

# Improvement in dyeing and water absorption properties of polypropylene and polyethylene

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## Abstract

The surface properties of polyolefin materials such as polypropylene (PP) and polyethylene (PE) were improved using a combination of activation treatment and polymer or monomer grafting. These materials obtained have a high water absorption property, and improved dyeing and painting properties, bonding with usual adhesives, etc. and are expected to be used widely in many fields. The technique is useful for the improvement of other polymeric materials.

*Keywords:* Polyolefin; Polypropylene; Polyethylene; Water absorption; Bonding property; Dyeing property

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## 1. Introduction

Polyolefins such as polypropylene (PP) and polyethylene (PE) have high tensile strength and high resistance to chemical reagents. Therefore, they are used in manufacture of strings, tubes, bags, containers, etc. However, polyolefins cannot be bonded to other materials using standard adhesives and have no water absorption properties because of their stable chemical structure. Thus, their use is limited to rather narrow fields compared with other polymers such as polyvinyl chloride, polystyrene, acrylonitrile-butadiene-styrene (ABS) resin and acrylic or methacrylic resins.

Many techniques have been attempted to improve the surface properties of polyolefins such as polymer-blend method, corona discharge treatment,<sup>[1]</sup> ozone treatment,<sup>[2]</sup> plasma treatment,<sup>[3, 4]</sup> UV irradiation,<sup>[5, 6]</sup> treatments with sulfuric acid and hydrofluoric acid and other chemical reagents, and graft polymerization.<sup>[7-9]</sup> PP fabrics were also treated with hydrophilic resin in the presence of a persulfate salt.<sup>[10]</sup> Polymeric materials were treated by coating with polyvinyl alcohol,<sup>[11]</sup> polymer mixtures with or without additives, and some binders containing polymers after corona or plasma treatment.<sup>[12, 13]</sup> However, these techniques did not give effective and durable improvement for polyolefins, because chemical bonds did not form between polyolefins and coated polymers.

The author examined techniques to improve polyolefins, and developed a novel and effective method, which comprised an activation treatment step and a polymer or monomer treatment.<sup>[14-19]</sup> The activation step produces functional groups such as hydroperoxyl and carbonyl on the surface of treated polymeric materials by chemical reactions or energy irradiation. The energy irradiation techniques are as follows: UV irradiation, plasma treatment, high voltage electric discharge treatment and corona discharge treatment, etc. The polymer or monomer treatment is to react the activated materials with polymers or monomers under

given conditions. This article describes the developed method and its application.

## 2. Experimental

### 2.1 Materials

PP non-woven fabrics (unit weight 50 g/m<sup>2</sup>), PE plates (average molecular weight of 5000000, thickness 0.7 mm, unit weight 467 g/m<sup>2</sup>), polyester (PET) non-woven fabrics (unit weight 57 g/m<sup>2</sup>), PET/PE core sheath type non-woven fabrics (unit weight 50 g/m<sup>2</sup>), PP film (unit weight 17 g/m<sup>2</sup>), PET film (unit weight 72 g/m<sup>2</sup>), poly(ether sulfone) film (thickness 170 μm, unit weight 50 g/m<sup>2</sup>).

### 2.2 Activation step

The energy techniques that were used to activate polymeric materials for 5 s to 10 min at room temperature were UV irradiation, plasma treatment, high-voltage electric discharge treatment, and corona discharge treatment. Polymeric materials were also activated by treatment with chemical oxidants such as ozone, peroxides, and sodium hypochlorite, etc. It is sometimes effective to impregnate the material with an appropriate solvent or solution, before the activation step. The impregnation step is to dip polymeric materials in a solvent or solution in which it has poor solubility under the condition that the material does not dissolve over a period of about 10 s to 60 min and in a temperature range from room temperature to about 100°C. The materials undergo a weight increase of 0 to 20% of the original weight without any deformation. This step was completed by drying the material quickly after dipping.

### 2.3 Treatment with polymer or monomer

Polymeric materials obtained after the activation step were treated with a solution of polymers in the presence or absence of catalysts or initiators for a given time at a given temperature. The following polymers were used: hydrophilic such as poly(vinyl alcohol) (PVA), cellulose derivatives, ethylene-vinyl alcohol

copolymer, poly(hydroxyethyl methacrylate), poly( $\alpha$ -hydroxyl vinyl alcohol), poly(acrylic acid), poly( $\alpha$ -hydroxyl acrylic acid), poly(vinyl pyrrolidone), polyamines, poly(alkylene glycol)s, starch, glucomannan, silk fibroin, agar, gelatin, egg white, sodium arginate, poly(acrylic ester)s, poly(methacrylic ester)s, poly(styrene), poly(vinyl acetate), polyamides, polyesters, polyimides, polyphosphates, etc. Copolymers and many other kinds of polymers were selected considering the aim of the improvement.

Monomer grafting was carried out as follows. Activated or activated and polymer-treated polymeric materials were mixed with a monomeric solution containing initiators or sensitizers. The reaction mixture was set in a bath for a given time at a given temperature in the case of a heating reaction. These ranged from 5 min to 3 h at 80°C. On the other hand, in the case of photopolymerization, a Pyrex glass reaction vessel containing the reaction mixture was irradiated with UV light from 1 min to 4 h at 30°C. A high pressure mercury lamp (H400P, Toshiba Co., Ltd.) was used as UV light source. The whole range of the UV light or the monochromatic UV light of approximately 360 nm obtained through a filter were irradiated. The distance between the reaction vessel and light source was between 5 and 30 cm. If the polymer material did not sink in the reaction mixture, an appropriate glass plate or vessel was placed on it for it to sink. An example of a typical mixture of reactants is as follows: 40–80 g of polymeric material, 0.10–1.0 g of initiator, and 400–800 ml of solvent. As an example of a monomeric mixture including a hydrophilic monomer, a mixture of 8 volumes of acrylic acid and 2 volumes of methyl methacrylate was applied. In the case of polymerization of vinyl acetate, methyl methacrylate, and styrene, an appropriate organic solvent such as methanol, acetone, or toluene, or a mixture of several solvents was used.

The following catalysts or initiators were used: peroxides such as benzoyl peroxide and potassium or ammonium persulfates, oxidation-reduction initiators, oxidants such as cerium ammonium nitrate (IV), hydrogen peroxide, cumene hydroperoxide and *t*-butyl peroxide, etc., inorganic reductants such as copper salts, iron salts, sodium hydrogen sulfite, sodium thiosulfate, etc. or organic reductants such as dialkyl peroxide, diacyl peroxides, etc. and other standard initiators of radical polymerization.

#### 2.4 Cross-cut test

The treated polymeric materials were coated with standard acrylic resin paint and the bonding force between the paint and polymeric materials was estimated by the cross-cut test. In this test, a coated area of 1.0 cm<sup>2</sup> was cut into 100 sections of 1.0 mm<sup>2</sup> area using knife, and adhesive tape was bonded to the sections. After peeling off the tape, the number of coated sections was counted. When the number was 100, the bonding was judged to be sufficient.

#### 2.5 Peeling strength test

An untreated PE plate and PE plates treated by each step of impregnation, activation, and grafting, or the combination of these steps were examined by the peeling strength test. A PE plate (size 5 x 30 mm) was bonded to a plywood board plate (size 10 x 20 mm) with 1.5 g of a commercial poly(cyanoacrylate) adhesive (Toa Gosei Co., Ltd.); the bonded area was 5 x 5 mm. A weight (500g) was put on the bonded part. Thus, a test piece was obtained. After the bonded test piece was dried, the energy required to peel it off was measured with a tensile tester (AGS-H of Shimadzu Seisakusho Co.

Ltd.) under a given condition. This energy was considered the peeling strength, which was relative assuming the value for untreated PE plate to be 1.0.

### 3. Results and discussion

Figure 1 shows IR spectra of untreated PP and activated PP fiber by oxidation with ozone. The treated PP gives an absorption peak based on carbonyl groups around 1710 cm<sup>-1</sup>. When the area ratio at a peak at around 1710 cm<sup>-1</sup> to that at 1167 cm<sup>-1</sup> was plotted against time, a straight line was obtained.

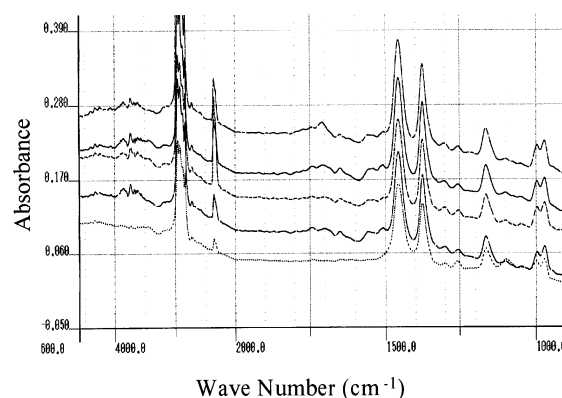


Fig.1 Change in IR spectra of PP fiber by the activation process. Activation times: 0, 15, 30, 45 min from the bottom.

As the tensile strength of oxidized PP fiber decreased with increase in treatment time, it is important to apply the activation treatment only to the surface area of the materials. When thick PP film (0.1 mm or more) or plate was treated, the decrease in tensile strength might be negligible compared with other fibers.

PP non-woven fabric (weight, 0.3 g) was activated with ozone and treated with an aqueous solution of PVA containing an initiator for 2 h at 50°C; the obtained material was called "Sample A." A similar PP was activated and treated with an aqueous solution of fibroin for 2 h at 80°C; the obtained material was called "Sample B." Yet another similar PP was treated with an aqueous solution of PVA and a persulfate salt for 2 h at 80°C according to the method used in the patent application;<sup>[10]</sup> the obtained "Sample C" gave a comparative example. Each sample had high water absorption properties. However, when these samples were washed with hot aqueous solution of the standard fatty acid salt (soap) (ratio of fabric to water = 1:100, soap concentration = 5%), the improved properties changed. Table 1 shows the relationship between the water absorption percentage and the number of washings for each sample. The water absorption of Sample C significantly decreased after washing, which suggests that chemical bonds are not formed between the materials and polymer by this method.

Table 1 Change in water absorption % of treated PP fabrics with washing

Sample	Number of washings					
	1	2	3	4	5	6
A	1060	950	820	800	780	780
B	650	620	610	610	605	605
C	760	460	330	320	300	260

The effect of each step and the combination of steps were examined in the treatment of PE plate with high molecular weight, which was known to be a difficult material to improve. The PE plate was treated with impregnation step in appropriate liquid, activation step, monomer grafting, and combination of these processes. The relative peeling strength and contact angle of water for the material are given in Table 2. Combination of the three steps is apparently the most effective among the treatments examined.

Table 2 Peeling strength test of adhesion and contact angle of water in PE plate treated by each step

No.	Impreg-nation	Activation	Grafting	Peeling strength	Contact angle (°)
1	X	X	X	1	1.00
2	X	O	X	6	1.10
3	O	X	X	6	1.10
4	X	X	O	5	1.20
5	O	O	X	6	1.10
6	O	X	O	10	1.71
7	X	O	O	18	1.30
8	O	O	O	220	167

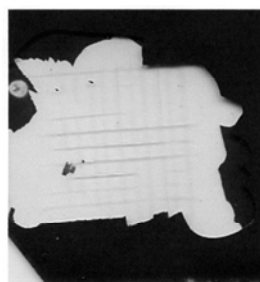
The step or test was done (O) or not done (X).

PP plates were treated by the usual methods and the present method. The plates obtained were coated with commercial acrylic resin paint. After drying, the cross-cut test was carried out to determine the bonding force between the paint and the plates. The test was carried out using each of the following PP plates: untreated, oxidized, one treated with a commercial primer that is usually sold as a reagent for prompting the bonding power of an adhesive for PP and PE materials, one treated with a toluene solvent treatment and UV irradiation according to reference, [5] one treated with graft polymerization of a hydrophilic monomer according to reference, [6] one treated with a corona-discharge treatment and coating with a hydrophilic polymer according to reference, [13] and one treated with the present method. Figure 2 shows each PP plate after the test. Only the PP plate treated by the present method gave a full 100 mark score in the cross-cut test.

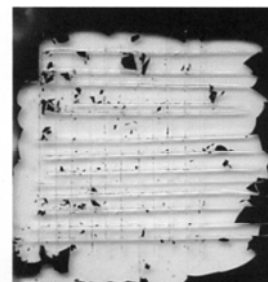
Graft polymerization is an old technique used to modify a polymer with a reaction of monomers. [20-22] Each graft polymer is considered to be grown from one active point on the main polymer chain. In contrast, the present activation step should produce many hydroperoxyl, hydroxyl, and carbonyl groups in polyolefins. [23] When PP is treated by an activation step, it is considered that propylene residues are oxidized and hydroperoxyl groups are mainly formed at  $\alpha$ -carbons to methyl groups; the structure is given by the formula,



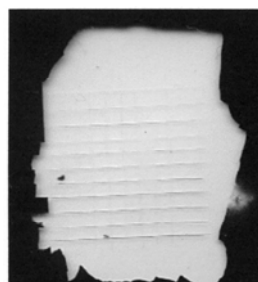
After the activation step, PP showed a weight increase of approximately 0.1–10%. We consider the case where PP fabrics of 100 g were oxidized to cause a weight increase of 6 g. When it is supposed that the PP of 100 g consists of propylene residues, values  $m = 2.19$  and  $n = 0.188$  are estimated from the weight increase of 6 g. In other words, about 13% of propylene residues is considered to be oxidized. When the oxidized PP was treated with PVA (with degree of polymerization, 2000), the obtained PP produced a weight increase of 2%, and the molar number of PVA bonded to the PP was estimated as  $2.39 \times 10^{-5}$  mole.



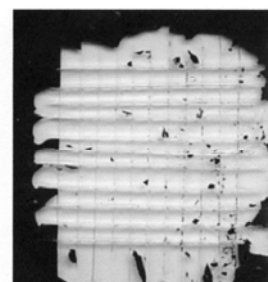
Untreated PP



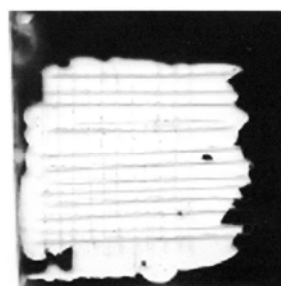
Oxidized PP



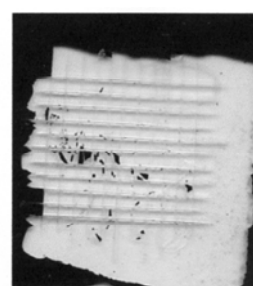
PP treated with a primer



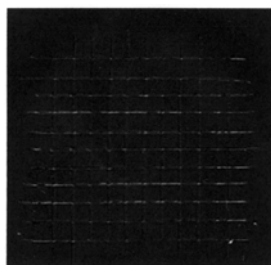
PP treated with toluene and UV irradiation



PP treated by the method described in reference [6]



PP treated by the method described in reference [14]



PP treated by the present method

Fig.2. Cross-cut test of an untreated PP plate and treated PP plates painted with an acrylic resin paint. Treatment methods are given in each photograph.

The molar ratios of PVA molecules to the original monomer residues of PP (2.38 moles) and oxidized monomer residues (0.188 mole) were calculated as 1.00:100000 and 1.33:10000, respectively. The molar ratios of vinyl alcohol residues to the original monomer residues of PP and oxidized monomer residues were calculated as about 20:1000 and 254:1000, respectively. As hydroperoxyl groups contained in PP are much more frequent than hydroxyl groups in PVA, the polymer is considered to be bonded to the PP at several points with the help of initiators.

PP fabrics grafted with methyl methacrylate (MMA) monomer or treated with polymer mixtures by the present method showed good dyeing affinity when dyed with disperse, cationic, and acid dyes in aqueous solutions. In particular, PP fabrics dyed with disperse dyes, Dianix Red AC-E and Dianix Blue AC-E (Mitsubishi Chemical Industries) did not fade even 13 years after dyeing, although, PET fabric dyed at the same time showed extreme discoloration through sublimation of the dye.

Similar effective improvements were obtained with the present method using PET non-woven fabrics (57 g/m<sup>2</sup>), PET/PE core sheath type non-woven fabrics, PP film, PET film, and poly(ether sulfone) film.

PP non-woven fabrics with high water absorption properties, shown in Table 1, had a high durability to alkaline solutions such as 40 wt% potassium hydroxide. These treated fabrics indicated suitable properties for use as a secondary battery separator, compared with commercial separators made of PP/PE fabric, glass fiber material, and nylon fabric.

Polymeric materials obtained with the present method have been applied in many areas; for example, wiping or cleaning fabrics, filters for medical use or food production, cloths with high water absorption, ink absorbers for writing materials, production of synthetic papers which can be written on with water-soluble ink, cosmetic tools, materials for microbial culture media, and binding materials for polymer composites. When the bonding properties of molded polymeric materials improve, the method will be applicable for production of plastic orthodontic brackets and other materials for dental use.

The present method can be applied to many kinds of synthetic polymeric materials such as polyester resin, acrylic resin, polystyrene, ABS resin, polyamides, polyimides, and rubbers and other natural polymeric materials, etc.

## 5. Conclusions

The present method provides an excellent modification for polyolefins and other polymers. Its application should be useful in many fields.

## Acknowledgements

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