was carried out at a 450-mm spraying distance, and the coating thickness was 1.5 mm with a neutral flame. However, in a neutral flame, the coatings showed similar bond results. Therefore, the flame type for this type of coating was very important for applications because of the good adhesion of EVOH to the substrate. The strong bond between the substrate and polymer coating was a function of the chemical nature of the polymer and metal surface characteristics as well as surface energies and wetting.¹² The experiments showed that the adhesion of EVOH to the substrate performed with a neutral flame was higher than that of the coatings performed with oxidizing and carburizing flames, as shown in Figure 4(a-c), respectively. Figure 6 (shown later) shows the IR spectra of powder and coated surfaces and indicates changes in the structural characteristics of the powder and coatings. Polymer materials are very sensitive to high temperatures, and it is believed that the heat capacity of the neutral flame causes negligible degradation. IR spectra of the coatings performed with neutral flames clarified these results. A 1050–

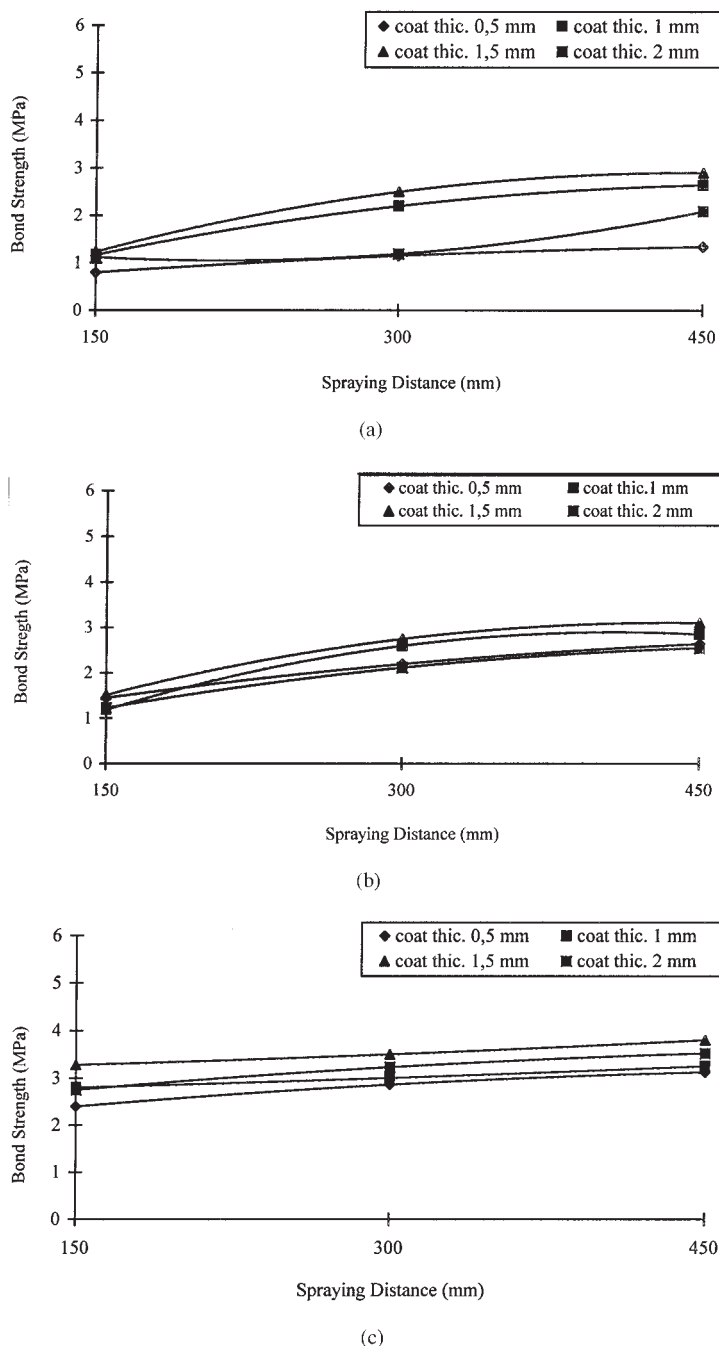


Figure 4 Bond resistance values for coatings performed with flame spraying: (a) oxidizing flame, (b) carburizing flame, and (c) neutral flame.

1100-cm⁻¹ peak can be observed [Fig. 5(b)] that did not change at all in comparison with Figure 5(a).

While the coating thickness increased, the bond strength decreased because of the porosity of the coatings. Also, the exothermic reaction and changing crystalline contents in the coatings were important for the final properties. The properties of the polymer materials strongly depended on crystallization. The changes in the crystallization controlled the morphology.¹⁶ Consequently, the weakening of the bonds among the molecules of the EVOH coating caused the

bond strength to decrease and caused the fracture to occur at lower stresses. IR spectra of the coated surfaces justified these results [Fig. 5(b)]. The IR spectra show the thickness and distance did not play vital roles for the coatings created with an oxidizing flame because of degradation. Moreover, the same degradation also existed in the 150-mm-distance coatings. This established that this degradation was caused only by the oxidizing flame. The EVOH coating with an oxidizing flame was not ideal for the flame-spraying process.

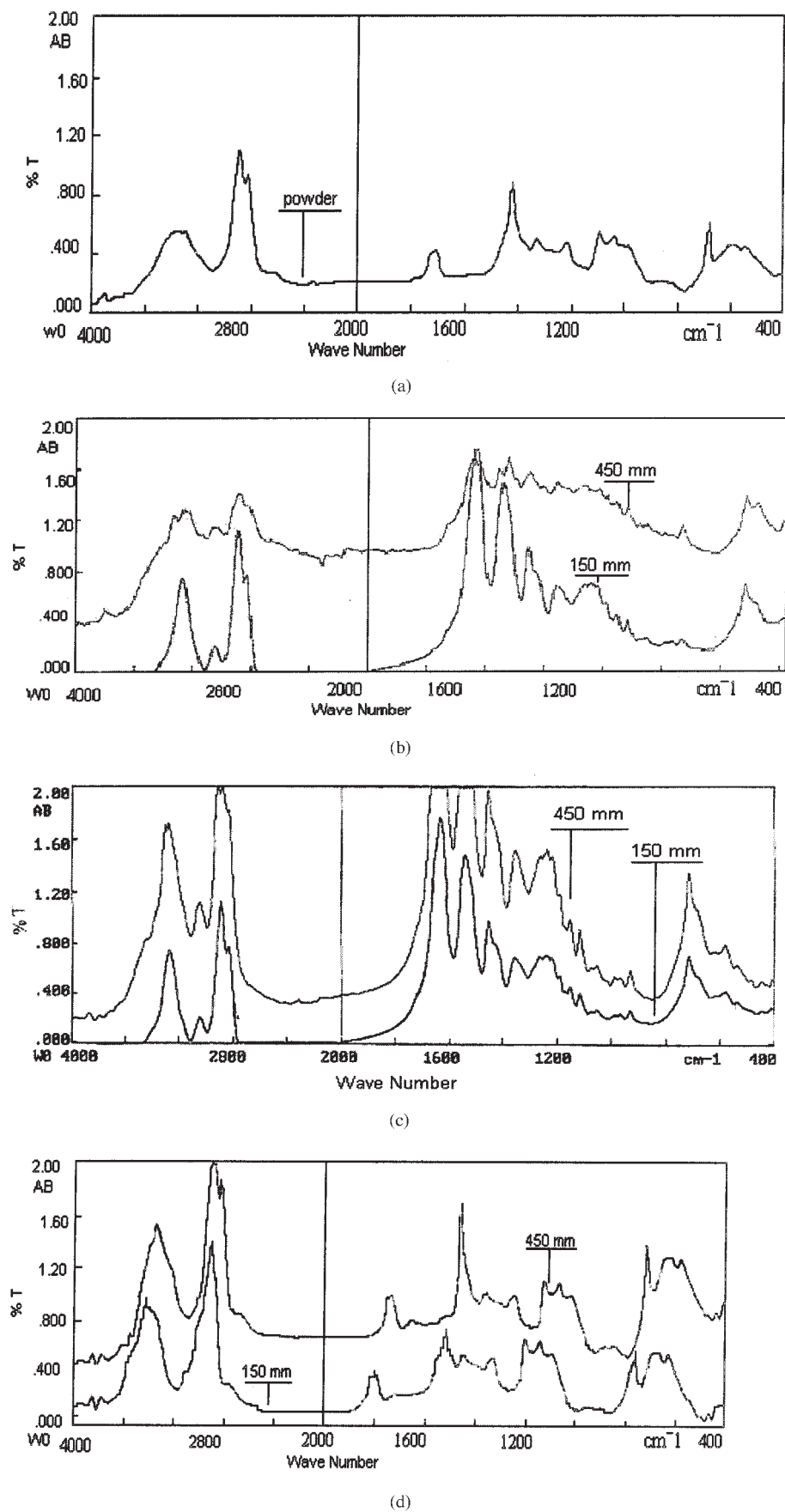
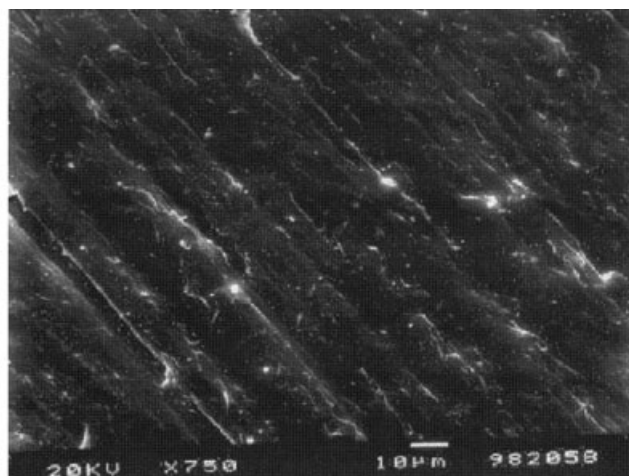


Figure 5 IR spectra of powder and coated surfaces: (a) powder, (b) oxidizing flame coating, (c) carburizing flame coating, and (d) neutral flame coating.

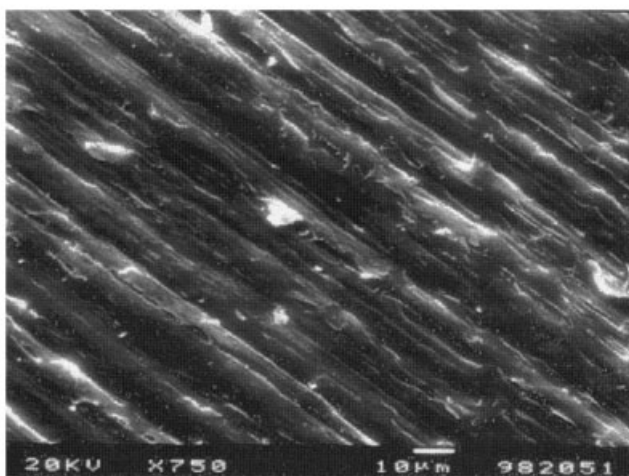
Furthermore, the bond strength of the coatings carried out with a carburizing flame was higher than the bond strength of those carried out with an oxidizing flame. However, coatings carried out with a carburizing flame were subject to degradation. This was indicated by the IR spectra of the surfaces of coatings carried out with a carburizing flame [Fig. 5(c)]. The reduction and deformation (shift) of the C—O peak volumes at $1050\text{--}1100\text{ cm}^{-1}$ and the deformation of the O—H peaks at $3200\text{--}3400\text{ cm}^{-1}$ clearly demonstrate degradation. The adhesion usually depended on the conditions that enabled the polymer to oxidize.

The bond strength of the coatings carried out with a carburizing flame tended to increase toward the distance range of 150–450 mm [Fig. 4(b)]. This was also indicated by IR spectra [Fig. 5(c)]. The change in the C—O peaks at $1050\text{--}1100\text{ cm}^{-1}$ in Figure 5(c) also verified this result. The reason for the increase in degradation in the 150-mm-distance range was thought to be the rising effect of the C_2H_2 gas.

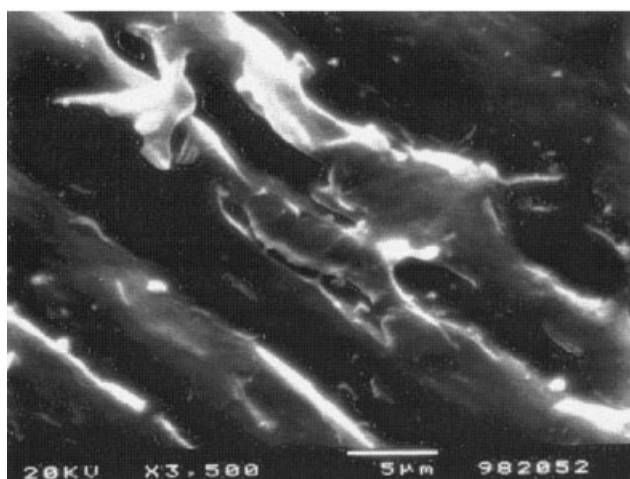
Moreover, the bond resistance of the coatings carried out with a neutral flame was higher than that of the coatings carried out with oxidizing and carburizing flames [Fig. 4(c)]. The coatings carried out with a neutral flame experienced almost negligible degradation and thus were ideal coatings. IR spectra of the coatings carried out with a neutral flame clearly indicated this result [Fig. 5(d)]. In these spectra, the $1050\text{--}1100\text{ cm}^{-1}$ peak did not change at all in comparison with the original peaks [Fig. 5(a)]. Furthermore, there were differences in the coatings carried out at 150 and 450 mm, and the structural changes of the coatings carried out with a neutral flame did not necessarily depend on distances [Fig. 5(d)]. The bond strengths of the coatings carried out with a neutral flame did not strongly depend on the distance [Fig. 4(c)], which did not play as important a role as it did for the oxidizing flame. During the tensile testing (adhesion), much elongation was monitored for the neutral flame coating. Therefore, the optimum coating, which provided good adhesion, was possible with the neutral flame in the flame-spraying process.¹ The coating thickness was also important for the bond strength. When the coating was greater than 1.5 mm, the bond strength decreased. The increasing thickness reduced the bond strength because of the stress applied to the coating. Thus, stress from the surface to the coating inside moved within a larger area and broke out with less force. Better results were obtained when the coating thickness was between 1 and 1.5 mm. This was due to fewer or no microstructure cracks and minimal pores and gaps. Therefore, the flame type had to be chosen carefully for good bond strength. In this respect, the oxidizing and carburizing flame types yielded no acceptable bond strength. The results presented in Figures 4(c) reveal that the EVOH-coated substrate had good adhesion. This was believed to be due to the physical adsorption between



(a)



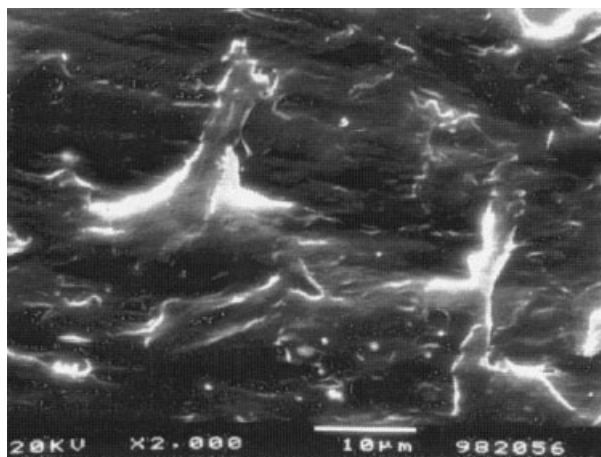
(b)



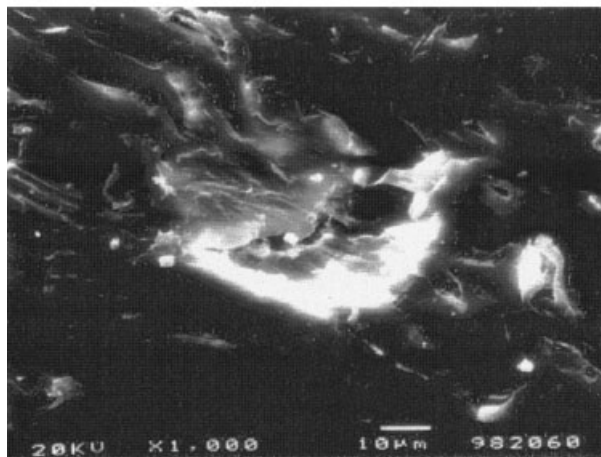
(c)

Figure 6 SEM micrographs showing the surfaces of EVOH coatings: (a) oxidizing flame coating, (b) carburizing flame coating, and (c) neutral flame coating.

polar groups formed during the thermal oxidation of the coating material and the surface of the substrate as well.^{12,13}



(a)



(b)

Figure 7 SEM micrographs showing coatings with porosity: (a) carburizing coating (2 mm thick) and (b) oxidizing coating (2 mm thick).

Figure 6 shows the structure of the EVOH copolymer coating obtained by SEM. The surface whiteness was due to the high vacuum of the SEM equipment. The distribution and fusion were good. The bond strength and IR spectra of the coatings carried out with a neutral flame clearly indicated this result [Figs. 4(c) and 5(d)]. The coatings carried out with a neutral flame contained almost negligible degradation. In these spectra, the $1050\text{--}1100\text{-cm}^{-1}$ peak did not change at all in comparison with the original IR peaks [Fig. 5(a)]. The SEM examinations showed various indentations [Fig. 6(a–c)] and pores [Fig. 7(a,b)] on the coating surfaces. Figure 6(a–c) indicates that the fracture marks on the surfaces of the coatings made with a neutral flame were higher in number and more frequent than those of the coatings made with an

oxidizing flame. Because of the structural degradation of the coatings made with an oxidizing flame, the fracture surfaces were more indented. The coatings made with an oxidizing flame contained pores [Fig. 7(a)]. This may have been due to the high temperature. Pores can be seen in the SEM micrographs of Figure 7(a,b).

CONCLUSIONS

In this study, substrate surfaces were coated with a flame-spraying process with an EVOH powder, and the changes in the bonding properties and structure were studied. The changes in the bond strength, macrosurfaces and microscales, and structural properties of the coatings were investigated. In terms of the bond strength, the EVOH powder coating performed with a neutral flame was more suitable than the coatings performed with oxidizing and carburizing flames. Moreover, the bond strength of the coatings increased from 150 to 450 mm. The surface color changes (discoloration and fading) and structural stability changes depended on the spraying distance of the coatings performed with oxidizing and carburizing flames. The surface characteristics and structural stability of the coatings performed with a neutral flame did not change with the spraying distance.

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