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A new method for preparing high impact polypropylene and polyethylene

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Summary

The impact strength of polypropylene was improved by adding propylene-vinylsilane copolymer(PVS) in the presence of tris(triphenylphosphine)rhodium chloride(TPR). The impact strength of polyethylene at low temperature was also improved by adding TPR and PVS which is brittle at low temperature. These phenomena were not observed when polymers were mixed without TPR.

Introduction

Polypropylene has a good stiffness but low impact strength at low temperature. To improve the impact strength of polypropylene ethylene-propylene copolymer was added or ethylene and propylene were copolymerized after the polymerization of propylene. Adding ethylene-propylene copolymer is very effective in improving impact strength but stiffness deteriorates because the ethylene-propylene copolymer has high impact strength but low stiffness.

We propose a new method for improving the impact strength of polypropylene in this report.

Experimental

A polypropylene-vinylsilane copolymer was prepared in the same way as previously reported(1). The xylene insoluble fraction(XIF) was measured by extracting the mixed polymer in 400 mesh wire using boiling xylene for six hours.

Two types of polypropylene were used, the first type is propylene homopolymer(PHP), the second type is propylene-ethylene block copolymer(PBC) prepared by first polymerizing propylene and then copolymerizing ethylene-propylene in a second step.

The first type of polypropylene used in this experiment was Mitsui Norblen JHH-G sold by Mitsui Toatsu Chemicals INC.(MFI at 503K is 8.0 g/10 min), and containing phenolic antioxidant. The isotactic pentad fraction observed by ^{13}C-NMR is 0.935. The second type of polypropylene was Mitsui Noblen BJHH-G sold by Mitsui Toatsu Chemicals, INC.(MFI at 503K is 8.2 g/10 min, ethylene content 8.5 wt%), and containing phenolic antioxidant.

The high density polyethylene(HDPE) was Nisseki Staflen E750(C) sold by Nihon petrochemicals, INC(MFI at 463K is 5.3g/10 min, and density is 0.963g/cm^3) was used as purchased.

High impact polypropylene and polyethylene were prepared by mixing PVS pellets, the catalyst master pellets and PHP, PBC or HDPE pellets and molding. The catalyst master pellets were prepared by mixing TPR with PHP, PBC or HDPH for preparing high impact PHP, PBC or HDPE respectively.

The TPR contents of the master pellets is 1 wt%.

The mechanical properties are measured on injection molding sheets. The injection molding sheets were prepared using an injection molding machine(Komatsu Manufacturing Co., FKS-55) having an inline screw:D=25 mm and L/D=4.6. The molding and mold temperature are 603 and 323K for PHP and PBC, and 563 and 323K for HDPE, respectively. ASTM tests D638, D638, D747, D790, and D256 were used for evaluating the mechanical properties, yield strength, elongation at break, flexural rigidity of elasticity, flexural strength of elasticity and Izod impact strength, respectively.

Differential scanning calorimetry(DSC) was measured at heating and cooling rates of 10K/min under a nitrogen atmosphere using a Perkin Elmer model 4. Transmission electron microscope(TEM) photographs were made using an electron microscope H-300(Hitachi Manufacturing Co.). Wide angle X-ray scattering(WAXS) measurements were performed using Ni-filtered Cu-Kα radiation generated from a RAD-2C(Rigaku Denki Co. Ltd.,Japan).

RESULT AND DISCUSSION

Table 1 shows the physical properties of the injection molding sheets of PHP and its mixtures. Run No. 3 is the mixture of PHP and TPR. No reaction occurred on mixing PHP and TPR, and the physical properties of the mixture were the same as that of PHP. The physical properties were improved a little by mixing PVS as shown as Run No. 4. The improvement found by mixing PVS with PHP was due to PVS acting as nucleating agent. Addition of the crosslinking catalyst TPR to the mixture of PHP and PVS results in the crosslinking of PVS and PVS with PHP as shown as Run No.5(2). By using a crosslinking catalyst the physical properties of both stiffness and Izod impact strength are improved. The physical properties are improved by increasing the weight fraction of PVS. Yield strength and flexural stiffness are not further improved when the weight fraction of PVS is over 3 weight %, but the impact strength especially at 296K increases with PVS weight fraction. When PVS was used alone, the physical properties were almost the same as that of Run No. 7 containing 17 weight fraction PVS.

Table 1

RUN NO.	wt fraction			XIF wt%	Yield Strength MPa	Elongation at break %	Flexural rigidity MPa	Flexural strength MPa	Izod impact strength J/m		Crystallinity	
	PVS wt%	PHP wt%	TPR ppm						296K	263K	①[1]	②[2]
1	0	100	0	0	36.0	720	1295	32.3	28.4	16.7	56	44
2	100	0	0	0	38.3	492	1540	40.3	96.2	30.4	59	50
3	0	100	500	0	36.1	720	1295	32.4	28.4	16.7	56	43
4	1	99	0	0	37.8	680	1354	34.3	29.4	17.7	58	47
5	1	99	500	1	39.7	522	1579	39.4	44.1	26.5	60	51
6	3	97	500	4	42.2	439	1903	44.7	51.0	20.6	63	56
7	17	83	500	44	42.7	434	1893	44.6	82.4	27.5	68	55
8	100	0	500	98	43.9	100	1854	43.7	88.3	24.5	65	54

①:calculated from densities
②:calculated from XRD

Table 2 shows the physical properties of PBC and its mixtures. The effect of addition of PVS and TPR is the same as that of PHP. Increasing the weight fraction of PVS improves yield strength, flexural stiffness and Izod impact strength. In this case improvement of Izod impact strength at 296K is small, but that at 263K was enormous.

Table 2

RUN NO.	wt fraction			XIF wt%	Yield Strength MPa	Elongation at break %	Flexural rigidity MPa	Flexural strength MPa	Izod impact strength J/m	
	PVS wt%	PBC wt%	TPR ppm						296K	263K
9	0	100	0	0	28.4	659	1050	26.6	86.3	37.3
10	1	99	500	2	31.1	614	1275	30.8	90.2	51.0
11	3	97	500	3	32.6	614	1363	32.6	96.1	58.8
12	17	83	500	24	34.2	360	1491	35.3	109.8	66.7

Table 3 shows the physical properties of HDPE and its mixtures. In this case, the yield strength and flexural stiffness of PVS and crosslinked PVS are better than those of HDPE and the Izod impact strength of PVS and crosslinked PVS is smaller than that of HDPE. However, the yield strength of the crosslinked mixtures of PVS and HDPE is the same as that of HDPE, and flexural stiffness of the mixture is better than that of HDPE. Also the Izod impact strength of the mixture is better than that of HDPE.

Table 3

RUN NO.	wt fraction				XIF wt%	Yield Strength MPa	Elongation at break %	Flexural rigidity MPa	Flexural strength MPa	Izod impact strength J/m		Crystallinity by XRD %
	PVS wt%	PHP wt%	HDPE wt%	TPR ppm						296K	263K	
13	0	0	100	0	0	27.4	591	902.5	18.8	92.2	78.5	59
14	0	0	100	500	0	28.0	659	873.1	18.7	87.3	76.5	60
15	2	0	98	500	2	27.4	551	853.5	18.2	115.7	104.0	59
16	0	7	93	500	0	27.4	680	892.7	18.7	89.2	79.4	59
17	7	0	93	500	4	27.6	496	794.6	17.8	155.9	128.5	60
18	24	0	76	500	65	31.7	31	657.3	15.3	377.6	241.3	

The PVS used in this study is a high crystalline copolymer(3), and the crosslinked PVS is also crystalline as shown in Table 1 and Fig. 1. It is reasonable to assume that combining PVS whose stiffness and impact strength are better than those of PHP with another crystalline polymer will improve the stiffness and impact strength. Without catalytic crosslinking the combination improves stiffness but affects impact strength very little. However, mixing and crosslinking of PVS improves not only the stiffness but also the impact strength.

In the case of PHP, the value of stiffness and Izod impact strength are almost the same as that of crosslinked PVS when a small fraction of PVS was used.

In the case of PBC, the value of stiffness is worse than that of crosslinked PVS, but the impact strength of the mixture is better than that of both PBC and PVS.

In the case of HDPE, the values of the stiffness of the mixture are worse than both HDPE and crosslinked PVS. The values of impact strength of the mixture, however, are better than that of both PVS and HDPE.

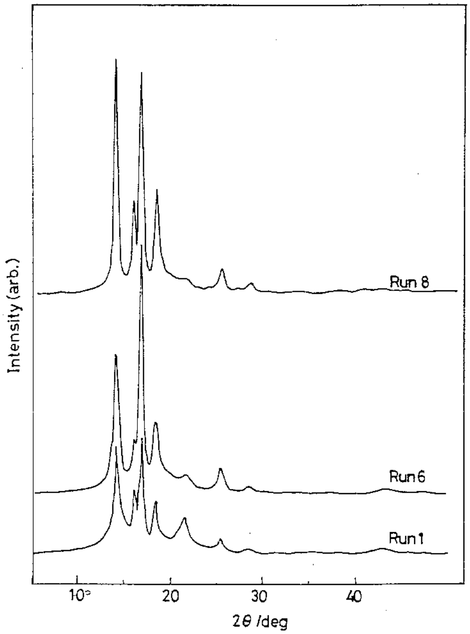

Fig.1 WAXS patterns of Run 1,6 and 8.

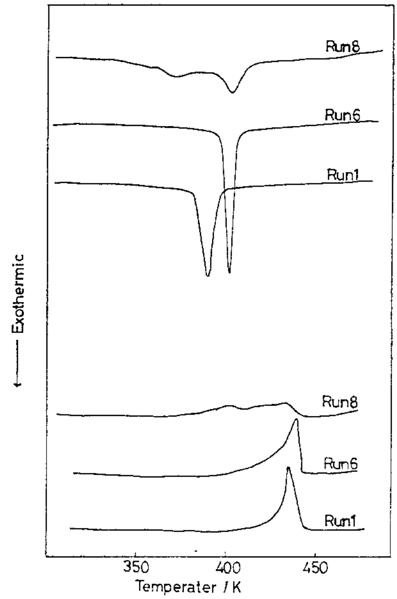

Fig.2 DSC diagram of Run 1,6 and 8

Fig.1 shows the WAXS patterns of Run 1, 6 and 8. The WAXS patterns show that the crystallinity of Run 8 was very high.

Fig.2 shows the DSC curves of the same samples. The crystallization and melting temperatures of Run 6 are higher than those of Run 1(PHP). However, the crosslinked PVS(Run 8) shows broad curves, and these data suggest that the usual crystallization or melting of the crystalline polypropylene was no longer observed.

The TEM photographs of Run 1, 2, 7 and 8 are shown in Fig. 3 to Fig.6. The length of the lamella of PVS is very long compared with that of PHP. The lamella length of the crosslinked PVS or the crosslinked mixture is thick compared with uncrosslinked ones, and the numbers of lamellae are greater than that of uncrosslinked ones.

The reason is unclear, but improving the stiffness of the mixture depends on high crystallinity of the mixture. Improving the impact strength depends on having the numerous large lamella which are characteristic of PVS or a high polymer molecular weight by crosslinking.

References
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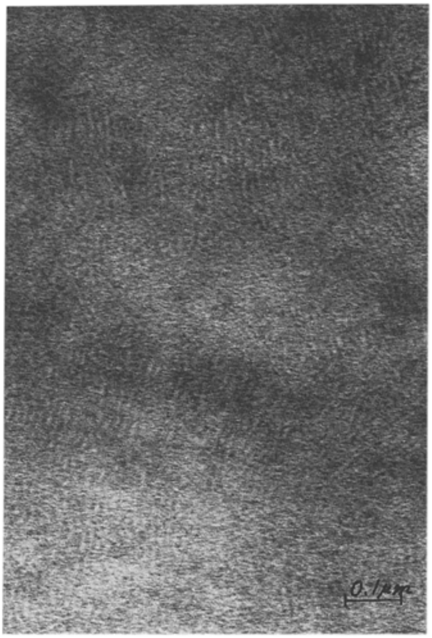

Fig.3 TEM photograph of Run 1.

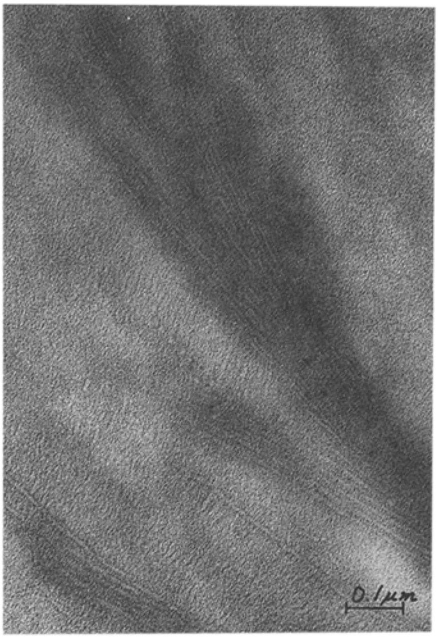

Fig.4 TEM photograph of Run 2

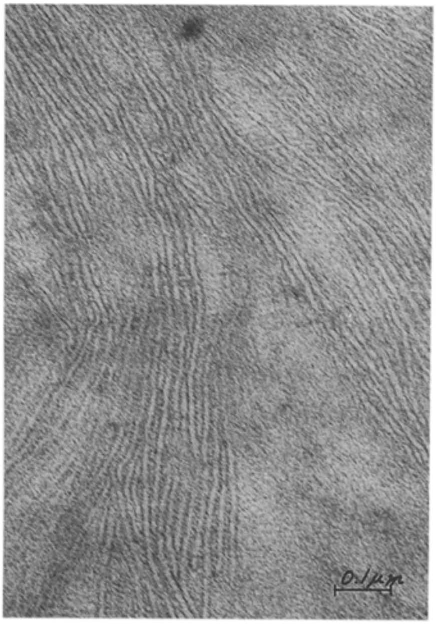

Fig.5 TEM photograph of Run 7

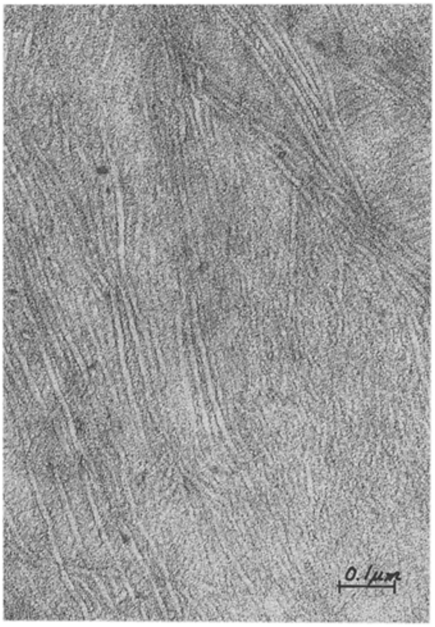

Fig.6 TEM photograph of Run 8

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