

Plasma-Graft Polymerization of Vinyl Monomers with Reactive Groups onto a Surface of Poly(*p*-phenylene terephthalamide) Fiber

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SYNOPSIS

The mechanical properties of a fiber-reinforced plastic are influenced by the adhesion between a reinforcing fiber and a matrix resin. In this work we tried to obtain strong adhesion between Kevlar 49TM yarn and a matrix resin through the formation of covalent bonds. Reactive groups were introduced onto a surface of the yarn by means of plasma-graft polymerization and then reacted with an epoxy resin/curing agent mixture as a matrix resin to form covalent bonds. Glycidyl methacrylate and acrylamide were used as monomers for plasma-graft polymerization. The degree of grafting was increased with increasing polymerization time. The grafted yarns enclosed with diglycidyl ether of bisphenol-A/triethylenetetramine 2.2 : 1 mixture were pulled out to obtain pull-out force after curing. The pull-out force increased with increasing degrees of grafting. The covalent bonds formed between the graft polymer and the matrix resin result in an increment of pull-out force. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of cold, high-frequency plasmas is exceedingly effective for modifying a surface of solid materials.¹⁻⁶ A plasma-graft polymerization method is one technique for surface modification of polymers by using plasmas. Acrylamide was graft-polymerized onto a surface of polyethylene film treated with an oxidative plasma, inert gas plasma, or corona discharge, followed by exposure to air.^{7,8} Peroxides formed by the plasma treatment are likely to be responsible for initiating the graft polymerization. The amount of the peroxides corresponds to the amount of the graft poly(acrylamide). The grafted film becomes hydrophilic.

The mechanical properties of a fiber-reinforced plastic are influenced by the adhesion between a reinforced fiber and a matrix. Good adhesion is crucial for the strength of the material, as the load is transferred from one fiber to the other via the

interface and matrix.⁹ A strong interface is also necessary to bear the shear stresses resulting from different expansions caused by temperature changes in manufacture and use.⁹ Plasma treatments were carried out onto a surface of aramid fiber to improve the adhesion between the fiber and matrix resin.⁹⁻¹¹ Various microwave plasma treatments were applied to KevlarTM 29 in the form of multifilament fabric; and significant increases in the bond strength of laminates which were constructed by using the plasma-modified fabrics may be attributed to the plasma treatments.¹⁰ To modify the interface between bisphenol-A epoxy and KevlarTM 49 fiber or TechnoraTM fiber, argon, nitrogen, and carbon dioxide gas plasmas were used.⁹ The plasma treatment of KevlarTM fiber resulted in a slight improvement of interfacial shear strength, whereas the plasma treatment of TechnoraTM fiber lowered the interfacial shear strength.⁹ To improve the adhesion between silicone rubber and KevlarTM 49 fiber, combining the plasma treatment and coupling agent treatment for the fiber was found to be effective.¹¹ Oxygen plasma treatment led to the formation of oxygen functionalities, including C—O and C=O,

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and the interaction between the silicone adhesive and the oxygen functionalities contributes to the adhesion between the silicone rubber and the fiber.

In this work we tried to obtain stronger adhesion between Kevlar™ 49 yarn and a matrix resin through the formation of covalent bonds. Thus functional groups reactive with an epoxy resin/curing agent mixture as the matrix resin need to be introduced onto a surface of the yarn; therefore, vinyl monomers with the functional groups are plasma-graft polymerized onto a surface of the yarn. The functional groups are then reacted with the epoxy resin/curing agent mixture to form covalent bonds. Pull-out force of the yarn is measured to evaluate the adhesion between the yarn and the matrix resin.

EXPERIMENTAL

Plasma-graft Polymerization

Glycidyl methacrylate (GMA) and acrylamide were used as monomers for plasma-graft polymerization.

Glycidyl Methacrylate

The yarn used in this work was Kevlar™ 49 [poly(*p*-phenylene terephthalamide)]. Kevlar™ 49 was supplied by E. I. du Pont de Nemours & Co. (VA) in the form of an 1140-denier, 768-filament yarn. Kevlar™ 49 yarn was washed with successive hot-water, methanol/acetone mixture, and trichloroethylene baths before plasma-graft polymerizing. GMA was diluted with a methanol/water 95 : 5 mixture to prepare a 2.3M solution, since GMA is not dissolved in water alone. Figure 1 shows a schematic representation of the apparatus for plasma-graft polymerization. The yarn was suspended in the upper plasma-irradiation vessel and irradiated for 1 min with plasma which was generated at 100 W at 13.56 MHz in an atmosphere of 20 Pa argon, and then immediately immersed for the prescribed time at 300 K in the GMA solution, which had been freeze-vaporized to remove dissolved oxygen gas and poured into the lower graft-polymerization vessel. The yarn was washed successively with methanol and *N,N*-dimethylformamide after graft-polymerizing and then dried *in vacuo* at room temperature.

Acrylamide

Acrylamide was diluted with water to prepare a 2M solution. *N,N'*-methylene-bis(acrylamide), in a 97 : 1 mole ratio, was added to the acrylamide solution

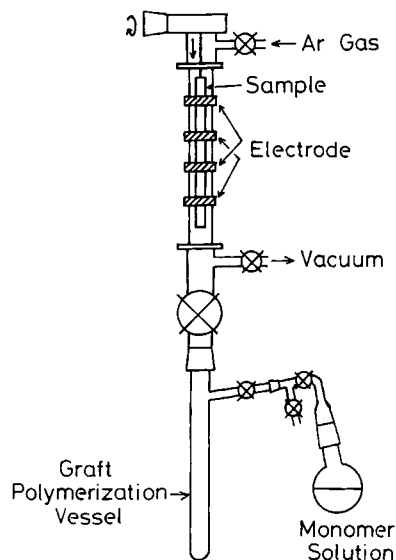


Figure 1 Schematic representation of apparatus for plasma-graft polymerization.

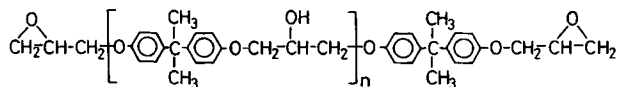
as a crosslinking agent. The yarn was plasma-grafted in the same manner as the GMA. The plasma-grafted yarn was washed with successive water and methanol baths and then dried *in vacuo* at room temperature.

Surface Analysis of Plasma-grafted Yarn

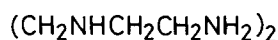
X-ray photoelectron spectroscopy (XPS) measurement was carried out with a Shimadzu ESCA750 X-ray photoelectron spectroscope (Shimadzu Co., Ltd., Kyoto, Japan) to clarify the species of atoms constituting the graft layer. An infrared spectrum was measured with a 5DXB Fourier transform infrared spectroscope (Nicolet Analytical Instruments, WI) equipped with a Barnes analytical diffuse reflectance accessory to clarify the chemical structure of the graft layer. The surface morphology of the yarn was observed by using a Nihondenshi JSM-T200 scanning electron microscope (Nihondenshi Co., Ltd., Tokyo, Japan).

Evaluation of Adhesion between Plasma-grafted Yarn and Matrix Resin

Figure 2 shows the chemical structures for diglycidal ether of bisphenol-A and triethylenetetramine (TETA), which were used as the epoxy resin and the curing agent, respectively. The average molecular weight of diglycidal ether of bisphenol-A was about 330 before curing. Figure 3 shows a schematic representation of the specimen used in measuring the load necessary to pull out the yarn. To prepare the specimen, the yarn was embedded in the epoxy



(a)



(b)

Figure 2 Chemical structures of (a) diglycidyl ether of bisphenol-A and (b) TETA.

resin/curing agent mixture to form a fiber-reinforced plastic and the mixture was cured at 300 K over 120 h. The mole ratio of the epoxy resin/curing agent was 2.2 : 1. The width of the yarn embedded in the mixture was 4 mm or 2 mm, considering that the width is small enough to achieve a pull-out before yarn breakage. The yarn was pulled out with a Tensilon UTM-III tensile tester (Toyo Baldwin Co., Ltd., Tokyo, Japan) to obtain pull-out load. Pull-out speed was 2 mm/min and gauge length was 15 mm. Pull-out force was evaluated by dividing pull-out load by the embedded width of the yarn.

RESULTS AND DISCUSSION

Plasma-graft Polymerization

Figure 4 shows the degree of grafting as a function of polymerization time for plasma-graft polymerizations of GMA and acrylamide. The degree of grafting G was evaluated as follows:

$$G = (W - W_0)/W_0 \times 100 (\%)$$

in which W_0 and W are weights of the yarn before and after plasma-grafting, respectively. The degree of grafting was increased with increasing polymerization time. An increase in the degree of grafting means that the number of graft chains per unit of surface area or/and the degree of polymerization of graft chains increase. An increase in the degree of polymerization is presumed from the results of plasma-induced polymerization of methyl methacrylate, as below: the plasma-induced polymerization will proceed with radical polymerization, but the degree of polymerization increased with increasing

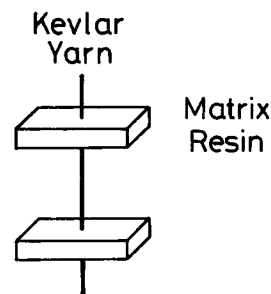


Figure 3 Schematic representation of specimen used in measurement of load necessary to pull out Kevlar yarn.

percentages of polymerization and an ultra-high molecular weight polymer, over a molecular weight of 10 million, was obtained.¹² The acrylamide polymerization rate was much higher than that of GMA, as shown in Figure 4. In the plasma-induced polymerization of acrylamide the rate of polymerization in water was much higher than that in methanol. It will be considered, therefore, that water as a solvent of the monomer enhances the rate of polymerization of acrylamide, compared with the methanol/water mixture as a solvent of GMA.

GMA

Figure 5 shows scanning electromicrographs of the yarn before and after plasma-grafting of GMA. It was observed that aggregations of graft polymers were developed on a surface of the yarn after plasma-grafting. Figure 6 shows XPS spectra of a surface of the yarn before and after plasma-grafting. The N_{1s} peak disappeared after plasma-grafting, and the XPS intensity ratio C_{1s}/O_{1s} also decreased. The ablation of the surface layer of the yarn, which is induced by plasma-irradiation, was not brought into the disappearance of the N_{1s} peak shown in Figure

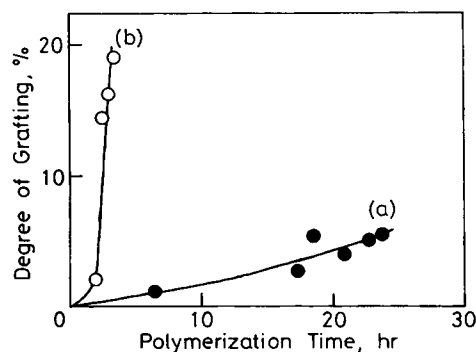
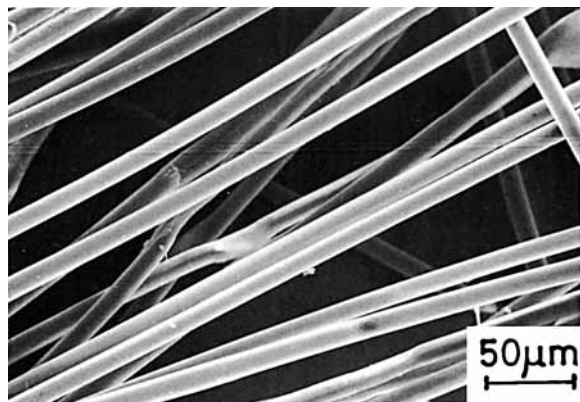
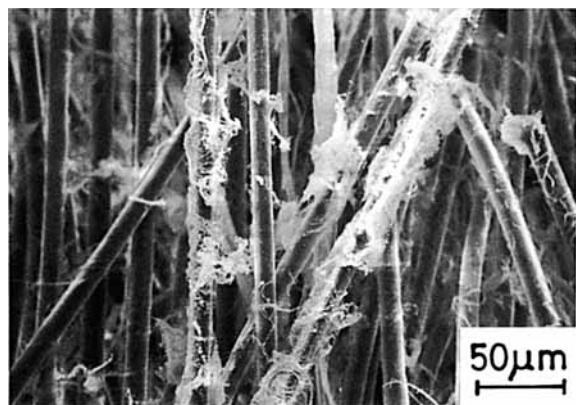


Figure 4 Degree of grafting as a function of polymerization time for plasma-graft polymerizations of (a) GMA and (b) acrylamide.



(a)



(b)

Figure 5 Scanning electromicrographs of Kevlar yarn: (a) before and (b) after plasma-grafting of GMA (degree of grafting was 5%).

6. Figure 7 shows the XPS intensity ratio C_{1s}/O_{1s} as a function of the degree of grafting. The intensity ratio C_{1s}/O_{1s} corresponds to the atomic ratio C/O. The intensity ratio C_{1s}/O_{1s} decreased with increased degrees of grafting and became almost constant above the degree of grafting of 3%. The intensity ratio C_{1s}/O_{1s} above the 3% degree of grafting was close to 2.3, which is the theoretical value of the atomic ratio C/O in poly(glycidyl methacrylate).

Figure 8 shows infrared spectra of a surface of the yarn before and after plasma-grafting. The absorption peaks which are attributable to $C=O$ stretching vibration and $C-O$ stretching vibration of the ester group appeared at 1730 cm^{-1} and 1270 cm^{-1} , respectively, after plasma-grafting. It becomes apparent from the results of Figures 4 through 8 that poly(glycidyl methacrylate) chains

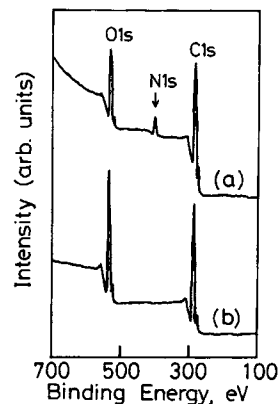


Figure 6 X-ray photoelectron spectra of a surface of Kevlar yarn: (a) before and (b) after plasma-grafting of GMA (degree of grafting was 5%).

are plasma-grafted onto a surface of the yarn as shown in Figure 9.

Acrylamide

It was observed from the scanning electromicrograph of the yarn after plasma-grafting of acrylamide that aggregations of graft polymers were formed on a surface of the yarn by plasma-grafting. According to the infrared spectrum of a surface of the yarn after plasma-grafting, the absorption peaks which are attributable to the CH stretching vibration of the methylene group appeared at 2940 cm^{-1} , whereas the strength decreased in the absorption peaks which appear at 1020 cm^{-1} and 820 cm^{-1} and are attributable to CH out-of-plane bending of the benzene ring. Therefore it becomes apparent that poly(acrylamide) chains can also be plasma-grafted onto a surface of the yarn.

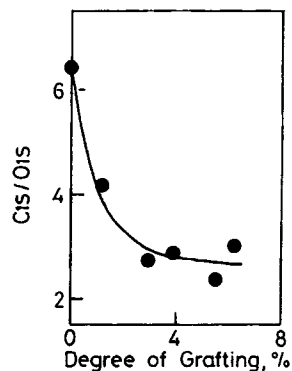


Figure 7 XPS intensity ratio C_{1s}/O_{1s} of a surface of Kevlar yarn as a function of degree of grafting of GMA.

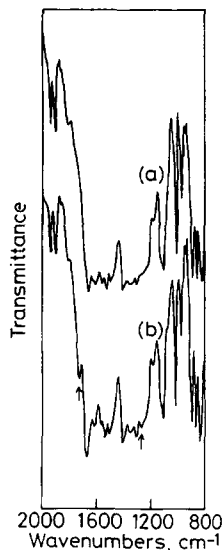


Figure 8 Infrared spectra of a surface of Kevlar yarn: (a) before and (b) after plasma-grafting of GMA (degree of grafting was 5%).

Reaction of Functional Groups of Graft Polymer Chains with Epoxy Resin or Curing Agent

Polymers such as poly(glycidyl methacrylate) and polyacrylamide, which were synthesized by plasma-induced polymerization, were used instead of the graft polymers to clarify the reactivity of functional groups of the graft polymer chains with the epoxy resin or the curing agent. The solutions of GMA and acrylamide for polymer-induced polymerization were the same as those used in the plasma-graft polymerization and freeze-vaporized to remove dissolved

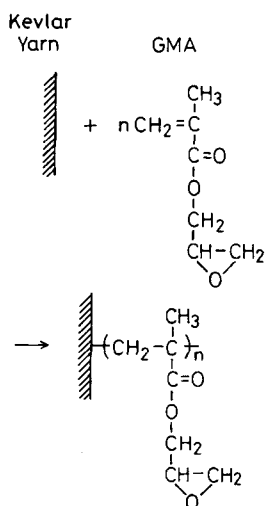


Figure 9 Plasma-graft polymerization of GMA onto a surface of Kevlar yarn.

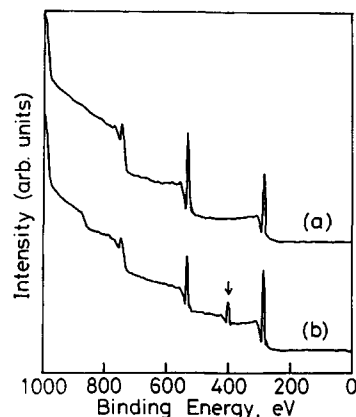


Figure 10 X-ray photoelectron spectra of a surface of poly(glycidyl methacrylate) aggregations: (a) before and (b) after reacting with TETA.

oxygen gas before plasma-induced polymerization. The plasma was generated at 100 W at 13.56 MHz for 1 min in the vessel containing the monomer solution and the polymerization was then initiated. Aggregations of poly(glycidyl methacrylate) and poly(acrylamide) were obtained by polymerizing at 300 K for 40 h.

Reaction of Poly(glycidyl methacrylate) with TETA

Aggregations of poly(glycidyl methacrylate) synthesized by plasma-induced polymerization were reacted with TETA as a curing agent at 300 K for 20 h and then washed sufficiently with methanol to remove unreacted TETA. Figure 10 shows X-ray photoelectron spectra of a surface of the poly(glycidyl methacrylate) aggregations before and after reacting with TETA. The N_{1s} peak appeared at 401 eV after reacting. Figure 11 shows infrared spectra of a surface of the poly(glycidyl methacrylate) aggregations before and after reacting with TETA. The absorption peaks at 3010 cm^{-1} and 2960 cm^{-1} are attributable to CH stretching vibrations of the epoxy group and methylene group, respectively. The absorption peak at 3010 cm^{-1} decreased after reacting, whereas that at 2960 cm^{-1} increased. It is confirmed from the results of Figure 11 that the epoxy groups of poly(glycidyl methacrylate) react with TETA at 300 K. Therefore the following inference is made: when the graft-polymerized yarn is enclosed with the epoxy resin/TETA mixture and then cured, covalent bonds are formed in the surface layer of the yarn by reacting the epoxy groups of graft poly(glycidyl methacrylate) chains with the amino or/and imino groups of TETA, as shown in Figure 12.

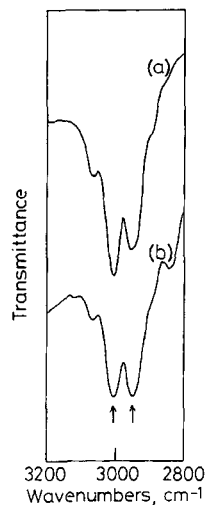


Figure 11 Infrared spectra of a surface of poly(glycidyl methacrylate) aggregations: (a) before and (b) after reacting with TETA.

Reaction of Polyacrylamide with Diglycidal Ether of Bisphenol-A

Aggregations of polyacrylamide synthesized by plasma-induced polymerization were reacted with 30 wt % diglycidal ether of bisphenol-A in toluene at 300 K for 24 h and then washed sufficiently with toluene to remove unreacted diglycidal ether of bisphenol-A. Figure 13 shows infrared spectra of a surface of the polyacrylamide aggregations before and after reacting with diglycidal ether of bisphenol-A. The absorption peaks at 1510 cm^{-1} and 1250 cm^{-1} are attributable to in-plane skeleton vibration of the benzene ring and to the C—O stretching vibration

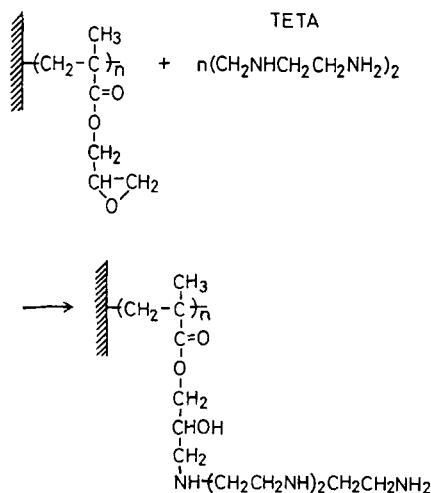


Figure 12 An example of reactions of graft poly(glycidyl methacrylate) with TETA.

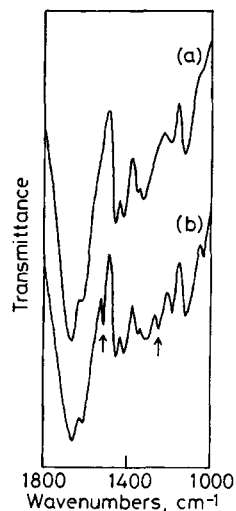


Figure 13 Infrared spectra of a surface of polyacrylamide aggregations: (a) before and (b) after reacting with diglycidal ether of bisphenol-A.

of the epoxy group, respectively. Therefore it is confirmed that the amino group of polyacrylamide reacts with the epoxy group of diglycidal ether of bisphenol-A.

Pull-out Force of Plasma-Grafted Yarn

Figure 14 shows pull-out force of the yarns which are embedded in the epoxy resin/TETA 2.2 : 1 mixture cured, as a function of the degree of grafting. Pull-out force was increased with increasing degrees of grafting. For example, the pull-out force in the ungrafted yarn was 22 kg/cm, but those in the yarns grafted by poly(glycidyl methacrylate) and polyacrylamide were 30 kg/cm and 54 kg/cm, respectively, at a 5% degree of grafting. This fact shows that the covalent bonds formed in the graft layer result in an increment of pull-out force.

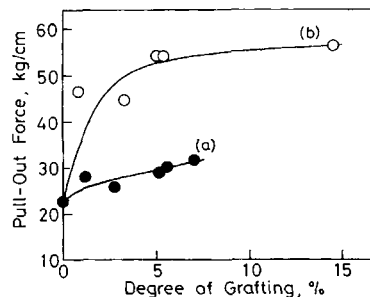


Figure 14 Pull-out force of the yarns grafted by (a) poly(glycidyl methacrylate) and (b) polyacrylamide, as a function of degree of grafting.

The pull-out force of the yarn grafted by polyacrylamide was always higher than that grafted by poly(glycidyl methacrylate) at the same degree of grafting. The density of the functional group in polyacrylamide is twice that in poly(glycidyl methacrylate), taking into account the molecular weights of monomeric units in the polymers. This means that the density of the functional group in the graft layer of polyacrylamide is twice that in the graft layer of poly(glycidyl methacrylate). In the diglycidyl ether of bisphenol-A/TETA mixture as a matrix resin, the density of the epoxy group reactive with polyacrylamide is 1.1 times that of amino and imino groups reactive with poly(glycidyl methacrylate), taking into account the mole ratio of the epoxy resin/curing agent mixture. Therefore the reaction frequency of graft polyacrylamide with diglycidyl ether of bisphenol-A is higher than that of graft poly(glycidyl methacrylate) with TETA, and the possibility of the formation of covalent bonds between graft polyacrylamide and the matrix resin becomes higher.

The surface structure of the polyacrylamide-grafted yarn after pulling out was investigated by infrared spectroscopy to clarify a failure mode in pulling out from the matrix resin. In the grafted yarn after pulling out, absorption peaks appeared at 2940 cm^{-1} and 1510 cm^{-1} ; these peaks did not appear in the yarn before grafting. The absorption peak at 2940 cm^{-1} originates from the methylene group of polyacrylamide as the graft polymer and that at 1510 cm^{-1} comes from the benzene ring of the diglycidyl ether of bisphenol-A/TETA mixture as the matrix resin. The strength of the peak from the matrix resin tended to increase with increasing degrees of grafting. It becomes apparent from the results of the infrared spectroscopy that the failure in pulling out of the grafted yarn is cohesive and the cohesive failure becomes more remarkable with increased degrees of grafting.

CONCLUSION

GMA and acrylamide can be plasma-graft polymerized onto a surface of KevlarTM 49 yarn. In the graft-

polymerization of GMA, the covalent bonds are formed in the graft layer by reacting epoxy groups of poly(glycidyl methacrylate) chains with amino and imino groups of TETA as a curing agent. In the graft-polymerization of acrylamide, the covalent bonds are formed in the graft layer by reacting amino groups of polyacrylamide chains with epoxy groups of the epoxy resin. The formation of the covalent bonds results in an increment of pull-out force of the yarn enclosed by the epoxy resin/TETA mixture cured. The failure in pulling out the grafted yarn is cohesive.

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