Bonding Characteristics of Recycled Polyethylene Terephthalate (PET) Fibers Coated with Maleic Anhydride Grafted Polypropylene in Cement-Based Composites

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ABSTRACT: In this study, we sought to enhance the bond performance between recycled polyethylene terephthalate(PET) fibers and cement-based composites using a hydrophilization treatment with hydrophilic maleic anhydride grafted polypropylene (mPP). The bond performance was evaluated with bone-shaped specimens after the hydrophilization treatment. The effects of the concentration of mPP in the solution in which the PET fibers were immersed (0, 5, 10, 15, and 20%) and the three types of shapes on the surface energy of the recycled PET fibers were evaluated. The pullout behavior, bond strength, and interfacial energy all increased with the concentration of mPP to 15% but decreased at 20%. This occurred because 15% mPP coated the recycled PET fiber thoroughly, whereas a 20% mPP coating resulted in partial cracks, which led to fractures on application of a pullout load. Of the fiber shapes, the embossed fibers demonstrated the best bond behavior. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1908–1915, 2011

Key words: coatings; composites; fibers; hydrophilic polymers; interfaces

INTRODUCTION

Cement-based composites are often brittle and possess a low tensile strength, energy absorption, and crack resistance, but one way to overcome these limitations is to add reinforcing fibers to cement-based composites.[1–4] Reinforcing fibers prevent crack growth by a bridging effect and induce ductile fracture to increase the energy absorption capacity of cement-based composites.[1–3] The enhanced energy absorption capacity of fiber-reinforced cement-based composites is determined by a bonding mechanism between the fibers and composites. This bridging effect induces fiber debonding, fiber pullout, and fiber fracture.[4–7] The energy absorption capacity of cement-based composites is influenced by the bond mechanism of individual fibers,[8,9] and fiber bridging reduces the stress intensity and crack closure at crack ends.[1,8] Fiber debonding and pullout at the interface of cement-based composites also affects the total energy absorption capacity during crack propagation.[1,8,10] Therefore, the bonds between the fibers and cement-based composites stabilize crack propagation.[11–13]

Polyethylene terephthalate(PET) is a plastic used in various products, such as beverage containers.[14] However, waste PET bottles constitute an environmental problem, and the recycling of PET products is important from both environmental and economic perspectives.[14] Therefore, recycling PET in concrete can contribute to environmental preservation. At present, methods of recycling PET bottles in concrete-related fields include their conversion into unsaturated polyester and their application to polymer concrete or their use in the production of lightweight aggregates in lightweight concrete.[14,15]

However, the production of reinforcing fibers from waste PET bottles for cement-based composites has several merits and demerits in terms of their physical properties. The major concerns in the use of PET materials as reinforcing fibers are their poor bond performance with cement-based composites and durability under alkali conditions. Methods used to enhance the bond between reinforcing fibers and cement-based composites include the mechanical deformation of fibers (i.e., fibrillation, twisted, crimped, hooked), densification of the interface between the fibers and cement-based composites by the addition of silica fume, deformation of the

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surface shape of the fiber, and alteration of the surface properties with a plasma process.[6,8–10,13,16] In this study, we examined the effect of surface hydrophilization on the properties of recycled PET fibers. The method of hydrophilization was used to coat hydrophilic maleic anhydride grafted polypropylene (mPP) on the surface of the fibers. Polypropylene has excellent chemical stability, tensile strength, and impact strength. In addition, it has superior alkali resistance, which could be used to enhance the alkali resistance of recycled PET fibers. Polypropylene is a hydrophobic material that has poor bond strength with cement-based composites, and the addition of large numbers of fibers may result in dispersion problems.[17–20] In contrast, mPP has a very similar molecular structure except for the addition of grafted side groups.[17–20] The bond properties of the hydrophilized recycled PET fiber with cement-based composites were evaluated in terms of their effects of the concentration of mPP (0, 5, 10, 15, and 20 wt %) and the fiber shape (straight, crimped, and embossed).

EXPERIMENTAL

Geometry of the recycled PET fibers

The bond performance of three types of reinforcing fibers made from recycled PET bottles were evaluated: straight (smooth surface and linear form), embossed (indentations on the fiber surface), and crimped (a bent external shape) fibers (see Fig. 1). The embossed, crimped, and straight fibers measured 1.3 × 0.2 mm^2 (0.051 × 0.008 $in.^2$, Width × Thickness), 1.2 × 0.3 mm^2 (0.047 × 0.012 $in,^2$), and 1 × 0.5 mm^2 (0.039 × 0.019 $in.^2$), respectively.

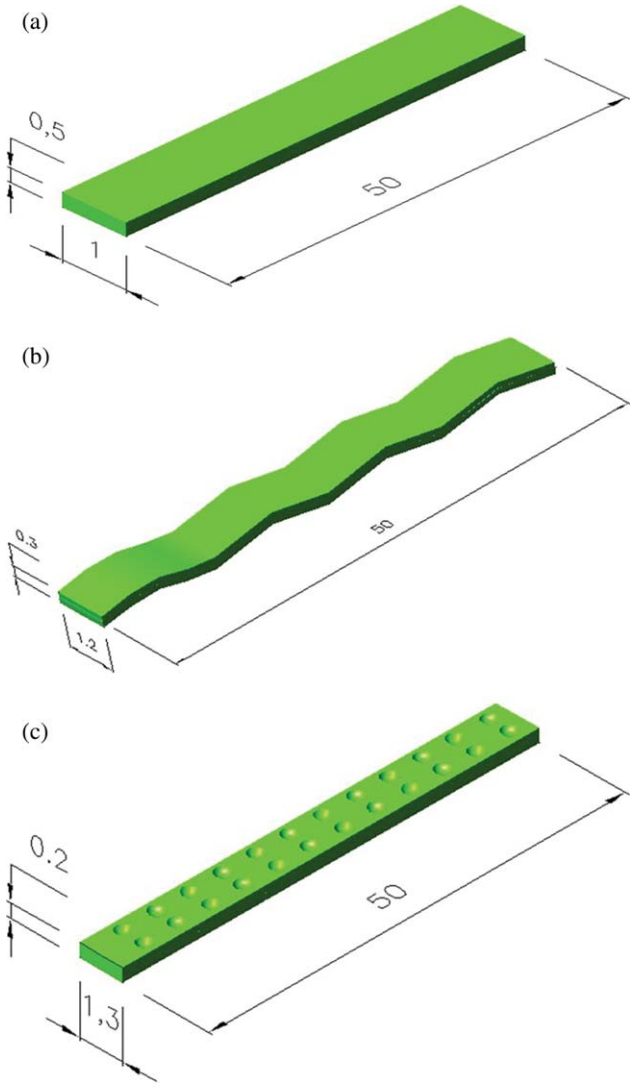


Figure 1 Shapes of the recycled PET fibers: (a) straight, (b) crimped, and (c) embossed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surface treatment methods

To hydrophilize the recycled PET fibers, mPP was dissolved in toluene in mixtures of 5, 10, 15, and 20 wt % at 80°C. The temperature of toluene was set to 80°C because mPP is not chemically affected at this temperature and can be 100% dissolved.[17] Because the other solvents, such as benzene, tetrahydrofuran, and dimethylformamide, could not be 100% dissolved in mPP, we used only toluene as a solvent. Then, the fibers were passed in the solution to hydrophilize the surface. Figure 2 presents photographs of the surface of PET fibers treated at each concentration. Figure 2(a) shows an uncoated surface. When coated in 5% mPP, large portions of the surface were not coated [Fig. 2(b)]. In contrast, the majority of the surface was coated with 10% mPP [Fig. 2(c)], and the entire surface was coated with 15% mPP [Fig. 2(d)]. With 20% mPP, a small area of the surface was not coated. Because the viscosity of the polymer solution increased with the amount of polymer and the molecular weight, the uneven coating at a 20% concentration of mPP was due to the increasing viscosity of the mPP solution. However, when the amount of mPP increased, the adhesion force between the mPP molecules also increased and became stronger than the adhesion force between the PET fibers and the mPP, so that the mPP bonded to itself and not the surface of the PET fibers. Therefore, the concentration level of mPP should not have exceeded 20% [Fig. 2(e)].

Pullout test

Dog-bone-shaped samples according to the Japan Concrete Institute SF-8 standards for test methods of fiber reinforced concrete[21] were used to evaluate the performance of the recycled PET fibers in relation to their type and hydrophilization treatment. As Figure 3 shows, a reinforcing fiber was placed in the

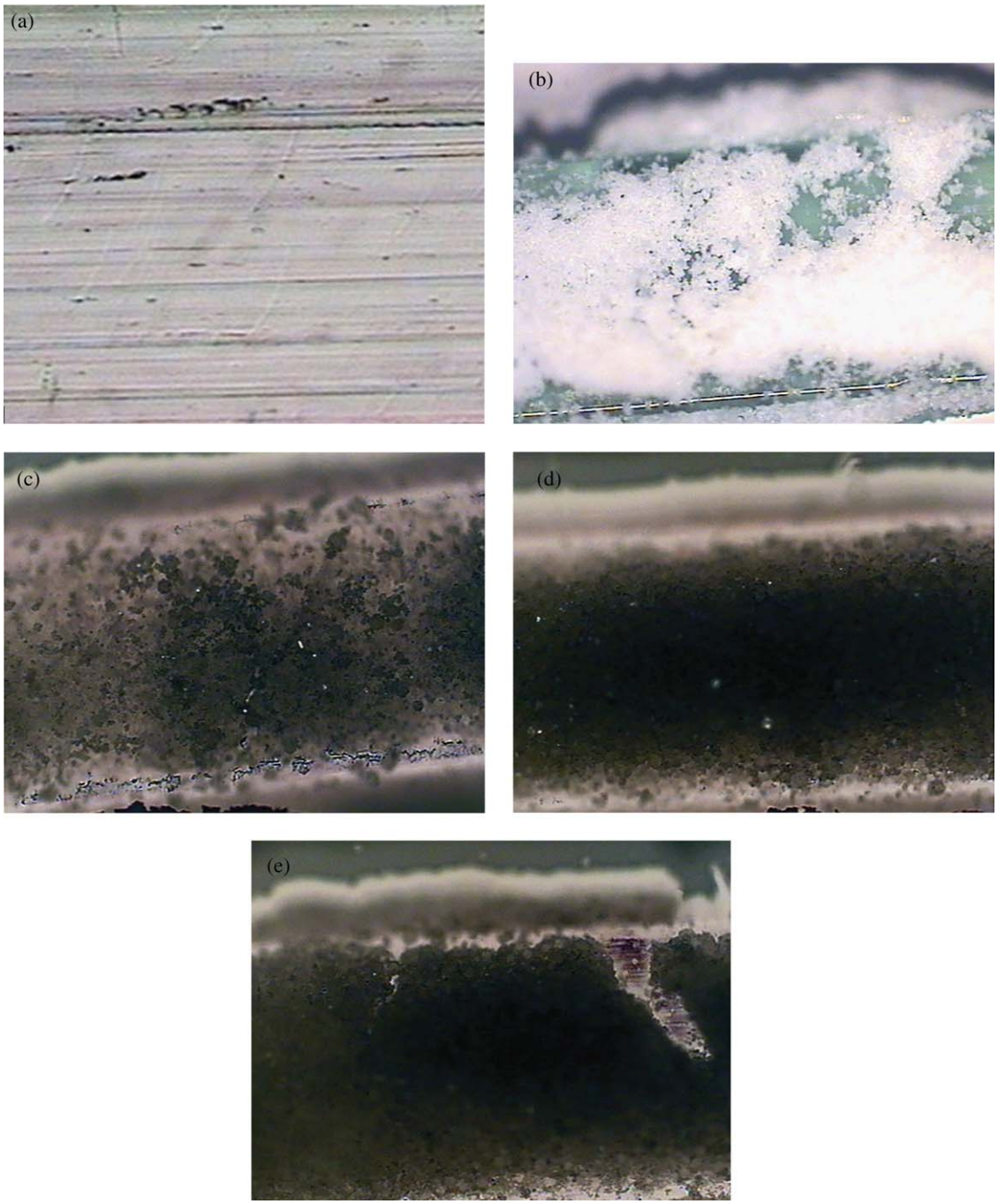
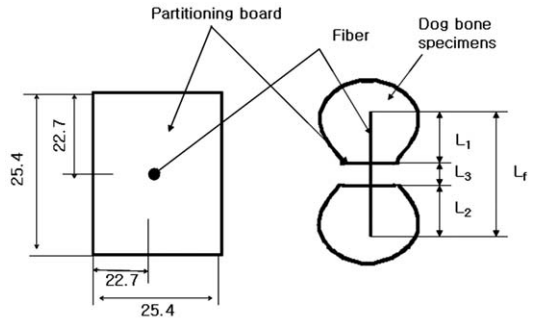


Figure 2 Photographs of the surfaces of recycled PET fibers treated with different concentrations of mPP (1000× magnification): (a) control, (b) mPP:5%, (c) mPP:10%, (d) mPP:15%, and (e) mPP:20%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

middle of a bone-shaped specimen. In this study, one fiber (25 mm or 0.984 in. long) was placed in the middle of the test specimen. The cross sections (Width × Thickness) of the embossed, crimped, and straight fibers measured 1.3 × 0.2 mm^2 (0.051 × 0.008 $in.^2$), 1.2 × 0.3 mm^2 (0.047 × 0.012 $in,^2$), and 1 × 0.5 mm^2 (0.039 × 0.019 in), respectively. The embedded length of all of the fibers was 15 mm (0.59 in.). The bond strength test results are presented as the mean values of six specimens.

The specimen was manufactured with a 1 : 1.2 ratio of cement to fine aggregate and a 0.55 ratio of water to cement. Fine aggregate with a specific gravity of 2.60, a fineness modulus of 2.1, and a maximum sand size of 0.595 mm was used in this study. After manufacturing, the specimens were cured for 24 h at 23 ± 2°C and 50 ± 2% relative humidity and were then cured in water at 23 ± 2°C for 28 days before the experiment.[22] After curing, the pullout strength was evaluated with an installed displacement-



L_1: embedment length (15 ㎜)

L_2: anchored length (15㎜)

L_3: unbonded length (20㎜)

L_f: fiber length (50㎜)

t: thickness of the partitioning board (0.5㎜)

Figure 3 Arrangement of the partitioning board and fibers and their placement in the mold (values are presented as millimeters).

adjustable 50-kN universal testing machine (Instron model 3369, Massachusetts, US) with a loading rate of 0.5 mm/min.

After the pullout tests, the maximum bond strength (τ_{max}) was calculated as follows:

$$\tau_{max} = \frac{P_{max}}{2(b+h)l} \quad (1)$$

where P_{max} is the maximum pullout load, b is the width of the fibers, h is the thickness of the fibers, and l is the embedded length of the fibers.

RESULTS AND DISCUSSION

Pullout behavior

Figure 4 shows the pullout behavior according to the fiber shape with the concentration of mPP. As shown in Figure 4, the maximum pullout load

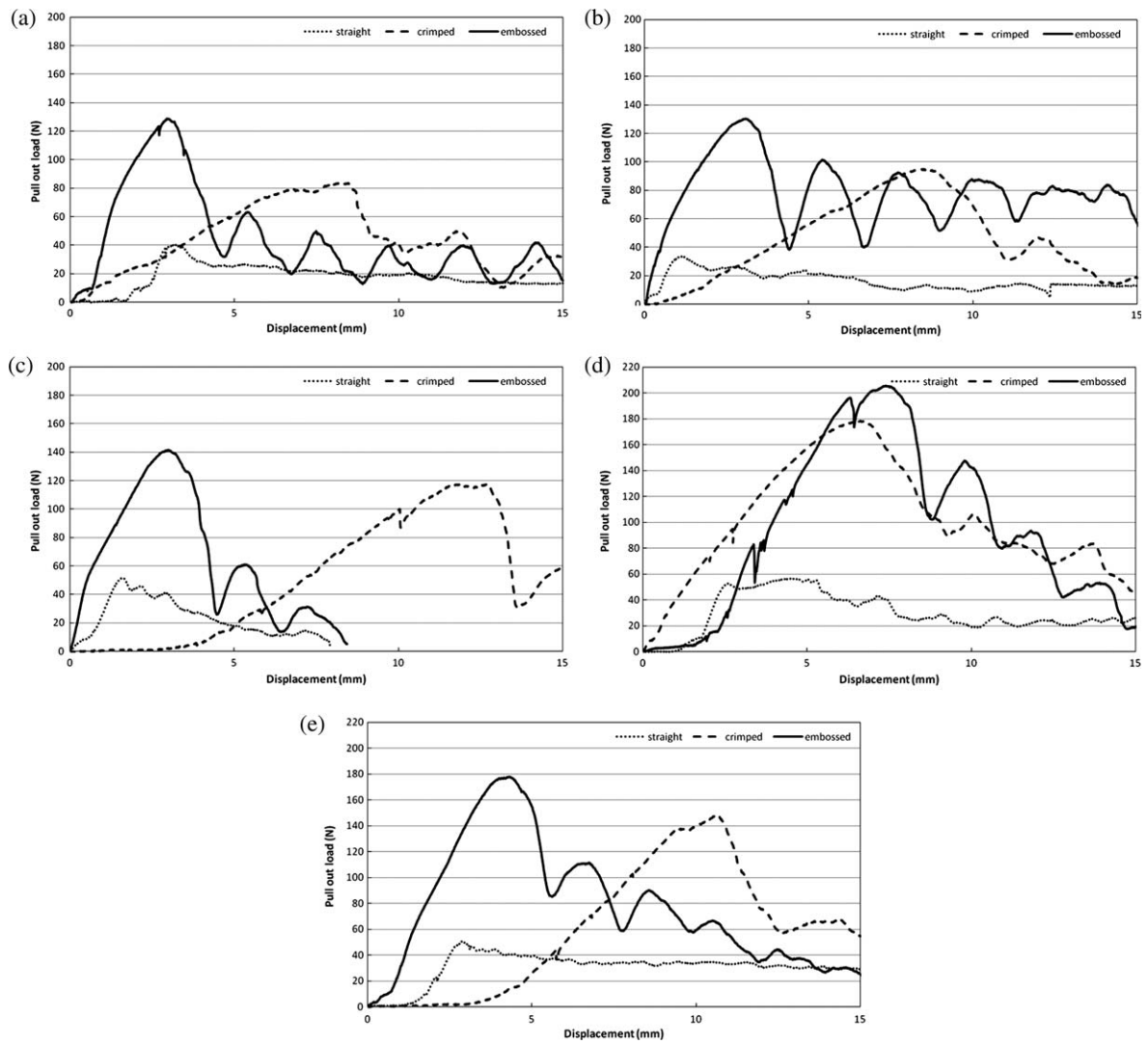


Figure 4 Pullout behavior of recycled PET fibers according to the concentration of mPP: (a) control, (b) mPP:5%, (c) mPP:10%, (d) mPP:15%, and (e) mPP:20%.

TABLE I
Results for the Bond Strength

Fiber geometry	Concentration of mPP (%)	Bond strength (MPa)[a] 1	2	3	4	5	6	Mean	Standard deviation	Increase in bond strength with surface treatment (%)[b]
Straight	0	0.67	0.69	0.55	0.68	0.68	0.59	0.64	0.06	—
	5	0.86	0.86	0.85	0.95	0.90	0.75	0.86	0.07	34
	10	0.98	0.89	0.89	0.75	0.92	0.85	0.88	0.08	37
	15	1.21	1.12	1.07	1.10	1.18	1.16	1.14	0.05	78
	20	0.88	0.92	1.10	0.94	0.82	0.93	0.93	0.09	45
Crimped	0	2.10	2.04	1.78	1.90	2.01	2.12	1.99	0.13	—
	5	2.08	2.18	2.08	2.20	2.05	2.19	2.13	0.07	7
	10	2.17	2.47	2.42	2.28	2.15	2.30	2.30	0.13	15
	15	3.52	3.42	3.64	3.97	3.52	3.59	3.61	0.19	81
	20	2.87	2.82	2.68	2.93	2.83	2.87	2.83	0.08	42
Embossed	0	2.56	2.23	2.82	2.63	2.46	2.52	2.54	0.19	—
	5	2.85	2.86	2.85	2.75	2.57	2.61	2.75	0.13	8
	10	3.20	3.15	2.99	2.99	3.25	2.99	3.09	0.12	22
	15	3.95	4.23	4.36	4.40	3.84	4.49	4.21	0.26	66
	20	3.46	3.54	3.32	3.15	3.66	3.42	3.42	0.18	35

[a] 1 psi = 0.0069 MPa.
[b] Increase = (Bond strength of the specimen with mPP/Bond strength of the control specimen) × 100% − 100%.

occurred in the embossed-type fiber regardless of the concentration of mPP, and in all of the types of fiber, the maximum pullout load appeared at 15% mPP. In this study, we observed a linear relationship between the pullout load and displacement until the fibers and cement matrix started to debond, and then, we observed a nonlinear relationship until the full pullout state or fiber fracture was reached. A similar pattern was observed for all fiber types, with some differences from displacement. The straight fibers showed a short linear period before the maximum pullout load when the minimum displacement was reached because of the rapid debonding between the fibers and cement matrix caused by their smooth surface. In contrast, the embossed fibers showed a long nonlinear period because of the uneven surface and the straightening of the fiber at the interface between the fibers and matrix; this resulted in a constant resistance to the pullout load until the full pullout state or fiber fracture was reached. It was difficult to distinguish the displacement under the linear region or nonlinear periods for the crimped fibers. When the pullout load loaded, the crimped sections started to unfold before the maximum pullout load was reached. Therefore, the displacement under the maximum pullout load was bigger than that of the other fibers, as displacement was increased by unfolding.

A clear relationship was observed between the pullout behavior and the concentration of mPP. A different behavior was observed in the section in which the fiber and cement matrix debonded. Before the fiber and cement matrix debonded, the pullout behavior increased linearly. For the straight and embossed fibers, however, the nonlinear phase increased with the concentration because the enhanced bond strength with the increased concentration of mPP delayed debonding at the bond surface between the fibers and cement matrix. Nevertheless, the period of nonlinear behavior with 20% mPP was shorter than that with 15% mPP. Because partial crack occurred on the surface of the 20% mPP coated fiber, debonding occurred on the interface between the coated part and PET fiber along this crack when we loaded the pullout load. To closely examine the initial pullout load and the displacement behavior according to the concentration of mPP, the maximum displacement was set to 2.0, 10.0, and 7.0 mm for the straight, crimped, and embossed fibers, respectively. The embossed fibers had the best bond load for different concentrations of mPP, and the pullout at the maximum bond load was gradual, not rapid. Only the straight fiber affected the concentration of mPP. The other fibers were affected by the concentration of mPP and geometry. The embossed fibers resisted rapid debonding until the maximum bond load was reached. For the crimped fibers, the load increased with the displacement and concentration of mPP until the maximum bond load was reached, after which a rapid decrease in the bond load occurred because this probably occurred when the crimped part of the fibers was stretched out. Thus, the stretch of the crimped part of the fiber influenced the decrease in the initial elastic modulus and the rapid decrease in the bond load once the maximum bond load was reached.

Table I shows the results of the bond test for each type of fiber. The bond strength of the recycled PET

TABLE II
Results for the Interfacial Energy

Fiber geometry	Concentration of mPP (%)	Interfacial energy (J) 1	2	3	4	5	6	Mean	Standard deviation	Increase in interfacial energy with surface treatment (%)[a]
Straight	0	16.3	16.6	17.0	16.3	15.8	16.3	16.4	0.39	—
	5	21.5	16.2	15.7	18.8	17.1	17.4	17.8	2.12	8
	10	25.3	25.0	25.5	25.6	24.7	24.2	25.0	0.54	53
	15	28.9	28.7	29.3	27.0	29.1	27.8	28.5	0.88	74
	20	25.6	24.5	23.3	21.9	23.1	20.4	23.1	1.85	41
Crimped	0	69.1	66.9	72.5	69.6	72.2	68.1	69.7	2.26	—
	5	87.6	93.6	88.8	87.8	91.1	86.2	89.2	2.71	28
	10	105.2	109.5	107.8	116.3	108.9	99.4	107.8	5.55	55
	15	126.1	133.3	133.3	134.0	135.0	128.3	131.7	3.59	89
	20	87.8	93.6	84.3	83.8	95.9	93.1	89.7	5.15	29
Embossed	0	84.8	86.7	80.5	81.3	81.5	91.9	84.5	4.34	—
	5	121.0	116.3	123.2	103.9	104.7	118.2	114.6	8.27	36
	10	126.2	122.7	131.2	124.1	124.0	129.3	126.3	3.38	49
	15	143.6	143.0	141.2	141.7	143.2	135.9	141.4	2.86	67
	20	93.3	91.4	90.2	87.3	90.9	93.6	91.1	2.32	8

[a] Increase = (Interfacial energy of the specimen with mPP/Interfacial energy of the control specimen) × 100% − 100%.

fibers increased with the concentration of mPP to a concentration of 15% because of the improved coating. However, the bond strength decreased with the concentration of mPP up to 20% because of the mPP self-bonding.

As the concentration of mPP increased to 5, 10, 15, and 20%, the increase in the bond strength due to surface hydrophilization of the straight fibers increased by 34, 37, 78, and 45%, respectively, compared to the control specimen. The bond strength of the crimped fibers increased by 7, 15, 81, and 42%, whereas that of the embossed fibers increased by 8, 22, 66, and 35%, respectively.

The best performance was attained when the recycled PET fibers were coated with 15% mPP. This pattern was observed for all types of fiber. With regard to the fiber geometry, the embossed fibers showed excellent bond behavior at all concentrations of mPP. Because of the uneven surface, such a strong bond was obtained that the cement matrix was still observed on the surface after the bond test. The crimped fibers also resulted in increased bond strength compared to the straight fibers because of their greater specific surface area and uneven surface. The unfolding behavior of the crimped sections lowered the bond strength compared to the embossed fibers because of insufficient anchorage to the cement matrix.

The interfacial energy is a very important factor related to the enhanced ductility of cement-based composites, which results from reinforcing fibers, which inhibit crack propagation by giving rise to a constant tensile stress when fibers are pulled from the cement matrix. The interfacial energy is also critical after cracks occur, with a higher interfacial energy ensuring ductile behavior in cement-based composites. The *interfacial energy* is usually defined as the energy consumed during fiber pullout and can be determined by the integration of the area under the fiber pullout curve. In this study, for the crimped fibers, a displacement of up to 10 mm was used as the pullout measurement range. This value was chosen so that it would include all maximum bond loads, which had a maximum displacement of 9 mm. Table II shows the interfacial energy results, in which the interfacial energy increased with the concentration of mPP. The range of increase was 8.5 to 35.6%, 49.5 to 54.7%, 67.4 to 88.8%, and 7.9 to 41.1% for 5, 10, 15, and 20% for the various fiber shapes, respectively. The best results were obtained with 15%, and the interfacial energy decreased at 20%, as did the bond strength, because 15% mPP resulted in a perfect coating. The self-bonding of the mPP at a concentration of 20% occurred for all fibers types. The embossed fibers gave the best results, regardless of concentration of mPP. Overall, the embossed fibers coated with 15% mPP exhibited the best bond performance.

Observation of the fiber surface after the pullout test

The fiber surface was examined after the pullout test to analyze the frictional resistance during the pullout process according to the concentration of mPP under optical microscopy at 1000× magnification.

Figure 5 shows the surface of the embossed fibers after the pullout test according to the concentration of mPP. The surface roughness increased with the concentration of mPP, and surface rupture was observed with 15% mPP. Hydrophilic mPP has a high bond strength with a cement matrix, so it bonds well to the

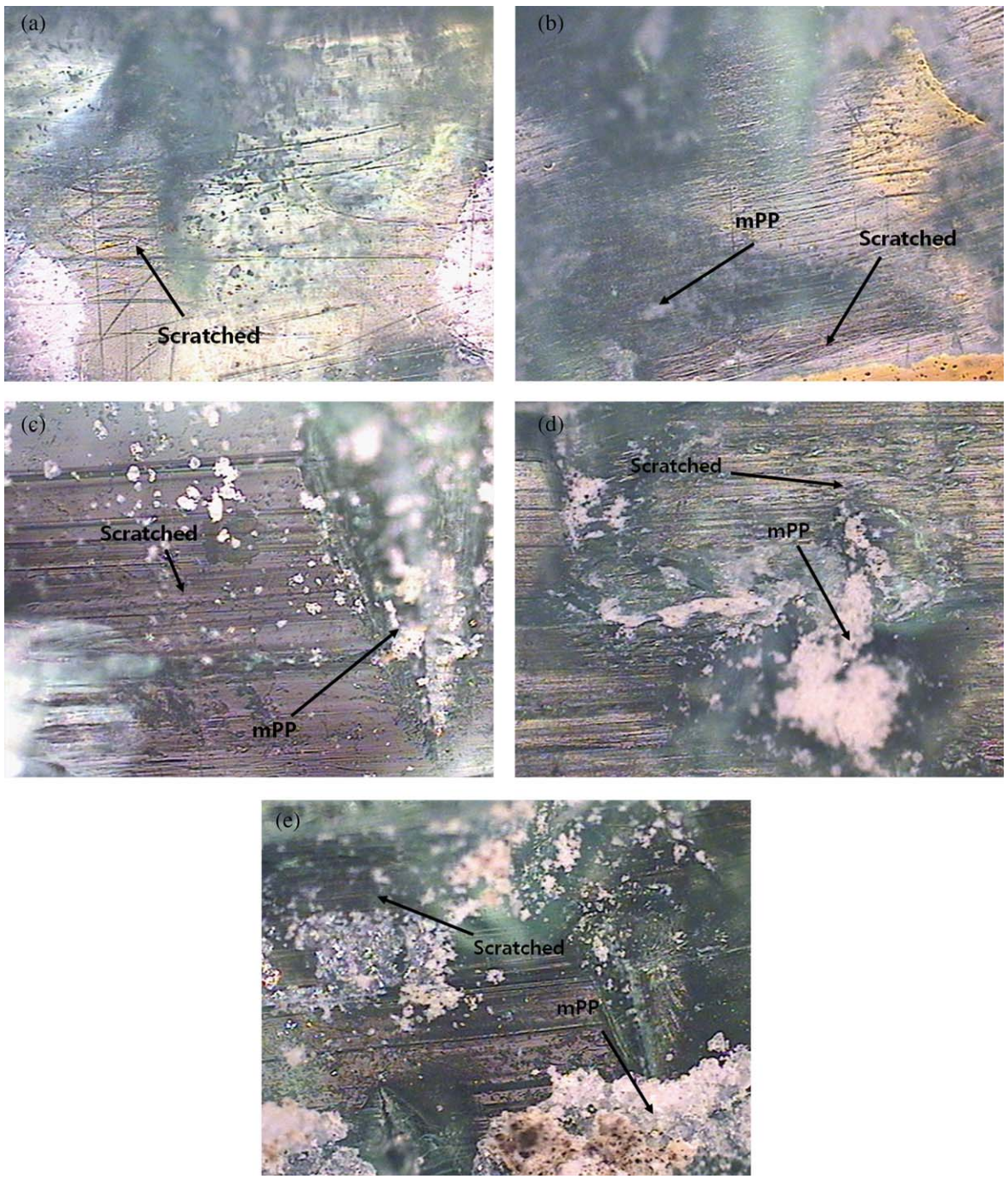


Figure 5 Photographs of the surfaces of embossed fibers according to the concentration of mPP after the pullout tests (1000×magnification): (a) control, (b) mPP:5%, (c) mPP:10%, (d) mPP:15%, and (e) mPP:20%.

surface of PET fibers when an appropriate amount is coated. The results suggest that the hydrophilization of the recycled PET fibers enhanced the bond performance by increasing the friction with the cement matrix during the pullout process.

CONCLUSIONS

In this study, we evaluated the effect of chemical hydrophilization on the bond performance between recycled PET fibers and cement-based composites. Bond experiments with dog-bone-shaped specimens containing fibers treated with various concentrations of mPP (0, 5, 10, 15, and 20 wt %) and with three fiber shapes (straight, crimped, and embossed) were performed. The results were as follows:

1. The bond strength increased with the degree of surface hydrophilization by mPP for all fiber types. The best results were attained with

the 15% mPP coating, but when the concentration of mPP reached 20%, the indentation decreased. This pattern was observed for all types of fibers.

2. The interfacial energy showed the best result at 15% mPP. The embossed fibers were superior in terms of bond strength to any other type of fiber for all concentrations of mPP.
3. Observations of the surface of the recycled PET fibers after the pullout tests showed that the number of scratches on surface increased with the concentration of mPP. At 15% mPP coated, we observed not only scratches but also tear-off.

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