Macromol. Symp. ***159**, 131–141 (2000)*

Surface Improvements of Aramid Fibers By Physical Treatments

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SUMMARY: The application of the low-temperature plasma method, the excimer laser treatment method and the corona-discharge method to aramid) were discussed, presenting an overview of current trends and developments in this area.

Introduction

New applications and improved applicability of the many fibers used for industrial materials require the new properties in such area as adhesive ability and the additional properties increase the value of fibers. Chemical treatment methods are most often used in actual practice. Physical treatment processes are dry, and make it possible to preserve certain properties intrinsic to fibers. Since 1960 this has been extensively studied.

The studies initially focused on electron beam irradiation and ultraviolet light irradiation, but electron beam irradiation required too much energy. Chemical treatment methods make use of large amounts of water and/or organic solvents, require high thermal energy for drying and curing, and pose such problems as the disposal of drained water and recovery of organic solvents. Therefore, it may be assumed that studies aimed at the eventual implementation of physical treatment methods will continue.

Para-type aramid fibers (abbreviated as aramid fibers) are useful as reinforcing fibers for matrices of rubber, resin etc.. However, the surfaces of the aramid fibers are relatively inactive, and their adhesive properties to rubbers, resins are insufficient. In order to enhance the adhesive properties for the rubbers and resins and attain the highest quality composite materials, the activation of the aramid fiber surfaces is extremely important.

The applications of the low-temperature plasma method and the excimer laser irradiation method to aramid fibers were discussed.

CCC 1022-1360/00/$ 17.50+.50/0

Experimental

Materials

The aramid fibers used in this study were PPODPTA yarn, made by Teijin Ltd. and PPTA yarn, made by Toray-DuPont Inc. The chemical structures are shown in Fig.1.

PPODPTA; co-polyparaphenylene/3,4'-diaminodiphenylene terephthalamide

PPTA; Polyparaphenylene terephthalamide

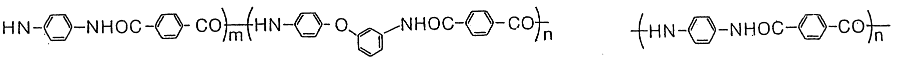

Fig.1 Chemical structures of aramid fibers

These were 1000 denier drawn yarn, and a plain weave fabric woven at 31 threads per inch for both warp and weft was applied. Scouring and de-oiling the fabric were done in the usual way. Table 1 gives the physical properties. These fibers are characterized by high tenacity and high degree of orientation and crystallinity. This was confirmed with wide-angle X-ray diffraction measurements.

Table 1. Physical properties of aramid fibers

	Density	Diameter	Young's modulus	Tensile strength
PPODPTA	1390 Kgm^{-3}	12.4 μm	73.5GPa	3.04 GPa
PPTA(Type 29)	1440	12.1	58.8	2.79
PPTA(Type 49)	1450	12.0	127.4	2.79

Low Temperature Plasma Treatment

The aramid fabric samples were treated for predetermined time with the RFIP (radio frequency ion-plating) apparatus, as shown, at frequency of 13.56 MHz, at a discharge output of 200 W and at a vacuum of 10^{-3} torr using oxygen or nitrogen gases.

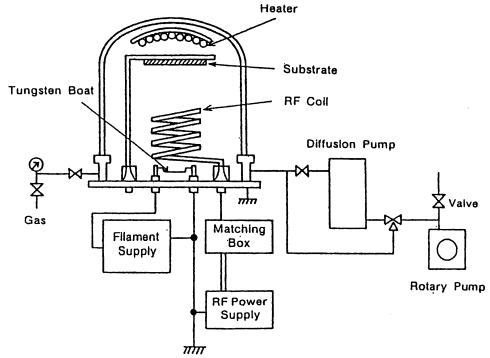

Fig. 1 Apparatus for Plasma Treatment

On the other hand, for RFIP, the aramid fabric samples were previously treated with low temperature plasma for 5 minutes under the same conditions as described above, using oxygen or nitrogen gas.

Different types of nylon were then melted at a current of 100A by the resistance-heating method, method, the shutter was opened, and oxygen or nitrogen gas was used as the carrier for a predetermined time, so that the different types of nylon were ion-plated on the aramid woven fabrics.

This treatment is based on the action of different active seeds, which results in etching (the developing of micro-irregularities) on the surface of fibers, the introduction of functional groups, and bridge building on the surface. However, there are problems such that the quality of the treated surfaces possibly degrades with times$^{1)}$. Therefore, it is said that the low temperature plasma treatment is not a stable method.

In this study, in order to improve the adhesive properties of aramid fibers to rubber as a matrix, nylon thin films were securely formed on the surface of the aramid fibers by RFIP technique, which was one application of the low temperature plasma treatment. The fibers were treated with a RFL (resorcin-formalin-latex) adhesive having a high affinity to nylon and rubbers. The adhesive properties of the fibers to rubber, were evaluated, and the effects of the treatment were confirmed by comparison with those obtained by the low temperature plasma treatment. The usefulness of the surface modification as a novel fiber surface activation method was discussed.

Excimer Laser Irradiation Method

This method can be applied in a normal atmosphere. Irradiation was carried out with a Lambda-Physik/Germany excimer laser apparatus filled with a mixture of krypton, neon and fluorine gases (wavelength 248nm). Each pulse of 20ns duration, delivered irradiation of 40, 50 or 100mJ/cm^2 above the threshold value.

In order to clarify the effects of the surface improvement on the adhesion performance with rubber, the following procedure was carried out. After being dipped in to an epoxy compound solution (5 wt-%), a sample of plain weave fabric was irradiated immediately with KrF excimer laser or was heated in an oven at 200℃. This was followed by dipping the sample in a RFL rubber adhesive and curing with heat (200℃ for 4 min).

To compare the adhesive performance, an alternative procedure was also applied. After being irradiated with a KrF laser, the sample was dipped into an epoxy compound solution and then cured in an oven at 200℃. This was followed by dipping in a RFL adhesive and curing with heat(200℃, for 4 min).

Estimation of Adhesion Performance

Test piece for adhesion strength evaluation were prepared by sandwiching a blended rubber (containing natural rubber/SBR) sheet, between two fabric samples placing the press in a mold and vulcanizing in a hot press at 150℃ for 30 min (for original adhesion) and at 180℃ for 60 min (for over-cured adhesion). An adhesive strength was measured by peeling (1 inch width) at a speed of 100 mm/min using a Model 5565 tensile tester made by INSTRON Corp/England.

Results and Discussion

Low Temperature Plasma Treatment

Changes in Fiber Surface

The changes in the aramid fibers at the surface[2], in the case of PPODPTA and PPTA, the oxygen gas low temperature plasma treatment produced so-called "Seashore Structure" perpendicular to the fiber axial direction. It was presumed that these convex and concave structures might be attributed to etching. The XPS analysis showed that the ratio of oxygen in the case of oxygen plasma was increased, thus indicating activation. It should be noted that such surface changes are not always observed, and depend on the type of gas.

Adhesive Properties

For the purpose of improving the adhesive properties, few reports on improvement of the adhesive properties to rubbers were found[3]. In the case of the low temperature plasma treatment using oxygen and nitrogen gases are shown in Fig. 3. These gases exhibited almost the same effect. By over-vulcanization, the aramid fibers exhibited less reduction or in some cases, an increase in adhesive properties, which is different from PET fibers of which the adhesive properties are reduced by over-vulcanization.

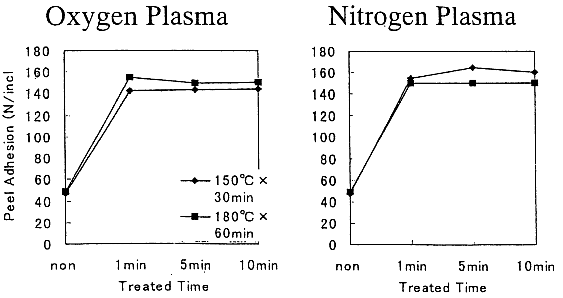

Fig.3 Adhesive properties to rubber

This is because the surfaces of the PET fibers deteriorated due to water and amine type vulcanizing agents contained in the rubber when the fibers were over-vulcanized. On the other hand, these behaviors of the aramid fibers are probably because they had less heat shrinkage and less degradation with heat generated during the vulcanization or rather had the interfaces strengthened by the anchoring effect due to good penetration of the rubber among the fibers by heating. In comparison, PPODPTA woven fabrics had higher adhesive properties than the PPTA woven fabrics. The reason, while not completely understood, may lie in the fact that PPODPTA has a chemical structure more ready to be activated by the low temperature plasma treatment as compared with PPTA. In the case of PPTA, fibrils are more readily formed as compared with PPODPTA, which is a copolymer, and also weak boundary layers are produced by the low temperature plasma treatment.

Adhesive Properties of Nylon Coated Aramid Fibers

Thin Film Formation Condition

Till now, studies of thin film formation by the RFIP method have been made for addition polymerization type polymers such as polyethylene, polydiacetylene, polyvinylidene fluoride, etc.$^{4)}$. On the other hand, few reports of thin film formation using condensations type polymers such as polyesters, nylons, etc. were found. This is probably because such polymers may be pyrolyzed when they are heated to melting and then vaporized under vacuum conditions. Nylon 6 chips placed in a tungsten board in the RFIP were melted with the resistance-heating system, with the plasma atmosphere generated by flowing-in oxygen or nitrogen gas at a vacuum of $10^{-4} \sim 10^{-3}$ torr, and then discharged of 150 W. The shutter was opened, and the melted nylon 6 was vaporized and was deposited on an aluminum foil substrate (as a model test). The aluminum foil was dissolved in alkali, and the remaining vaporized matter was observed by SEM. It consisted of continuous thin films.

Characteristics of Nylon Thin Films

As previously reported, the thickness of the thin films formed under the above conditions, determined by the SEM observation, were 100～200 nm. Also, the examination results of the dissolution properties of the thin films shows that there existed two parts of the thin film which were soluble and insoluble in formic acid, a solvent for nylon. The analytical results of the thermal properties show that the soluble part had a melting point of 214℃ and a heat of fusion of 8 mcal/mg. These values are lower than the melting point of 225℃ and the heat of fusion of 17.4 mcal/mg for the original nylon. Based on the TGA results, it is presumed that the heat-reduction in weight of the formed thin films begun when the temperature of the films was considerably lower, that is, the films had such structures that are readily decomposed at low temperature. In the FT-IR spectra, all of the characteristic absorption bands of nylon were observed, though the absorption intensities were rather different from those of' the original nylon 6. In contrast to the nylon 6 specific gravity of 1.1519, that of the soluble part of the thin films was 1.3857, and that of the insoluble part was 1.2583. The X ray analysis reveals that the thin films are unoriented and noncrystalline. Based on these analytical results, it is presumed that nylon 6 is different from its original configuration and is a cross linked, uncross linked nylon 6 having a low molecular weight nearly the same as the original nylon 6. Moreover, a similar examination of nylon 66 was made. The results show that these nylons gave thin films similar to those formed in the case of nylon 6.

Types of Nylon and Adhesive Properties

The surfaces of PPODPTA woven fabrics were ion-plated with nylon 6 and 66 using the previously described conditions, and were RFL treated. The adhesive properties were then evaluated (shown in Fig.4) The nylon formed on the surfaces improved their adhesive properties. On the whole, the bonding strength and rubber coverage on the treated PPODPTA woven fabrics after peeling tests were relatively high.

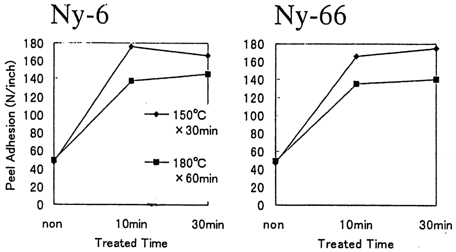

Fig.4 Adhesive properties

Comparison of Adhesive Properties due to Ordinary- and Over-Vulcanization

For, RFL treated nylon 6 and 66 fibers to be used in tire cords, the reduction of the adhesive properties, caused by over-vulcanization, was small and comparable to those due to the ordinary vulcanization. In the case of the aramid woven fabrics coated with the nylon thin films, the adhesive properties obtained by the over-vulcanization were relatively high, though a reduction was observed in some cases. The rubber coverage was also high.

Comparison of PPODPTA and PPTA

It has been also confirmed that PPTA takes almost the same behaviors as PPODPTA but with a difference in the adhesion level (shown in Fig.5).

More particularly, in the case of not only the low temperature plasma treatment but also the RFIP of the nylons, the adhesive properties of' PPODPTA fibers were higher than those of PPTA fibers. As for the probable reason of this behavior, the affinities of nylon thin films to the RFL adhesive are estimated to be equal, and it is assumed that the adhesion properties of' the nylon thin films to the PPODPTA substrate are

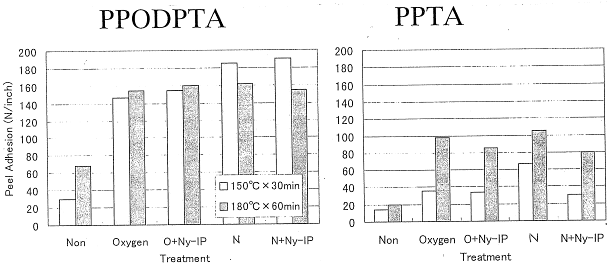

Fig.5 Comparison of PPODPTA and PPTA on adhesion level

higher than those to PPTA. In fact, PPODPTA exhibited very high rubber coverage, showing its cohesion failure. The PPTA showed very low rubber coverage, mainly causing failure at its interface. It may be concluded that the PPTA has relatively low-level adhesive properties though some improvement is seen when compared with the untreated PPTA.

Excimer Laser Irradiation (Ablation) Method

Changes in Fibers on Surface

Fig.6 shows the scanning electron micrographs of the irradiated aramid fiber surfaces after the laser pulse irradiation at 100 mJ/cm^2 with (a) non-irradiation, and (b) 10 shots. Small ripples were observed by the radiation. However, we found in this experiment that the ripples on the surface of PPODPTA are clearer than that of PPTA at the same conditions.

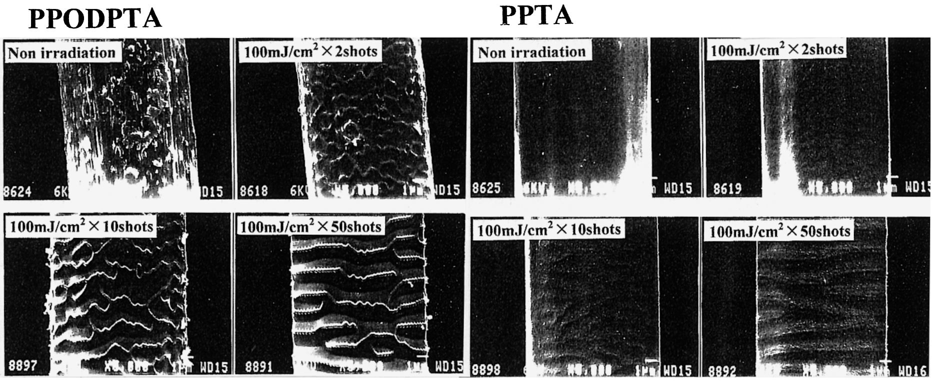

Fig.6 SEM micrographs of the fiber surfaces

Surface Chemical Composition studied by XPS Analysis

The content of O and C atoms at the aramid fiber surface after excimer laser irradiation was analyzed by XPS (ESCA). The ratio of O to C atoms decrease for PPODPTA and not change for PPTA. It may depend on the existing of ether bond of PPODPTA.

Adhesive Properties

Generally, as adhesives for fiber reinforced rubber composite, a first treating agent containing an epoxy compound having an affinity to the fibers and a second treating agent containing RFL are applied. The RFL comprises resorcinol-formaldehyde•-rubber latex and is reactive with the matrix rubbers through its methylol groups. Both of the treating agents, after they have been applied to the fibers, are cured with heat. The heating conditions exhibit a great influence on the adhesion performances of the fibers.

The authors have examined the application of an epoxy acrylate as the first treating agent. The acrylate compound, which is sensitive to UV rays, has a structure relatively similar to the epoxy compound used as the first treating agent. In order to reveal the effects of an excimer laser, the irradiation timing was examined. Before or after addition of a glycerol triglycidyl ether or its acrylate adducted-compound to the fibers, these were irradiated with an excimer laser (in the wet state) to compare the performances. In any case of the fibers, the KrF laser irradiation frequency was set that it slightly exceeded the threshold value and fine concave and convexes could be formed at the surfaces of the fibers. The irradiation was conducted at 100 mJ/cm^2×10 shots for the aramid fibers.

In the case that the laser irradiation was conducted beforehand, and then the first treating agent was applied and heated to be cured, differences between the adhesive properties of the fibers were observed. On the other hand, in the case that the compounds were applied and then cured by the laser irradiation, no changes in the adhesive properties were observed for the epoxy compound, but significant improvements in adhesive properties of the PPODPTA fibers were exhibited when the acrylate compound was used. However, in this case, no effects on the PPTA fibers were recognized. There was such tendency found with respect to the original and over-cured adhesive properties.

Irradiation conditions of KrF laser and adhesive properties

It was recognized that the adhesive properties can be enhanced when the epoxy acrylate is used as the first treating agent and cured with the KrF laser, followed by the RFL treatment and the heat curing. The adhesive properties were shown in Fig.7.

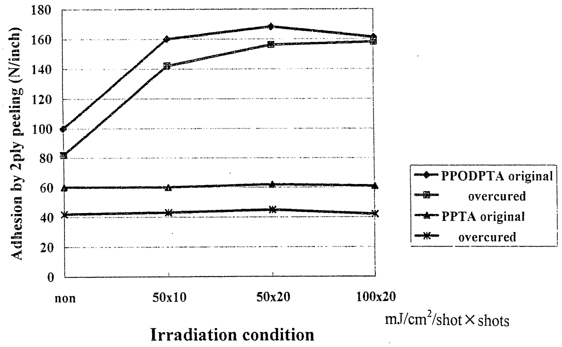

Fig.7 Adhesive properties of aramid fibers at various conditions

As to the observed rubber coverage at the peeled surfaces, PPODPTA presented the cohesive failure at about 50 mJ/cm^2 and also a desirable rubber coverage ratio. When the irradiation energy was increased, little changes in the apparent bonding strength of PPODPTA were shown, and the cohesive failure of the rubber was partially observed at the peeled surfaces. On the other hand, PPTA had a low bonding strength, showing the interfacial peeling and less rubber coverage.

Comparison of PPODPTA and PPTA

The aramid fibers PPODPTA and PPTA presented different adhesive properties. A reason was assumed as follows. In PPODPTA fibers, copolymer components compose crystalline domains independently of each other, and are oriented sufficiently. The copolymer components constitute crystalline domains, leaving almost no non-crystalline state in which molecules remain relaxed5), whereas PPTA fibers comprise highly oriented skin layers and a core layer stacking up fibril groups in blocks. So there is a non-crystalline phase containing relatively many end groups of molecules between the blocks, which is likely to become fibril6•. Such a difference in orientation of the non-crystalline phase seems to result in differences in susceptibility to ablation and in affinity of an epoxy acrylate compound to fibers, which is considered to be finally expressed as a difference in adhesion performance.

In addition, it is possible that the differences of the peeling-adhesion properties were caused by the different bonding energies of the fibers. In the PPODPTA fibers, the aromatic rings are linked together through amide and ether linkages; in the PPTA fibers, the aromatic rings are linked together only through amide linkages. The bonding energies are different and the fibers show different susceptibilities to the ablation. This might result in the different peeling-adhesion properties of the fibers.

When the laser irradiation was conducted after the epoxy acrylate was applied, a larger amount of fibrils were observed in the PPTA fibers at the peeled surface than in the PPODPTA fibers. It is estimated that the PPTA fibers present the low peeling-adhesion properties because they are readily fibrillated.

Conclusion

It has been revealed that the adhesive properties of the aramid fibers can be enhanced by low temperature plasma treating, and immediately after the treatment, carrying out the RFL treatment. It is important that the aramid fibers are subjected to the succeeding process as soon as possible before changes in the surface properties occur.

Based on the acknowledgment that nylon 6, one of the typical condensation type high polymers, can be formed into thin films by the RFIP method. The mechanism by low temperature plasma treatment on aramid fiber surface is shown in Fig.8.

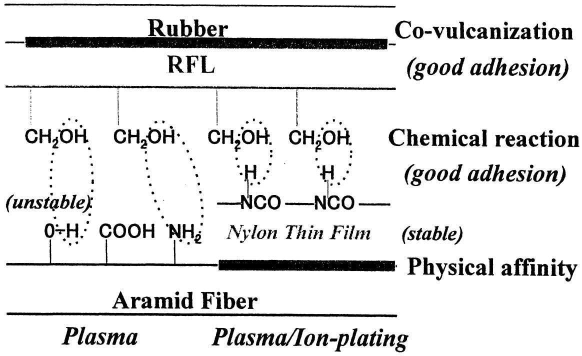

Fig.8 The mechanism by low temperature plasma treatment on aramid fiber surface

1) It has been confirmed that, as in the case of nylon 6, thin films made of un-oriented, noncrystalline nylons cross linked or uncross linked, having structures different from those of the original nylons and low molecular weight, are formed. According to the RFIP method, nylon thin films were formed on the fibers of which the surfaces are inactive, followed by treatment with RFL generally used fort rubber, thus having a high affinity to the nylon.

2) PPODPTA exhibited high adhesive properties such as, rubber coverage and bonding strength. As for PPTA, the bonding strength, though it was higher as compared with that of the untreated PPTA, was on a relatively low level. This is probably because the adhesion properties of PPODPTA and PPTA toward the nylon thin films were different. It is estimated that the RFIP method has a higher stability than the low temperature plasma treatment.

An examination was also made on the improvement of adhesion performances by a surface modification with an excimer laser. The following has been revealed. The mechanism by laser ablation on aramid fiber surface is shown in Fig.9.

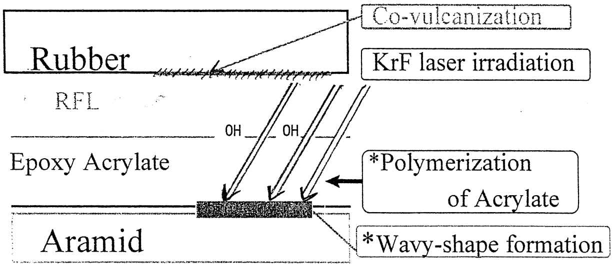

Fig.9 The mechanism by laser ablation on aramid fiber surface

3) When an acrylic acid adducted-compound (acrylate) is employed as first treating agent, and is cured by KrF laser irradiation, followed by a RFL treatment and heat-curing, the adhesive properties of the PPODPTA fiber are improved, but no improvements are observed for the PPTA fiber.

4) For the PPODPTA fibers, the copolymer components constitute crystalline domains, independently, which are sufficiently oriented substantially without amorphous regions having the molecular chains relaxed. Therefore, it is speculated that the high adhesive properties of the fibers could be obtained because the fibers were readily ablated, so that the applied acrylate compound enhanced the affinity of the fibers.

5) It is speculated that the relatively low adhesive properties of the PPTA fibers are attributed to a skin layer and a core layer composed of fibrils stacked into blocks. Amorphous phases containing a relatively large number of molecular chain ends are present between the blocks so that the fibers are readily fibrillated and are difficult to be ablated. Accordingly, the affinity of the fibers to the acrylate compound is insufficient.

We hope that the obtained knowledge will serve for the development of novel surface modification techniques for aramid fibers of which the surfaces are relatively inert.

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