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# Reactive Polyolefine

## 2. Properties of Propylene-Methyl-1,4-Hexadiene Copolymer

**Sadao Kitagawa**[1], **Isao Okada**[1] **and Ryoichi Itoh**[2]

[1] Central Research Laboratory, Mitsubishi Petrochemical Co., Ltd., Ami, Ibaraki 300-03, Japan

[2] Plastics Laboratory, Mitsubishi Petrochemical Co., Ltd., Toho-cho, Yokkaichi, Mie 510, Japan

## SUMMARY

A chemical reactivity of the pendant double bond of crystalline propylene-MHD(methyl-1,4-hexadiene) copolymer has been investigated for practical applications. The adhesion property of the copolymer was much increased by a surface treatment with ozone, aq. $KMnO_4$ solution or concd. $H_2SO_4$. Several types of paints can be coated on the copolymer with or without surface treatment according to the types of paints. The copolymer is also characterized by easy cross-linking by irradiation of electron beams. The cross-linking can be conveniently applied to foaming. These properties are of great importance from a practical view point for improving the disadvantages of a conventional polypropylene.

## INTRODUCTION

Because of lack of polar groups, conventional polypropylene is unable to be coated with paints or to adhere to itself or to other materials. Much attemps have been done to improve the disadvantage of polypropylene. However, their effects are limited, and the fundamental solution remains open. For example, although flame treatment of the polypropylene surface enables coating or printing, the method is restricted to only thick moldings. Corona discharge is suitable for films and sheets, but it is unsuitable for complicated moldings. In addition, the effect of corona discharge does not remain long. Polypropylene grafted with maleic anhydride permits adhesion only in molten state.

Another disadvantage of polypropylene is a lack of cross-linking with a radical mechanism. Degradation occurs in preference to recombination of the tertiary radicals because of $\beta$-fission(1). A mixture composed of polypropylene and a cross-linking agent is utilized for cross-linking(2). The cross-linking agents are usually divinylbenzene, diallyl phthalate and triallyl isocyanurate. The reproducibility of the cross-linking, however, is inferior on account of the blooming of the agent and ununiform cross-linking. The disadvantage is brought about by insufficient solubility of the agent in polypropylene.

We have reported a new crystalline thermoplastic copolymer of propylene with MHD(3). The tensile modulus of the copolymer is in the region of a conventional polypropylene. The present paper describes some novel approaches for overcoming the disadvantages of polypropylene. These approaches are based on the chemical reactivity of the pendant double bond of the copolymer.

## EXPERIMENTAL

### Materials

Propylene-MHD copolymer was obtained according to the procedure described in the previous paper(3). Homopolypropylene was a commercial polymer. All these polymers were subjected to the tests mentioned below in the form of injection-molded sheets with stabilizers.

### Surface Treatment with Aq. $KMnO_4$ Solution

Test pieces of polymers were soaked in a saturated aq. $KMnO_4$ solution acidified with 5% $H_2SO_4$ at 15°C for one minute. The test pieces were then washed with acidic $NaHSO_3$ solution, washed with water and finally dried in air.

### Surface Treatment with Concd. $H_2SO_4$

Test pieces were soaked in a concd. $H_2SO_4$ at 15°C for 30 minutes, washed with water and finally dried in air.

### Surface Treatment with Ozone

Test pieces were exposed to air containing 34g ozone/$m^3$ for one minute.

### Adhesion

The surface-treated test pieces were adhered to each other with epoxy-resin adhesive at 80°C for 3 hours.

### Measurement of Adhesive Strength

The adhered test pieces were subjected to tensile tests during surface removal.

### Coating

Test pieces with or without surface treatment were coated with commercially available paints. The paints were acrylic emulsion(Acronal YX 2730 D; Yuka-Badische Co., Ltd., Japan), epoxy-resin paint(Eponics #3,100; Dainippon Paint Co., Ltd., Japan) and polyurethane paint(Rethane PG-60; Kansai Paint Co., Ltd., Japan). Coating was performed according to the directions of catalogues.

### Evaluation of Paintability

The coated layer was cross-cut with a blade at 1 mm intervals to make 100 checks. Each groove reached to the surface of the base sheet. A cellophane adhesive tape was stuck on the checks, and the tape was removed at a breath. The paintability was expressed as x/100, where x was the number of unremoved checks.

### Irradiation of Electron Beams

Test pieces were irradiated in air at room temperature by the electron beams generated by a cascade type accelerator (Dynamitron IEA 300-25-2; Radiation Dynamics,Ltd.). The beam energy was 2 MeV and the current was 5 mA.

### Measurement of Gel Fraction

0.5g of the irradiated test piece was extracted with boiling xylene for 24 hours. The unsoluble part of the polymer was regarded as gel fraction.

Foaming

The test pieces for foaming were injection-molded with 15 phr of azodicarbonamide as a foaming agent. The irradiated test piece was subjected to foaming by heating at 200°C for 5 minutes.

Measurement of Expansion Ratio

The expansion ratio of the foamed polymer was calculated from the apparent density.

## RESULTS AND DISCUSSION

In Table 1 and 2 are summarized the adherent strength and the paintability, respectively. High adherent strength and high paintability of the copolymer were observed. On the other hand, these properties of homopolypropylene were inferior and practically of no value.

Table 1
Adherent Strength of Propylene-MHD Copolymer and Propylene Homopolymer with Epoxy-resin Adhesive

| Surface Treatments | Adherent Strengths (Kg/15mm x 10mm) | |
|---|---|---|
| | Propylene-MHD Copolymer*1 | Propylene Homopolymer |
| Ozone | >50*2 | 7.3 |
| Aq. $KMnO_4$ | >50*2 | 1.0 |
| Concd. $H_2SO_4$ | >50*2 | 1.0 |

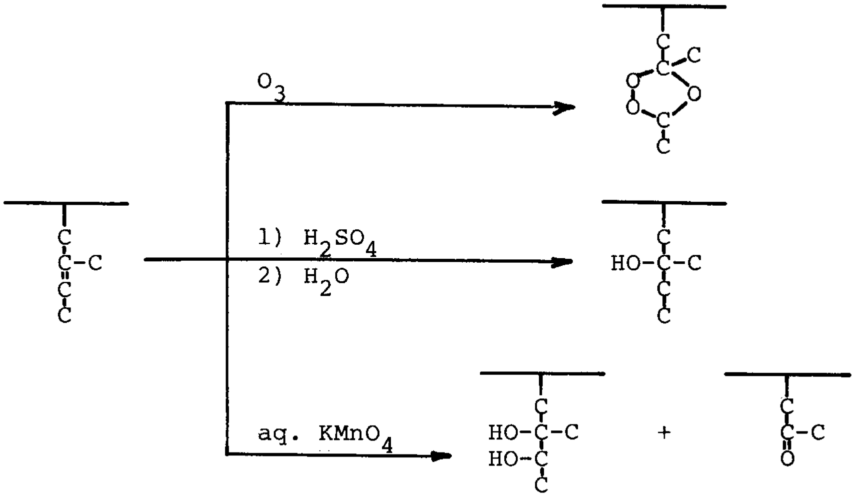
*1 MHD content: 8.4 mol%
*2 Adhered until test pieces were broken

Table 2
Paintability of Propylene-MHD Copolymer and Propylene Homopolymer

| Paints | Polymers*1 | Paintabilities*2 Surface Treatments | | |
|---|---|---|---|---|
| | | None | Aq. $KMnO_4$ | Ozone |
| Acrylic Emulsion | A | O | x | O |
| | B | x | x | x |
| Epoxy-resin Paint | A | O | O | O |
| | B | x | x | x |
| Polyurethane Paint | A | x | O | O |
| | B | x | x | x |

*1 A: Propylene-MHD copolymer; B: Propylene homopolymer
*2 O: 100/100; x: 0/100

These properties of the copolymer are regarded to be based on the polar groups. The polar groups are considered to be formed on the pendant unsaturation of the copolymer by surface treatments.



It is of interest to note that the copolymer can be coated with an acrylic emulsion or an epoxy-resin paint without surface treatment(Table 2). The paintability can be explained by a small amount of polar groups, which may be formed on the pendant unsaturation of the copolymer at the injection-molding conditions.

Another feature of the copolymer is the easy cross-linking by irradiation of electron beams(Figure 1). Irradiation on the copolymer with dose of only 5 Mrad gave 74% of gel fraction. The results reveal that the pendant radicals which are produced by irradiation are coupled with each other.

In contrast, homopolypropylene did not give any gel fraction even with dose of 20 Mrad. Furthermore, the melt flow rate of homopolypropylene changed from 7 to 250 g/10min by irradiation. The results indicate that irradiation leads to a degradation of homopolypropylene.

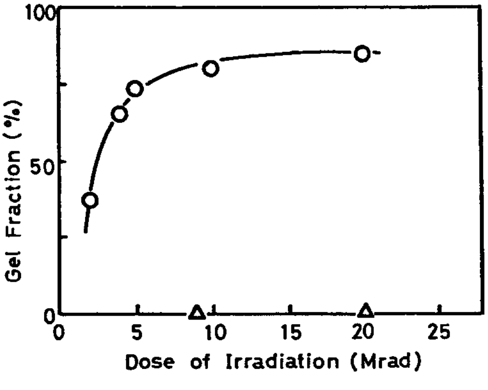


Figure 1. Gel fraction by irradiation of electron beams

○: Propylene-MHD copolymer
△: Propylene homopolymer

The cross-linking property of the copolymer can be applied to foaming. In Figure 2 is shown the relationship between expansion ratio and gel fraction. Adequate gel fraction is in the region of about 40 to 60%. Lower gel fraction is unsuitable, because low melt tension causes fracture of foams. Higher gel fraction, on the other hand, is also inadequate, because melt tension is too high to expand for foams.

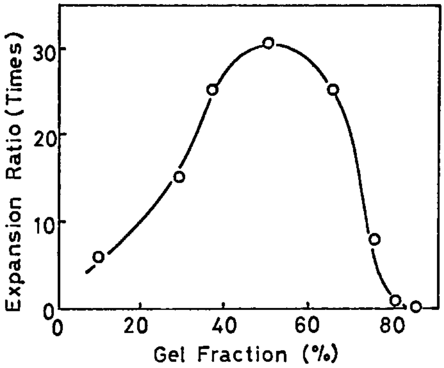


Figure 2. Expansion ratio vs. gel fraction of irradiated propylene-MHD copolymer(15 phr of azodicarbonamide)

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REFERENCES

1. A.R. Robinson, J.V. Marra and L.Amberg, Rubber Chem. & Technol., 35, 1083(1962).
2. Toyo Rayon Co., Ltd., Japan. Pat. 70 41,098(1970).
3. S.Kitagawa and I.Okada, This bulletin, in press.

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