Wetting and Adhesion Behavior of Armos Fibers After Dielectric Barrier Discharge Plasma Treatment

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ABSTRACT: To investigate the influence of atmospheric plasma treatment on aramid fiber wetting and adhesion behavior, an air dielectric barrier discharge (DBD) was applied to the Armos aramid fiber surface at different discharge power densities. Dynamic contact angle analysis indicated that the total surface free energy was increased from 49.6 to 68.3 mJ/m^2, an increment of 37.7%, whereas the single-fiber tensile strength testing showed that the mechanical properties of the Armos fibers were almost unaffected. With the enhancement of fiber surface wettability, the interlaminar shear strength, which was used to determine the interfacial adhesion in Armos-fiber-reinforced thermoplastic poly(phthalazinone ether sulfone ketone) composites, increased by 17.2% to 71.4 MPa. Scanning electron microscopy photos showed that the predominant failure mode of the composites changed from interface failure to matrix and/or fiber failure after the plasma treatment. Taken together, these results suggest that the air DBD plasma was an effective technique for improving the surface and interfacial performance of the Armos fibers without damaging their bulk properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 433–438, 2012

Key words: fibers; interfaces; matrix; strength; surface modification

INTRODUCTION

Compared to inorganic reinforcing materials, such as glass and carbon fibers, advanced composites filled with aramid fibers have excellent axial properties because the fibers have a unique combination of stiffness, high strength, and low density.[1] Armos fiber, a para-aramid material that incorporates imidazole functional groups, shows markedly higher mechanical properties than the rest of the aramid fibers.[2] On the other hand, the matrix resin used in this study, poly(phthalazinone ether sulfone ketone) (PPESK), is a novel thermoplastic resin with an extremely high glass-transition temperature, thermooxidative stability, and excellent mechanical properties,[3] which can satisfy the increasing demands of high-performance applications involving high-temperature resistance, damage tolerance, and flexibility that thermosetting resins always lack.[4] Additionally, PPESK shows better solubility in some common solvents, such as *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone, and chloroform. Armos-fiber-reinforced PPESK composites can thus be easily prepared by the solution impregnation technique, and the resulting high-performance composites are supposed to be capable of operating in extreme conditions. However, resin matrix composites reinforced by Armos fibers generally have low levels of fiber–matrix adhesion on account of the poor wettability of the inert and smooth fiber surface; this wettability can be improved by the introduction of more polar components and an increase in the fiber surface roughness.[5]

There are various methods for material surface modification, including mechanical, chemical, combustion, and plasma techniques. Because the diameter of an ordinary fiber is a few micrometers, the use of mechanical and combustion methods on the fiber surface is almost impossible. On the other hand, increasing concern about environmental pollution problems has limited wide industrial application of chemical surface treatments.[6] Plasma technology is, therefore, getting popular and has been used as an effective means of modifying material surfaces to improve their surface-wetting and adhesion characteristics.[7–9] In recent years, more attention has been paid to atmospheric plasma treatment, for example, atmospheric dielectric barrier discharge (DBD) plasma processing. Compared with other plasma

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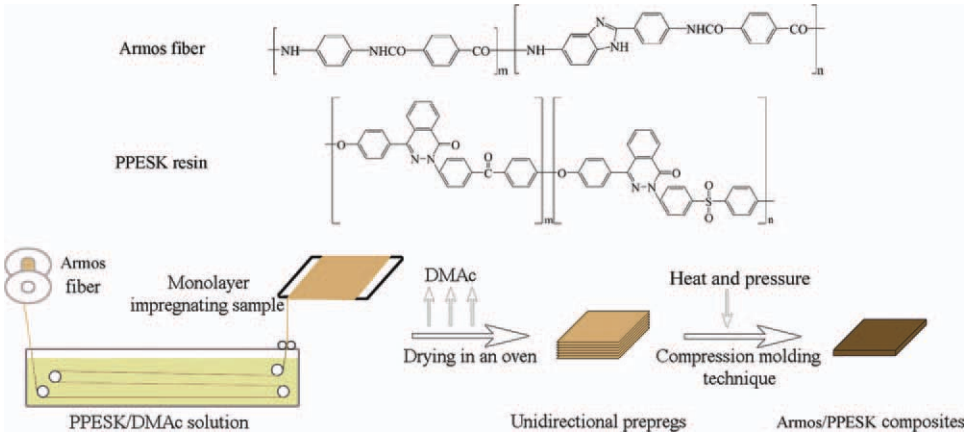

Figure 1 Schematic representation of the Armos/PPESK composite preparation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

methods, DBD plasma has a lot of advantages, including no need for vacuum equipment, scalability to a larger area, and online process capabilities, and has been widely used for the surface modification of varied materials.[10–15]

In this study, we investigated the DBD plasma treatment of Armos fibers to obtain fibers showing good wetting and adhesion behavior. The fiber surface wettability was measured with dynamic contact angle analysis (DCAA), and the influence of plasma treatment on the fiber mechanical properties was investigated by means of single-fiber tensile strength (SFTS) testing. The interfacial adhesion of the Armos/PPESK composites was determined through interlaminar shear strength (ILSS) testing, and the failure modes of the composites were analyzed by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials and composite specimen preparation

The Armos aramid yarn used in this study was received from Tverchimovolokno, J.-S. (Russia). The filament diameter was about 15 μm, and the density was 1.45 g/cm^3. To eliminate possible interference by contaminants and surface sizing, the fibers were washed with acetone at room temperature before the air plasma surface treatment, and then, they were dried in an air oven at 110°C for 3 h to thoroughly remove acetone. The thermoplastic resin used in our experiment was PPESK, which was supplied by Dalian Polymer New Material Co., Ltd. (China). The glass-transition temperature of the PPESK resin was 284°C.

PPESK resin was dissolved in DMAc to form a solution with a concentration of 15 wt % (PPESK/DMAc). Armos fibers were continuously passed through the PPESK/DMAc solution, were wound compactly on a frame, and then formed monolayer impregnating samples. We removed the solvent by drying the samples in an oven (120°C/1 h and 175°C/3 h) until they reached a constant weight and formed Armos/PPESK unidirectional prepregs, which were then molded into composite specimens with the compression-molding technique.[16] It is important to note that the volume fraction of Armos fibers in the composites was controlled at about 62%.

Figure 1 gives the chemical structures of the two materials and a schematic diagram of the composite specimen preparation.

Plasma treatment

The schematic diagram of the DBD apparatus was shown in a previous article.[17] It was a stainless hollow cylinder that provided the chamber where the fiber could be treated by plasma. Two identical circular stainless electrodes with a diameter of 4.7 cm were placed within the cylindrical enclosure, both covered with a quartz plate as the barrier. The lower electrode was connected to a power source, which provided a high alternating-current voltage continuously with an output frequency of 27 kHz, and the upper electrode was connected to earth. The discharge gap was set at 3 mm. When a high voltage was applied, a uniform filamentary DBD took place between the two electrodes. The Armos fibers were treated by means of going through the DBD plasma region at a constant speed of 1.56 cm/s. In this study, the sample treatment time was set at 18 s, with the discharge power density varied from 13.8 to 41.4 W/cm^3. The system was always exposed to atmosphere through the air hole during the plasma processing.

Dynamic contact angle measurements

The dynamic contact angles and surface free energy values of the Armos fibers were measured through a

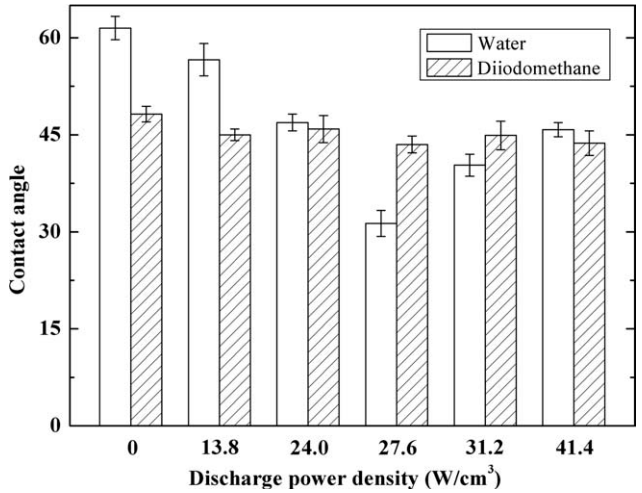

Figure 2 Advancing contact angles of the untreated and plasma-treated Armos fibers.

DCAA system (DCA-322, Thermo, America) according to the Wilhelmy technique. We cut a single-fiber sample to about 1 cm in length, fixed it indirectly to a wire hook suspended from the microbalance of the system, and then immersed it into the testing liquid media by raising the stage at a constant speed of 1 mm/min. The dynamic contact angles were then obtained schematically by measurement, and the surface free energy was calculated from eqs. (1) and (2):[18]

$$\gamma_1(1+\cos\theta) = 2\sqrt{\gamma_s^p\gamma_l^p} + 2\sqrt{\gamma_s^d\gamma_l^d} \quad (1)$$

$$\gamma_{\text{total}} = \gamma_s^p + \gamma_s^d \quad (2)$$

where θ is the dynamic contact angle between the fiber and testing liquid, which was calculated by a computer program, γ_1 is the surface tension of the testing liquid, γ_{total} stands for the total surface free energy of the fiber, and γ_s^p/γ_s^d and γ_l^d/γ_l^d are the polar/dispersive components of the fiber surface and the testing liquid, respectively, of the total surface free energy. In our experiment, water and diiodomethane were chosen as the testing liquids, with surface tensions of 72.3 mN/m ($\gamma_l^d = 18.7$ mN/m and $\gamma_l^p = 53.6$ mN/m) and 50.8 mN/m ($\gamma_l^d = 50.8$ mN/m and $\gamma_l^p = 0$ mN/m), respectively.

Fiber tensile strength testing

The tensile strength properties of the Armos fibers were analyzed with a tensile testing instrument (Instron 5567A, Instron, America) equipped with a 100-N sensor at room temperature. Each monofilament sample was mounted across a cardboard sample frame according to ASTM D 3379-75. Samples 25 mm in gauge length were tested under tension at a crosshead speed of 1.0 mm/min. Each data entry was the average of more than 10 measurements.

Interfacial adhesion

The ILSS of the composites was studied to estimate the interfacial adhesion strength between the Armos fiber and PPESK matrix; testing was conducted on a universal testing machine (AG-2000A, Shimadzu, Japan) with a three-point, short-beam bending test method according to ASTM D 2344. The tests were performed with a constant crosshead movement speed of 2.0 mm/min and a span-to-thickness ratio of 5. In our experiment, all of the ILSS values were taken as the average of more than five measurements.

SEM observations

SEM (QUANTA 200, FEI, Netherlands) was selected to observe the features on the shear failure plane of the composites. The composite samples were adhered to an SEM mount with a conductive adhesive. The microscope was operated at 60 Pa with an accelerating voltage of 25 kV. The magnification was set at 1000×.

RESULTS AND DISCUSSION

Surface-wetting behavior

A contact angle of zero indicates that spontaneous spreading occurs, whereas $0° < \theta < 90°$ shows that there are attractive interactions, and $\theta > 90°$ is indicative of repulsive interactions.[19] The dynamic contact angles were measured for both the untreated Armos fibers and those subjected to air DBD plasma treatment to show the interactions between the filament samples and the testing liquids. The mean values of the advancing contact angles for each Armos fiber sample in water and diiodomethane are shown in Figure 2, where the error bars represent ±1 standard deviation. The computed values of the surface free energy from eqs. (1) and (2) are illustrated in Figure 3.

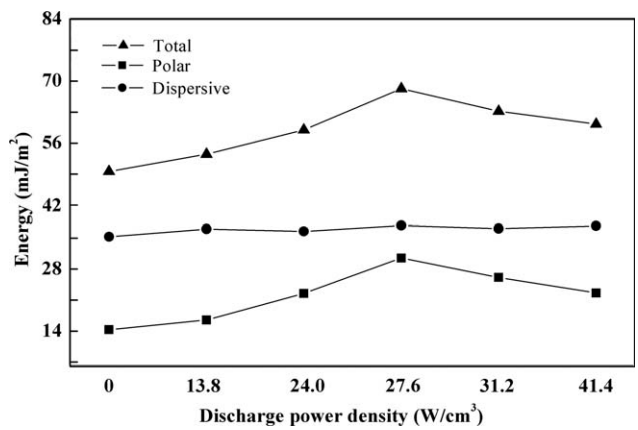

Figure 3 Surface free energy values of the untreated and plasma-treated Armos fibers.

From the untreated fiber to the samples after air DBD plasma treatment at power densities of 13.8, 24.0, 27.6, 31.2, and 41.4 W/cm^3 for 18 s, the contact angles of water declined sharply from 61.5° (untreated) to 31.3° (27.6 W/cm^3) and then rose to 45.8° (41.4 W/cm^3), whereas the advancing contact angles for diiodomethane changed from 48.2° (untreated) to 43.7° (41.4 W/cm^3). It was found that all of the fibers processed by the plasma showed lower contact angles for these two testing liquids than the original sample, with the fiber after the 27.6 W/cm^3 plasma treatment having the lowest values, which declined by 49.1% for water and 9.8% (from 48.2 to 43.5°) for diiodomethane. As mentioned previously, the decrease in contact angle indicated that there were increasing attractive interactions between the treated Armos fibers and the testing liquids. This could be explained by the increases in the surface polar functional groups and surface roughness of the materials after they experienced the plasma modification.[7,17,20,21]

In Figure 3, the variation trends of the resulting polar component, dispersive component, and total surface free energy for the fiber samples after plasma processing can be clearly observed. The polar component of the total surface free energy for the original fiber was about 14.3 mJ/m^2, and then, it increased to 16.5, 22.5, 30.5, 26.1, and 23.7 mJ/m^2 with the discharge power density increasing from 13.8 to 41.4 W/cm^3. The dispersive component of the total surface free energy had a slight increase as well for the samples after the air DBD plasma treatment. The polar component of the total surface free energy increased much more readily than the dispersive component; this was in accordance with the results obtained by Wu,[7] who employed oxygen plasma to modify aramid fibers. In the case of the total surface free energy, the trend was in accordance with the change of the polar component, which increased at the early stage from 49.6 mJ/m^2 for the untreated fiber to 53.5, 59.0, and 68.3 mJ/m^2 and decreased later to 63.2 and 60.3 mJ/m^2 with increasing discharge power density.

The surface free energy can be used to determine parameters such as adsorption, adhesion, and wetting. In general, high-energy surfaces wet better than low-energy ones for a given liquid.[19] The results show that the plasma-treated Armos fibers had a higher total surface free energy than the untreated one, which was supposed to have a better wettability and interfacial adhesion with the PPESK resin. In addition, the higher discharge power density could increase the amount of active species in the plasma and bring a closer contact between the Armos fiber surface and the discharges;[22] thus, increasing the power densities resulted in better surface-wetting behavior for the fibers. However, when an undue discharge power density was imposed on the fiber surface, there were decreases in the polar component and total surface free energy. The main reason might have been the removal of the polar groups by excessive plasma etching, which was introduced at an earlier stage of the treatment.[23]

TABLE I
Tensile Strength of the Armos Fibers Before and After DBD Plasma Treatment

Power density (W/cm^3)	Tensile strength (MPa)	Standard deviation	Decreasing rate (%)
0	5277	421	0
27.6	5175	461	1.9
41.4	4954	401	6.1

Tensile strength of the fibers

One of the most controversial issues is the influence of plasma treatment on the mechanical performance of fibers based on improved surface properties. Table I presents the results from SFTS testing for the original and the DBD plasma-treated Armos fibers. It could be seen that the treated fiber samples displayed lower average tensile strengths compared to the original one. The untreated Armos fiber had a tensile strength of about 5277 MPa, and the 27.6 W/cm^3 plasma-treated fiber had an average tensile strength of about 5175 MPa; this represented a minor reduction of less than 2%, whereas after the fiber was subjected to the 41.4 W/cm^3 plasma treatment, the tensile strength had a relatively obvious decrease by 6.1% to 4954 MPa. Nevertheless, it was evident that any modifications were within the error bars. As for the decreases in the average mechanical strength, the stress concentration in the flaws, which were introduced to the fiber surface by etching effects of the plasma, was one of the main causes,[21,24] and the level increased with increasing discharge power densities.

On the basis of the previous DCAA analysis, the results of SFTS suggest that the air DBD plasma treatment applied in this study improved the surface wettability of the Armos fibers to different degrees, whereas there were only slight declines in the fiber tensile properties. Exactly one conclusion could be made: that an appropriate plasma discharge power density, such as 27.6 W/cm^3, could achieve great improvements in the wetting behavior of the Armos fibers with the excellent fiber mechanical properties retained. The enhanced wettability then contributed to the interfacial adhesion between the reinforcing fiber and the matrix resin, as demonstrated in the following sections.

ILSS

In unidirectional fiber-reinforced composites, the matrix determines the chemical and thermal resistances

TABLE II
ILSS of the Armos-Fiber-Reinforced PPESK Composites After DBD Plasma Treatment at Different Power Densities

Power density (W/cm^3)	ILSS (MPa)	Standard deviation	Increasing rate (%)
0	60.9	2.5	0
13.8	64.5	2.7	5.9
24.0	66.8	1.3	9.7
27.6	71.4	2.6	17.2
31.2	67.1	2.5	10.2
41.4	62.3	1.2	2.3

of the composites, and the fibers provide strength and stiffness, whereas the overall properties of the composites and their durability with regard to combined moisture and temperature attack are dependent on the interface.[25,26] In this work, ILSS was applied to determine the interfacial adhesion properties between the Armos fibers and PPESK resin matrix.

The ILSS values of the Armos/PPESK composites with the standard deviation and increasing rate are shown in Table II according to the different discharge power densities. As a result, the effects of the fiber surface treatment conditions on the interfacial behavior of the resulting Armos fibers are clearly illustrated. With increases in the discharge power density to 13.8, 24.0, and 27.6 W/cm^3, ILSS increased obviously to 64.6, 66.8, and 71.4 MPa, respectively, with the largest increment being 17.2%. However, after the fibers were subjected to air DBD plasma treatment at power densities of 31.2 and 41.4 W/cm^3, the ILSS value decreased from 71.4 to 67.1 and 62.3 MPa. It should be noted that all of the ILSS values for the DBD plasma-treated Armos fibers reinforced composites were improved with respect to the ILSS value of the original fiber-filled composites, which was only 60.9 MPa. These changes were in good agreement with previous results derived by the DCAA.

The improved surface wettability of the Armos fibers after air DBD plasma treatment helped to increase ILSS of the composites. As the Surface-Wetting Behavior section explains, the improvement of fiber wetting could be partly attributed to the modifications of the fiber chemical structure. Polar groups introduced into the surface molecular chains contributed to the polarity and functionality of the treated Armos fibers, establishing more chemical interactions for the reinforcing fibers with the matrix. On the other hand, cracks in the surface layer caused

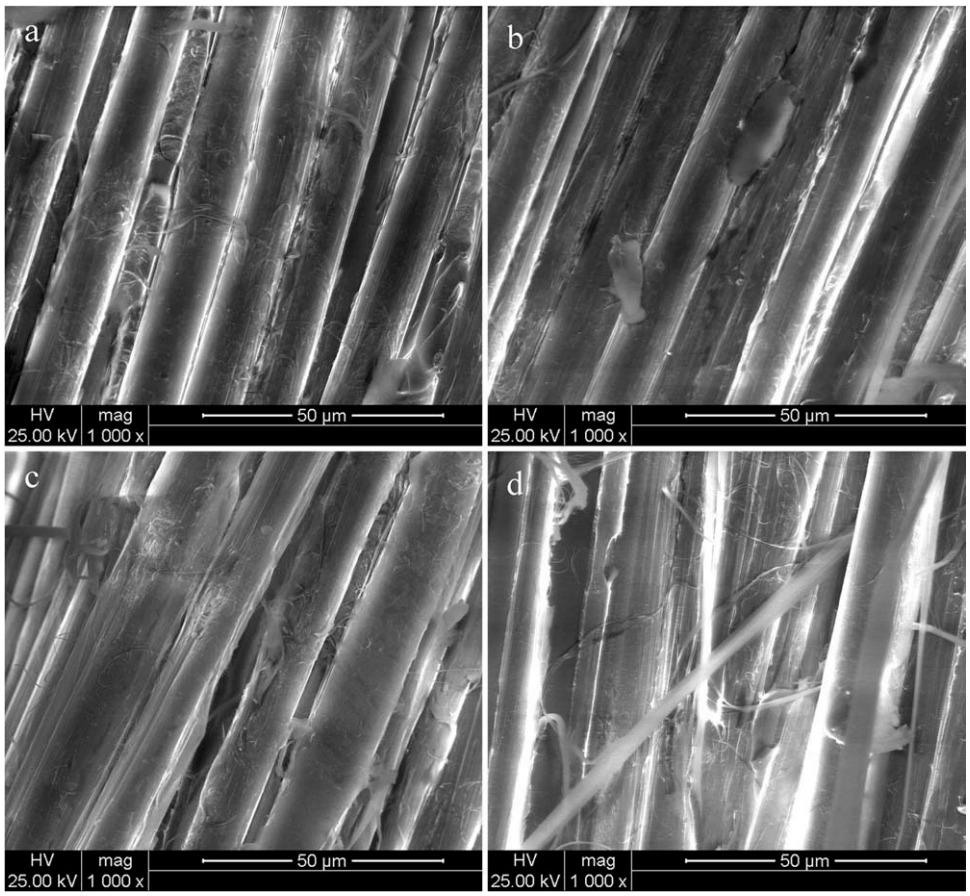

Figure 4 SEM images of the fractured Armos/PPESK composite specimens: (a) untreated fibers and plasma-treated fibers at (b) 13.8, (c) 27.6, and (d) 41.4 W/cm^3.

by plasma etching facilitated the penetration of the matrix resin into Armos fiber intermolecular areas; this may have provided for larger mechanical interlocking between the fibers and the PPESK resin. Both changes decreased the formation of traps in the resulting composites and enhanced the interfacial adhesion.[19]

Failure modes of the composites

Interfacial adhesion in continuous-fiber-filled composites not only plays the role of transferring the load between the fiber and the matrix but also influences the fracture behavior of the composites.[27] Figure 4 shows the fracture surfaces of the Armos-fiber-reinforced PPESK composites before and after the air DBD plasma treatment, which could, in turn, have sustained the interfacial adhesion variations in the composites.

For the untreated Armos-fiber-filled composites, as demonstrated by the SEM photo in Figure 4(a), most Armos fibers were pulled out from the matrix, and little PPESK resin was observed on the visible surface of the fibers. This observation indicated that the predominant failure mode was fracture at the interface between the fiber and the resin; the interface was relatively weak. Compared to the untreated specimen, the interfacial adhesion was supposed to be improved after the air DBD plasma treatment; this could have led to good stress transfer from the matrix materials to the fiber ones. Actually, there appeared to be more PPESK resin, as shown in Figure 4(b,c), and fewer locations of obvious separation between the Armos fiber and the resin are present in these photos. The primary failure mode shifted from interfacial failure to matrix and/or fiber failure because the interfacial strength was now greater than the failure shear strength of the matrix or the treated fibers.[24,28] However, after the treatment at a discharge power density of 41.4 W/cm^3 [Fig. 4(d)], fiber failure was evident, with several strips torn from the surface because of the excessive plasma processing, which introduced some larger defects on the fiber surface. Although the defects had no obvious influence on the fiber tensile strength, they made the fiber in the composites easily torn when bearing shear stress. This might also have been part of the reason ILSS decreased when the discharge power density overtook 27.6 W/cm^3 in our experiment.

CONCLUSIONS

The effects of atmospheric air DBD plasma treatment at various different discharge power densities on both the Armos fiber surface wettability and interfacial adhesion of Armos-fiber-reinforced thermoplastic PPESK resin composites were investigated. DCAA measurements showed that the plasma-treated Armos fibers had a markedly higher total surface free energy than the original fiber. More significantly, the SFTS test revealed that the fiber tensile strength could be retained while the fiber wetting behavior was greatly improved. With the enhancement in fiber wettability, ILSS testing showed that after plasma treatment, the interfacial adhesion between the fibers and the surrounding matrix was improved, and meanwhile, the composite fracture surfaces observed by SEM indicated that the composite failure mode changed from interface failure to matrix and/or fiber failure; this sustained the enhanced interfacial performance between the Armos fiber and PPESK matrix.

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