Chemical Modification of Synthetic Fiber. 1. Graft Copolymerization of Methyl Methacrylate onto Poly(propylene) and Poly(vinyl chloride) Fabrics.

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Abstract

Graft copolymerization of methyl methacrylate onto poly(propylene) and poly(vinyl chloride) fabrics was carried out by the successive treatments of ozone oxidation and UV irradiation. The resulting grafted fabrics had enough strength for a practical use and gave high dye uptake in the dyeing with a disperse dye.

1. INTRODUCTION

Since poly(olefin)s such as polyethylene (PE) and polypropylene (PP), poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) etc. are hydrophobic, they need the surface treatment by chemical or physical techniques for a general use. Recently, plasma or sputtering treatments are extensively carried out for the improvement of the surface property of these films.\(^1\)\(^-\)\(^4\) But, the dyeing of poly(olefin)s with usual water-soluble dyes has not been successfully carried out by these techniques.

On the other hand, graft copolymerization of vinyl monomers to various substrates have been made extensively to improve the physical or chemical properties of many kinds of polymers such as synthetic resin, natural and chemical fibers, proteins, carbon black and silica gel.\(^5\)\(^-\)\(^11\) Ultra-violet light (UV) irradiation is one of the effective methods to make graft copolymerization of various vinyl monomers onto rather inactive polymers.\(^12\)\(^-\)\(^16\) As a fact, graft copolymerization of methyl methacrylate or acrylamide onto PP or PE by the UV irradiation were carried out.\(^17\),\(^18\) \(\gamma\)-Irradiation is also an effective technique to carry out the graft copolymerization of vinyl monomers onto poly(olefin)s such as PP.\(^19\)

Ozone oxidation is also known as a conventional method to improve the surface property of many kinds of polymers. Several studies were reported on the graft copolymerization of vinyl monomers onto polymers including PP by ozone oxidation.\(^20\)\(^-\)\(^25\)

Usually, poly(olefin)s have excellent physical properties, but they are not used widely as textile fibers, because they cannot be dyed by general water-soluble dyes. Graft copolymerization seems effective for the improvement of the surface property and the dyeability of poly(olefin)s. But, the reaction conditions of the graft copolymerization were in most cases too vigorous to prepare grafted materials of practical value. In the graft copolymerization of vinyl monomers onto PP by ozone oxidation, the resulting product with high grafting (%) seems not to be used in practice because of low tensile strength.

The authors tried to improve the dyeing property of polypropylene and poly(vinyl chloride) by successive two treatments. This paper describes the grafting of methyl methacrylate onto these fibers by the ozone oxidation and the UV irradiation.
2. EXPERIMENTAL

2.1 Materials

Plain weave fabrics of poly(propylene) and poly(vinyl chloride) were obtained from Kansai Iseikatsu Kenkyu-kai. Fabrics of PP: 170 d yarns warp and weft (each yarn contained 20 filaments) and PVC: 75 d yarns warp and weft (each yarn contained 25 filaments). Both fabrics were washed with toluene and methanol five times at room temperature and dried at 60°C for six hr. Liquor ratio of the fabrics to toluene or methanol on each washing was 50.

Commercial reagent-grade methanol and toluene were used without further purifications. Methyl methacrylate (MMA) was distilled under reduced pressure in nitrogen atmosphere.

2.2 Ozone oxidation treatment

A Nippon Ozone ON-1-2 ozonizer was employed for making ozone gas. The amount of oxygen supplied into the apparatus was 1.5 l/hr and the voltage was 50 V. Ozone evolved was estimated to be 0.5 g/hr or 9.2 g/m³. PP or PVC fabrics of ap. 50 mm x 50 mm size are put in a 300 ml Erlenmeyer flask. The mixture of oxygen and ozone from the ozonizer was introduced to the flask for 45-60 min. The treated fabrics were used for the subsequent grafting process.

2.3 Grafting

MMA solution in methanol was put into a 300 ml Erlenmeyer flask containing a fabric treated with ozone. The mixing amounts of each materials were MMA 1.23 ml and methanol 12.3 ml for a PP fabric 0.2 g, and MMA 2.44 ml and methanol 9.77 ml for a PVC fabric 0.15g, respectively.

A Corning CS-7-51 filter was used to obtain around 365 nm light from UV light of a Toshiba H400P high pressure mercury lamp. The filter was 4 mm thick and placed at the position of 155 mm distance from the UV lamp. The reaction flask was put on the filter and the light was irradiated on it for 3 hr.

After the reaction time, the reaction mixture was poured into a large excess of methanol. All of the MMA homopolymer and MMA grafted fabrics were collected and dried in vacuo and weighed. The MMA homopolymer attached to grafted fabrics was removed by three times of washing with toluene for 1 hr using a magnetic stirrer. Total conversion (%), grafting (%) and grafting efficiency (%) were calculated from the following equations:

\[
\text{Total conversion} = \frac{\text{Homo and graft polymers (g)}}{\text{Monomer used (g)}} \times 100
\]

\[
\text{Grafting} = \frac{\text{Graft polymer (g)}}{\text{Original fabric (g)}} \times 100
\]

\[
\text{Grafting efficiency} = \frac{\text{Graft polymer (g)}}{\text{Homo and graft polymers (g)}} \times 100
\]

2.4 IR spectroscopy

Infrared spectra were recorded by a Shimadzu FTIR-8500 with the diffusion reflection method.

2.5 Dyeing

Original, ozone treated and MMA grafted fabrics of PP or PVC were dyed with a disperse dye, Dianix Blue AC-E produced by Mitsubishi Chemical Industries using sodium o-phenylphenol as a carrier. The carrier (20 mg) was dispersed in a flask with an anionic surfactant, ABS at 60°C and
the mixture was adjusted to pH 5.5 using acetic acid. The dye (20 mg) was dispersed in another flask containing 30 ml of water. Both of the dye and the carrier mixture were mixed in a flask and the original, ozone treated and MMA grafted fabrics of PP or PVC were put in the flask. The weight of each fabric was in the range of 40 mg to 50 mg. The dyeing temperature and time were 100°C, 30 min. for PP and 80°C, 10 min. for PVC. Dyed fabrics were washed in boiling water containing ABS.

2.6 Tensile strength

Tensile strength of yarns were measured by an Imada SV-55-0-20-M tester; full scale 0-20 kg, tensile rate 20 mm/min., specimen length 48 mm, and length of the part pinched by clamps 10 mm from both edges of a specimen. The tensile strength was measured with one yarn of PP or three yarns of PVC.

3. RESULTS AND DISCUSSION

3.1 Grafting

When PP or PVC fabrics were treated with ozone, hydroperoxyl groups (-O-O-H) are considered to be formed, which are converted into carbonyl or hydroxyl groups on the polymer chain. In IR spectra of ozone oxidized PP, strong absorption band due to stretching vibration of carbonyl group is observed at around 1710 cm⁻¹. In order to estimate the amount of carbonyl groups, the intensity ratio of the absorption at 1710 cm⁻¹ to that at 1167 cm⁻¹ which is due to -CH-CH₃ structure in the polymer was calculated for the IR spectra of PP oxidized for various times. Figure 1 gives the result. The amount of the carbonyl groups in PP increased linearly with oxidation time.

![Figure 1](image-url)

Fig. 1 Ratio of area of absorption at 1710 cm⁻¹ to that at 1167 cm⁻¹ in IR spectra of PP treated with ozone as a function of the treatment time.

IR spectra of PP, ozone treated PP (OPP) and MMA grafted PP are given in Figure 2. In the spectrum of MMA grafted PP, a very strong absorption is observed at 1738 cm⁻¹, which is due to the stretching vibration of carbonyl group in carbomethoxy group of MMA in the treated PP. The other absorptions based on MMA graft polymer are seen around 750, 1040 and 1150 cm⁻¹. Grafting (%) of MMA onto PP was 16.8%.
IR spectra of PVC, ozone treated PVC for 1 hr, and MMA grafted PVC are given in Figure 3. A small absorption peak at around 1736 cm⁻¹ suggests that the original untreated PVC was oxidized a little before the treatment. The PVC treated with ozone for 1 hr gives a small peak at around 1736 cm⁻¹, which shows that the PVC fabric was not so much oxidized. In the spectrum of the PP treated with oxidation and grafting, absorptions due to graft MMA polymer are seen at 1738, 1450, 1150, and 750 cm⁻¹ etc. In the grafting of MMA onto PVC, grafting (%), total conversion and grafting efficiency were 31.9%, 48.0% and 3.3%, respectively.

Thus, the graft copolymerization of MMA is regarded to be made by the successive processes of ozone oxidation and UV irradiation. As is shown in IR spectra, PVC was not oxidized so much with ozone. But, the grafting (%) of MMA onto PVC is higher than that onto PP. The UV irradiation on PVC seems to make radicals easily which initiate the graft copolymerization of MMA on the polymer chain.

Figure 4 gives the scheme considered for the grafting of MMA onto PP by the present treatments.

3.2 Tensile strength

Tensile strength of untreated and treated fabrics are summarized in Table 1. The PP treated with ozone decreased its strength, compared with the untreated PP. This suggests that some of polymer chains of PP are broken by the oxidation. As the strength of MMA grafted PP increased considerably compared with the OPP, graft polymer layer on the surface of PP is considered to enhance the strength of PP. On the other hand, PVC was strengthened by the oxidation. This reason cannot be explained at present. The strength of MMA grafted PVC was slightly smaller than that of OPPVC. The UV irradiation seems to cause some decomposition of polymer chains of PVC. It is possible to carry out the graft copolymerization of MMA onto PP by only the ozone treatment to some extent. But, in this case, the strength of resulting grafted fabrics seems too small to be used in practice. The grafted PP or PVC obtained in the present treatments seem to
have enough strength for fabrics of practical value. Further investigations are necessary to know the best experimental conditions for the preparation of grafted fabrics having large strength.

\[ \text{CH}_2\text{CHCH}_2\text{CHCH}_2\text{CH} \]  
Ozone treatment

\[ \begin{array}{c} \text{OH} \\
\text{CH}_2=\text{CCH}_3\text{COOCH}_3 \\
\text{UV irradiation} \\
\end{array} \]

\[ \begin{array}{c} \text{(CH}_2\text{C}_3\text{O}_3\text{H})_m \text{H} \\
\text{COOCH}_3 \\
\text{MMA grafted PP} \\
\end{array} \]

**Fig. 3** IR spectra of untreated PVC (PVC), ozone treated PP (OPVC) and MMA grafted PVC (MMA graft PVC).

**Fig. 4** Scheme of the reaction in the treatments of poly(propylene) fabrics with ozone oxidation and graft copolymerization of MMA by UV irradiation.
### Table 1 Tensile strength of untreated and treated fabrics

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Tensile strength (g/d)</th>
<th>Fabric</th>
<th>Tensile strength (g/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>6.18</td>
<td>PVC</td>
<td>3.73</td>
</tr>
<tr>
<td>OPP</td>
<td>5.47</td>
<td>OPVC</td>
<td>4.23</td>
</tr>
<tr>
<td>MMAGPP*3</td>
<td>6.06</td>
<td>MMAGPVC*2</td>
<td>3.53</td>
</tr>
</tbody>
</table>

*3 MMA grafted PP, *2 MMA grafted PVC.

### 3.3 Dyeing

Dyeing experiments were carried out on PP, OPP and MMA grafted PP or PVC, OPVC and MMA grafted PVC with a disperse dye, Dianix Blue AC-E. As a reference, a polyester (polyethylene terephthalate) fabric was put in the dyeing system. MMA grafted fabrics were dyed deeply and the fastness of dyeing was high enough for a practical use, but OPP and PP were not dyed deeply. Polyester was dyed in the deepest color among the fabrics.

Similar dyeing was made for PVC, OPVC and MMA grafted PVC. These three fabrics were dyed well. But, MMA grafted PVC was dyed rapidly in the deepest color. The fastness of dyeing was also high enough for a practical use. This improvement in the dyeing property is due to the layer of MMA graft polymer on PP or PVC fabrics. The disperse dye used here can diffuse into the graft polymer layer swollen by the carrier, similarly to the dyeing of polyester by usual disperse dyes.

### 4. CONCLUSION

Successive treatments of ozone oxidation and UV irradiation were very effective for the graft copolymerization of MMA onto PP or PVC fabrics. The resulting grafted fabrics gave a little decrease in the tensile strength, but showed the high dye uptake in the dyeing with a disperse dye. Further investigations will prepare poly(olefin)s with well improved properties.

### References

5) F. Ide, Kobunshi-Kako, 24, 192 (1975).