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Poly(ethylene terephthalate)에 대한 친수성 Monomer의 2단계 Grafting

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Two-Step Grafting of Hydrophilic Monomers onto Poly (ethylene terephthalate)

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요약 : 본 연구는 acrylic acid (AA), methacrylic acid(MAA) 및 AA/MAA 혼합물을 사용하여 그래프팅하므로써 poly(ethylene terephthalate) (PET)의 소수성을 개질하는 것을 목적으로 하였다. 상용 PET 섬유는 그래프팅에 대해 반응성이 낮기 때문에 1,1,2,2-tetrachloroethane을 swelling agent로 사용하여 반응성을 향상시켰다. 2단계 그래프팅에 있어서 제 1 단계는 개시제로 사용한 benzoyl peroxide(BPO)의 에멀젼으로 PET를 처리하는 것이고 제 2 단계는 전처리된 PET를 homopolymer 생성억제제인 cupric sulfate가 포함된 monomer의 수용액에서 그래프팅하는 것이다. PET 내부로 BPO의 확산과 전처리 과정에서의 BPO의 분해가 그래프팅 활성에 상반된 영향을 주며 따라서 이러한 관점에서 그래프팅에 대한 전처리 조건의 영향이 연구되었다. AA와 MAA의 혼합물은 각각의 monomer보다 높은 그래프트율을 나타냈고 AA/MAA의 몰비가 2/3일 때 최고 그래프트율을 나타냈다. 그래프트된 PET는 흡습성과 염색성이 상당히 향상되었다

ABSTRACT : To modify the hydrophobic property of poly (ethylene terephthalate) (PET) fiber such hydrophilic monomers as acrylic acid (AA), methacrylic acid(MAA), and AA/MAA mixture were grafted to PET. The grafting reactivity of commercial PET fiber was improved by swelling the fiber with 1,1,2,2-tetrachloroethane. Benzoyl peroxide (BPO) was the initator for the two-step grafting. The first step was the pretreatment of PET with an emulsion of BPO and the second was the grafting of the pretreated PET in an aqueous monomer solution containing cupric sulfate as a homopolymerization inhibitor. Diffusion of BPO into PET and decomposition of BPO during the pretreatment showed an opposite effect on the generation of the active species for

grafting, and so the conditions of pretreatment on grafting was emphasized on these effects. The mixture of AA and MAA gave a higher grafting yield than each monomer alone, giving the maximum yield at the mole ratio of 2/3 in AA/MAA. The grafting improved the moisture retention and dyeability of PET fibers.

INTRODUCTION

The chemical modification of poly (ethylene terephthalate) (PET) fibers through grafting with various vinyl monomers has attracted a considerable attention to improve the properties of PET fibers. Generally PET has strong physical and chemical resistance and is not decomposed by micro-organisms due mainly to their highly crystalline and chemically inert nature. In particular, PET is neither easily penetrated by dyes of large molecular weights nor combined with ionic dyes[1,2,3].

The strength is one of the most important characteristics of the fibers. The fiber strength has an infuluence on the strength of yarn or fabrics as well as such fabric characteristicsas crease and the sense of touch.

Some desirable properties of improved moisture regain, better dyeability and antistatic property could be imparted by grafting PET with acrylic acid and methacrylic acid[3~10,16,18,19], vinyl pyridine[1,7,11], acrylamide[7], and acrylonitrile[3,7,10]. Grafting can be done by either radiation or chemical means. Such ionizing radiation of PET as γ-rays from a 60 Co source [3,5,6,8,10,12~16], X-rays[17], or high energy electrons from accelerators[4,8,12,18,19] generates radicals, one of which was-CO-C_6H_4-COO-$CHCH_2$-via ESR study[20]. The radical provides the site for monomerreac-tion to form short chains. Similar PET radicals could be obtained at an elevated temperature in the presence of benzoyl peroxide [1,3,7,9,10], hydrogen peroxide[11], or ceric ion [5]. Grafting can be accomplished either by the direct irradiation of fiber with monomer or by the stepwise reaction of radical creation and the monomer addition[3]. In both radiation and chemical method for grafting, homopolymerization of vinyl monomers is suppressed by sutable additives[6,21~24].

A loose packing of chains is favored for the grafting due to easy accessibility of monomers for grafting. Swelling of fiber could be a way to allow monomers to easily diffuse into free-radical sites on the fiber[25].

EXPERIMENTAL

Materials

PET fiber samples (1.4d, degree of crystallinity 51.15%) were treated with methanol for 24hours to remove the oily impurities on the surface of fiber and then rinsed with hot water for 1hour, and dried at room temperature. Acrylic acid(AA) and methacrylic acid (MAA) were freshly distilled. Benzoyl peroxide (BPO) was purified via recrystallization.

Swelling

The PET fibers were treated with 1,1,2,2-tetrachloroethane as a swelling agent to increase the reactivity as follows: A PET fiber sample(0.3g) was placed into a 50m*l*-stoppered conical flask containing the swelling agent (6m*l*). The flask was immediately stoppered and placed in a water bath for a certain time period at the desired temperature. The contents were stirred on a shaker. The swelling agent was removed by treatment with warm methanol, and then with boiling water. The swollen samples were then used for pretreatment.

Pretreatment

The BPO emulsion was prepared in the ratio 1:8:2:1000 of BPO: monochlorobenzene: Tween 80: water, by weight. Tween 80 was added as an emulsifier. The swollen sample was introduced into a 50m*l*-stoppered conical flask containing 20m*l* of BPO emulsion. The flask was stoppered and placed in a water bath for a certain time period at the desired temperature. The contents were stirred on a shaker. After draining the excess emulsion solution by a centrifuge, the pretreated sample was obtained.

Grafting

A monomer solution was consisted of AA(or MAA, the mixture of the two), cupric sulfate as a homopolymerization inhibitor and water. The pretreated PET was introduced into a 50m*l*-stoppered conical flask containing 20m*l* of the aqueous monomer solution. The flask was stoppered and placed in a water bath for a certain time period at the desired temperature. The contents were stirred on a shaker. The by-product homopolymer was removed by rinsing with boiling water for 5 hours, and the grafted PET fiber was dried and weighed. The percent yield of grafting was calculated as follows:

$$\% \text{ graft yield} = \frac{\text{dry weight of grafted PET} - \text{dry weight of original PET}}{\text{original PET}} \times 100$$

Determination of moisture regain(M.R.)

The samples were dried in an oven at 110°C for 1.5 hours and weighed. They were then conditioned at 65% R.H. and 20°C for 72 hours and weighed.

$$\text{M. R.}(\%) = \frac{\text{weight of the conditioned sample} - \text{weight of the dried sample}}{\text{dried sample}} \times 100$$

Dyeing and determination of dye content

Dyeing of the PET fiber with basic dye of Malechite Green was carried out from 40°C to 98°C by a gradual increase for a period of 40 minutes. Then the dyeing was continued at 98°C for 40 minutes.

The dye content of a dyed fiber was determined by extracting the dye from a known amount of the fiber with DMF containing 0.4 mole of $ZnCl_2$, 8m*l* of conc. HCl, and 20g of hydroquinone in a liter. The extract was made up to a known volume, and the optical density was measured using a double beam spectrophotometer to determine the dye content of the dyed fiber. The standard solutions for the measurements of optical density were prepared with identical solvent and dye.

Determination of fiber strength

The strength of the original PET fiber and the grafted PET fiber was measured by a Pressley Strength Tester. The specific strength was determined from Pressley index(PI)

$$\text{Specific strength (g/den.)} = 0.596 \times \text{PI}$$

RESULTS AND DISCUSSION

The PET fibers pretreated in the present investigation consisted of long chain molecules which are rather irregularly distributed in a single filament and the grafting becomes favored. In other words, the PET fibers used possess higher portion of accessible domains improving the susceptibility toward grafting monomers.

The graph of swelling time vs. graft yield at various temperatures are shown in Fig.1. From Fig.1 it is apparent that the swelling of PET fibers makes the grafting more effective. Since it has been believed that the formation of radicals is confined to the amorphous part of PET[11], the swelling increases the degree of

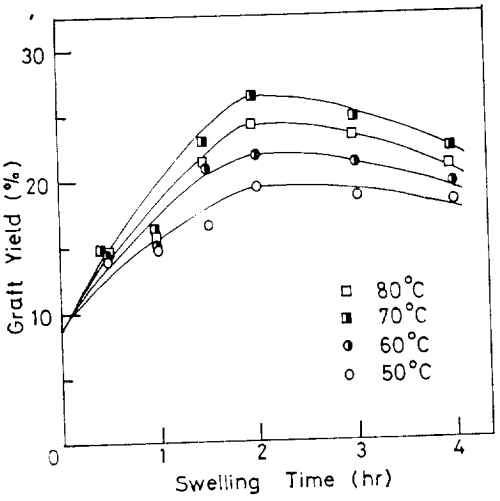

Figure 1. Relation between swelling time and grafting of AA/MAA onto PET at various temperature.
Pretreatment : emulsion (BPO/MCB/Tween 80/water=1/8/2/1000, by weight), 1hr at 70°C.
Grafting : AA/MAA(50/50 by vol.) 10% aqueous solution containing 0.04mmol/l of $CuSo_4$, 2hr at 80°C.

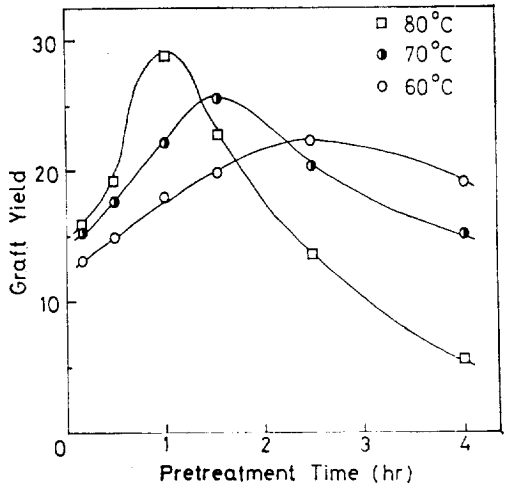

Figure 2. Relation between time of pretreatment and grafting of AA/MAA onto PET at various temperature.
Swelling : 1,1,2,2-tetrachloroethane, 1.5hr at 70°C.
Grafting : AA/MAA(50/50 by vol.) 10% aqueous solution containing 0.04mmol/l of $CuSO_4$, 2hr at 80°C.

freedom in chain motion at least in the amorphous region of PET, causing easy diffusion of monomer.

The amount of active species generated on PET fibers affects directly on the efficiency of grafting, and is determined from the diffusion rate of BPO into PET and the thermal decomposition rate of BPO or radicals[7].

BPO is decomposed to primary free-radical species ($C_6HC_5OO\cdot$) or secondary free-radical species ($C_6H_5\cdot$). These free radicals may participate in[1] (a) abstracting hydrogen atoms directly from the PET backbone to yield PET radicals capable of initiating the grafting reaction; (b) terminating growing polymer chains; (c) combining the other free-radical species, in particular, the secondary free-radical species; and (d) terminating the PET radicals. When(a) is predominant over the combined reactions of(b), (c), and (d), the graft yield will increase. It is known that the active species introduced from the pretreatment by BPO emulsion is not the radical but BPO itself entrapped in PET fibers[7].

Figure 2 shows that the higher temperature gives the faster and the hgiher maximum graft yield. The decomposition rate and the diffusion rate of BPO are also accelerated at the higher temperatures.

The effect of BPO concentration on graft yield is shown in Fig. 3. The increase in the BPO concentration up to 4.0×10^{-3} mole/l is accompanied by a rapid increase in graft yield. It suggests that only the BPO entrapped in PET fiber can be used for active species for grafting. Above the concentration of 4.0×10^{-3}mole/l, PET fiber may be saturated with BPO.

The effect of grafting temperature and time on graft yield is shown in Fig.4. The increase in grafting for the higher temperature can be

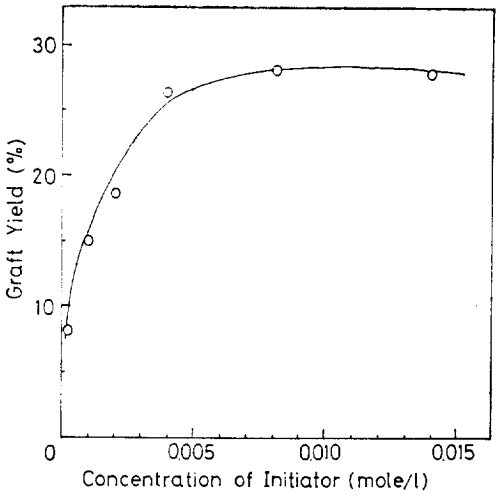

Figure 3. Relation between concentration of initiator and graft yield.
Swelling : 1,1,2,2-tertachloroethane, 1.5hr at 70°C.
Pretreatment : 1hr at 80°C.
Grafting : AA/MAA (50/50 by vol.) 10% aqueous solution containing 0.04 mmol/l of $CuSO_4$, 2hr at 80°C.

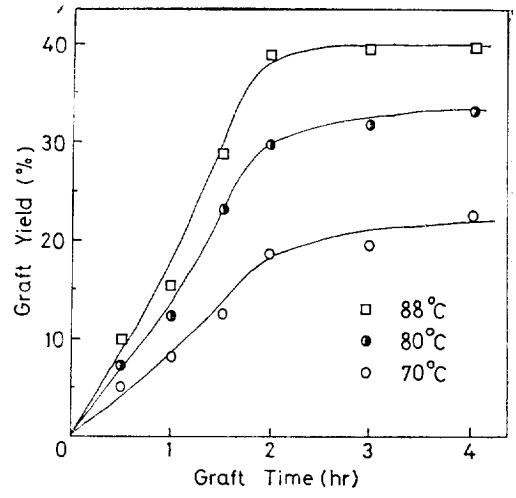

Figure 4. Relation between grafting time and graft yield at various temperature.
Swelling : 1, 1, 2, 2-tetrachloroethane, 1.5hr at 70°C.
Pretreatment : emulsion (BPO/MCB/Tween 80/water=1/8/2/1000, by weight), 1hr at 80°C.
Grafting : AA/MAA(50/50 by vol.) 10% aqueous solution containing 0.04mmol/l of $CuSo_4$.

interpreted by (a) faster BPO decomposition rate;(b) increased swelling of PET fibers and mobility of monomer molecules, both of them are the main controlling factors in monomer diffusion in the aqueous phase;(c) possible reaction between growing homopolymer chains with the PET and the PET radicals; and (d) increased initiation and propagation rate for grafting. The saturation graft yield was observed at all temperatures after a certain period. This means the depletion in monomer as well as the decrease in the available sites for grafting on the PET backbone as the reaction proceeds. In addition, it seems that large amount of grafted PET formed in the initial stage of the reaction retards the diffusion of monomer and initiator.

Figures 5 and 6 show the effect of monomer concentration and mixing ratio of AA/MAA on graft yield, respectively. As shown in Fig.5 MAA gives higher yield than AA, and the mixture of AA and MAA gives even higher yield than MAA. Although the graft yield varies with mixing ratio of two monomers, Fig.6 gives the maximum graft yield at 2/3 in AA/MAA mole ratio. In the case of monomer which propagates fast, the consumption of the monomer is increased due to fast homopolymerization and so diffusion of the monomer into PET fiber is insufficient, resulting in decrease of graft yield. Since grafting is dominated by the diffusion of monomer into PET fiber, the monomer which diffuses into PET fiber more easily is grafted preferentially at the initial stage of grefting in the case of mixed monomer. Therefore, it seems that the grafted PET shows an enhanced affinity toward the other monomer and makes the monomer diffuse into PET fibers more easily[7].

Figure 5 shows that the graft yield increases with monomer concentration up to about 10%

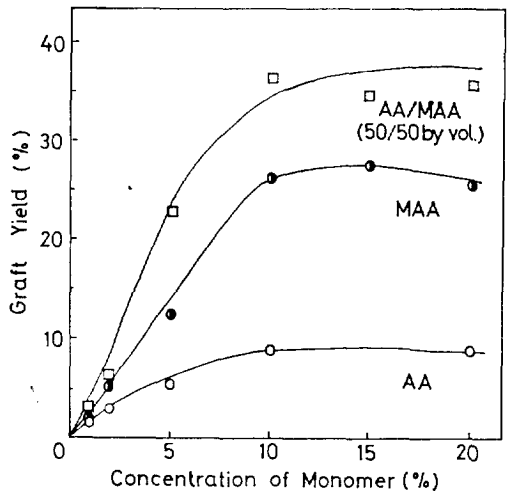

Figure 5. Relation between concentration of monomer and graft yield.
Swelling : 1, 1, 2, 2-tetrachloroethane, 1.5hr at 70°C.
Pretreatment : emulsion (BPO/MCB/Tween 80/water=1/8/2/1000, by weight), 1 hr at 80°C.
Grafting : aqueous monomer solution containing 0.04 mmol/1 of $CuSO_4$, 2hr at 88°C.

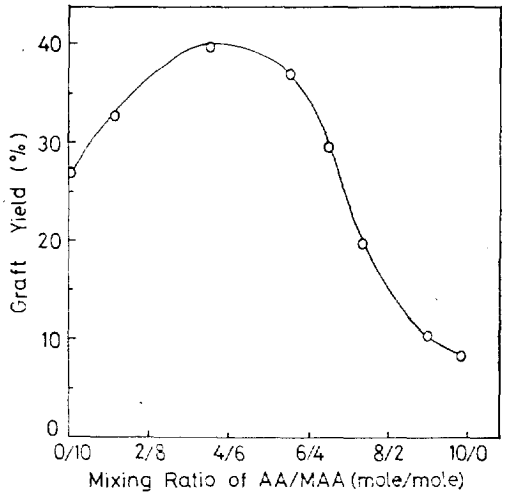

Figure 6. Relation between mixing ratio of monomers and graft yield.
Swelling : 1, 1, 2, 2-tetrachloroethane, 1.5hr at 70°C.
Pretreatment : emulsion (BPO/MCB/Tween80/water=1/8/2/1000, by weight), 1hr at 80°C.
Grafting : aqueous monomer solution containing 0.04mmol/1 of $CuSO_4$, 2hr at 88°C.

then levels off. At high concentration, the homopolymer, barrier for diffusion of monomer, seems to increase and to impede the rest of the monomer to diffuse into the fibers resulting in lowering the graft yield.

Previous works have reported that the presence of metallic ions such as Cu^{2+} and Fe^{3+} enhances grafting reactivity of free-radical significantly[6,23,24]. The initiating species in homopolymerization of acrylic acid is known to be the H-atom adduct of the monomer[6]. Therefore, the presence of H-atom scavengers may inhibit the formation of initiating species for homopolymerization. Although O_2 and H_2O_2 are good H-atom scavengers, they also inhibit grafting, perhaps due to giving species incapable of propagating the chain. Although both Fe^{3+} and Cu^{2+} inhibit homopolymerization of acrylic acid, only the latter is effective in the case of methacrylic acid[6]. This suggests that the addition of H-atom to acrylic acid is slower than scavenging of H-atom by either Cu^{2+} or Fe^{3+}, but the addition of H-atom to methacrylic acid is faster than scavenging by Fe^{3+}. In terms of attachment to PET fibers, Cu^{2+} seems to bond ionically and it can easily be broken, whereasFe^{3+} tends to form chelate type complex[1,26,27]. For this reason, cupric sulfate was used for both AA and MAA homopolymerization inhibitor.

Figure 7 shows the effect of cupric sulfate concentration on graft yield. A maximum grafting is seen at the Cu^{2+} concentration of 0.04 m mole/1. The increase in grafting yield by the addition of Cu^{2+} can be ascribed to the following two factors. First, Cu^{2+} accelerates the decomposition of BPO where reaction is well known[28,19]. Second, Cu^{2+} inhibits the formation of homopolymer giving reduced monomer loss and easy monomer diffusion. The decrease in graft yield for higher concentrations of cupric sulfate suggests that Cu^{2+}may act as a radical

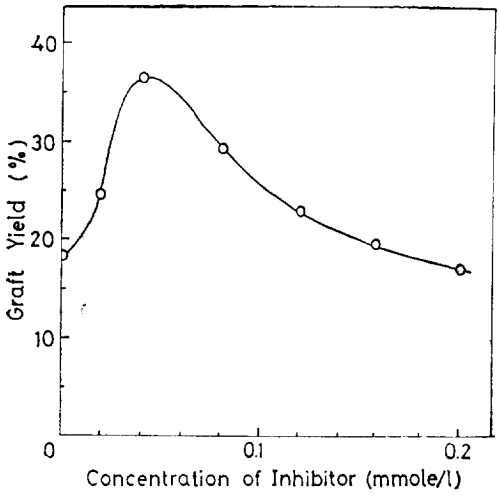

Figure 7. Relation between concentration of inhibitor and graft yield.
Swelling : 1, 1, 2, 2-tetrachloroethane, 1.5 hr at 70 °C.
Pretreatment : emulsion (BPO/MCB/Tween 80/water=1/8/2/10000, by weight), 1hr at 80°C.
Grafting : AA/MAA (50/50 by vol.) 10% aqueous solution, 2hr at 88°C.

trap[1] causing radical termination.

Figure 8 shows the moisture regain of various grafted PET fibers. The original(non-grafted) PET fiber is highly hydrophobic, and the moisture regain of the fiber is extremely low under normal conditions, 0.37% at 20°C and 65% relative humidity.

Grafting with acrylic acid or methacrylic acid increases hydrophilicity of the fiber by the introduction of hydrophilic groups such as carboxylic group into the fiber structure. The increase in the hydrophilic nature is responsible for the increase in moisture regain. As shown in Fig. 8, the moisture regain increases with graft yield for all monomers tested. Because the mixture of monomers gives higher graft yield than each monomer alone the grafting with the AA/MAA mixture is more effective to enhance the moisture regain.

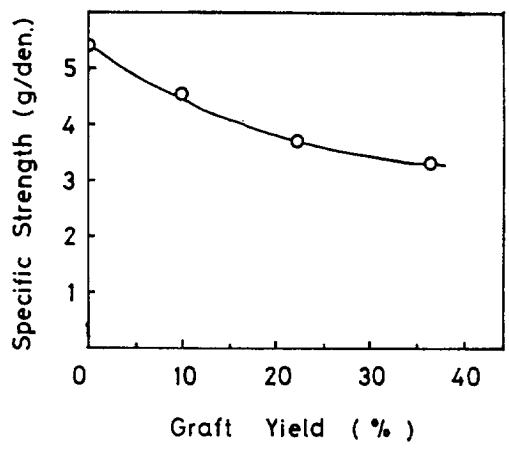

Figure 8. Relation between moisture regain and graft yield at 20°C, 65% R.H.

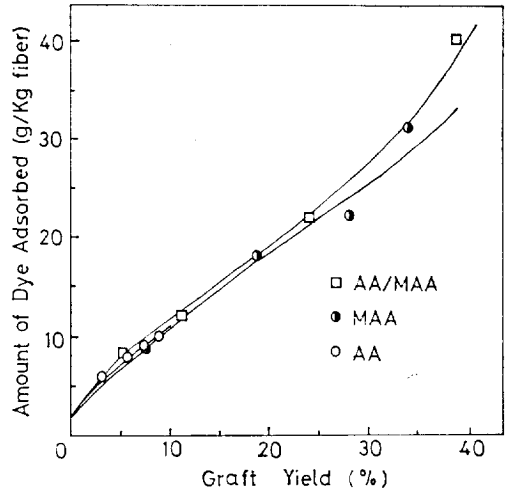

Figure 9. Relation between the amount of dye adsorbed and graft yield.

Figure 9 shows the dyeability of the grafted PET fibers. The grafted PET fibers show considerable uptake of basic dye giving almost equal degree of dye content corresponding to graft yield. It is considered that the carboxylic group introduced on PET fiber provides the acidic site to which the basic dye can be easily

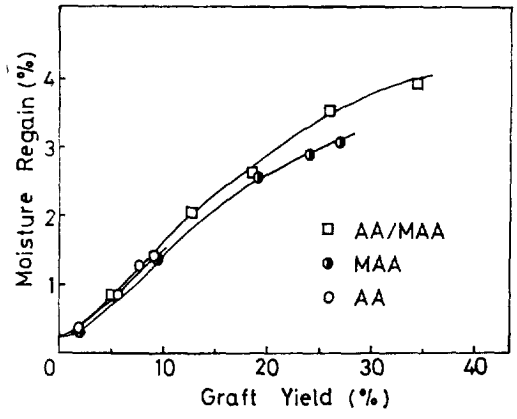

Figure 10. Relation between specific strength and graft yield.

adsorbed.

Figure 10 shows the relationship between the specific strength of the fiber and the graft yield for AA/MAA mixture. The strength is decreased with increasing the graft yield, due partly to loose structure by grafting PET fiber.

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