Melt Fracture Behavior of Polypropylene-Type Resins with Narrow Molecular Weight Distribution. II. Suppression of Sharkskin by Addition of Adhesive Resins

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ABSTRACT: Standing on a hypothesis that the sharkskin of a polymer with a narrow molecular weight distribution at extrusion processing originates from a stick-slip of the polymer at the die wall, the suppression of the sharkskin was tried by means of suppressing the slip by the addition of adhesives. To polypropylene (PP)-type resins with narrow molecular weight distributions such as a PP-type thermoplastic elastomer, PER and a controlled rheology PP were added small amounts of adhesives such as maleated PP, maleated PER, reactive polyolefin oligomers, ethylene/ethylacrylate/maleic anhydride (MAH) copolymer, ethylene/vinyl acetate copolymer, and styrene/MAH copolymer, and their melt fracture behaviors at capillary extrusion were observed. It was found that the sharkskin of the PP-type resins with narrow molecular weight distributions was suppressed by the addition of the adhesive resins with good adhesion to metal. The suppressive effect of the sharkskin was generally the more remarkable by the higher loading of the adhesives with the higher MAH content. This is the direction of increasing adhesion. From this fact, it was assumed that the sharkskin of the PP-type resins with narrow molecular weight distribution does not originate from a periodic growth and relaxation of tensile stress at the extrudate surface but from a stick-slip at the die wall. Based on this mechanism, it may be said that the sharkskin can be suppressed by both ways of directions of promoting and suppressing the slip at the die wall. The former way is the previously known method, and the latter way is the method proposed in the present study. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2120–2127, 2002

Key words: poly(propylene); adhesives; extrusion; melt; fracture

INTRODUCTION

Polypropylene (PP)-type resins with narrow molecular weight distribution, such as PP-type thermoplastic elastomer PER[1–3] and controlled rheology PP (CRPP) made by peroxide degradation of high molecular weight PP, have a problem of easy generation of sharkskin at extrusion. In the pre-

vious article,[4] the occurrence of skin roughness in PER and CRPP at extrusion was investigated with a capillary rheometer in a shear rate range of 12–6100 s^{-1} and a temperature range of 180–280°C, comparing with a homo PP (HPP) and a block PP (BPP) with usual molecular weight distributions. The following results were obtained.

HPP and BPP with usual molecular weight distributions show smooth extrudates at low shear rates and abruptly generate severe skin roughness "elastic failure" originated at the die entrance at a higher shear rate. PER and CRPP

Table I   Characteristics of Adhesives

Sample Code	Adhesive Name	Grade Name	Manufacturer	Content
EVA	EVA	Sumika EVA	Sumitomo Chemical Co., Ltd.	Ethylene/Vinyl Acetate Copolymer VA = 7.5 wt %, MFI = 2 g/10 min, ρ = 0.93 g/cm^3, Pellets
EEA-MAH	Bondine	TX8030	Sumitomo Chemical Co., Ltd.	Ethylene/Ethylacrylate/Maleic Anhydride Copolymer EA= 15 wt %, MAH = 3 wt %, MFI = 3 g/10 min, ρ = 0.94 g/cm^3, Pellets
MPP-1	MAH-PP	AD89G	Tokuyama Corp.	Maleated PP MAH = 0.5 wt %, MFI = 50 g/10 min, Pellets
MPP-2	MAH-PP	PH-200	Honan Petrochemical Corporation	Maleated PP MAH = 5.2 wt %, T_m = 151°C Powder
MPER	MAH-PER		Tokuyama Corp.	Maleated PER MAH = 1.7 wt %, MFI = 80 g/10 min, Pellets
RPOO-1	Umex	1001	Sanyo Chemical Industries Ltd.	Reactive Polyolefin Oligomer MAH = 2.3 wt %, ρ = 0.95 g/cm^3, MW = 15,000, η(160°C) = 16 Pa · s, Pellets
RPOO-2	Umex	1010	Sanyo Chemical Industries Ltd.	Reactive Polyolefin Oligomer MAH = 4.6 wt %, ρ = 0.95 g/cm^3, MW = 700, η(160°C) = 7 Pa · s, Pellets
SMAH	SMA Resin	SMA 1000	Elf Atochemi North America Inc.	Styrene/Maleic Anhydride Copolymer Styrene/MAH Ratio = 1/1, MW = 1600, Powder

with narrow molecular weight distributions are easy to generate "sharkskin" melt fracture originated at the die exit from a shear rate nearly one decade lower than those of elastic failure of HPP and BPP. The sharkskin becomes more severe with increasing shear rate, and attains to the elastic failure. The critical shear rate at which sharkskin occurs increases with increasing extrusion temperature. The critical shear rate is about 20 s^{-1} at 180°C, and about 120 s^{-1} at 280°C, which is in the range encountered by the molten resin at extrusion processing.

Two types of theories are proposed for the mechanism of sharkskin. One is based on the stick-slip at the die wall,[5–11] and the other is based on the periodic growth and relaxation of tensile stress at the extrudate surface at the die exit.[12–21] The following methods to suppress the sharkskin are known: (1) increasing the resin temperature;[12,13,22,23] (2) decreasing only the die part temperature;[13,24,25] (3) choosing the die material;[5,11] (4) fluorinating the die wall,[20] coating the die wall with Teflon[10] and fluorocarbon elastomer,[19] and coating the die exit part

$\dot{\gamma}\,(s^{-1})$ 12.2 24.3 60.8 122 243 608 1220 2430 6080

Content (wt%)

0

1

3

5

10

20

30

5 mm
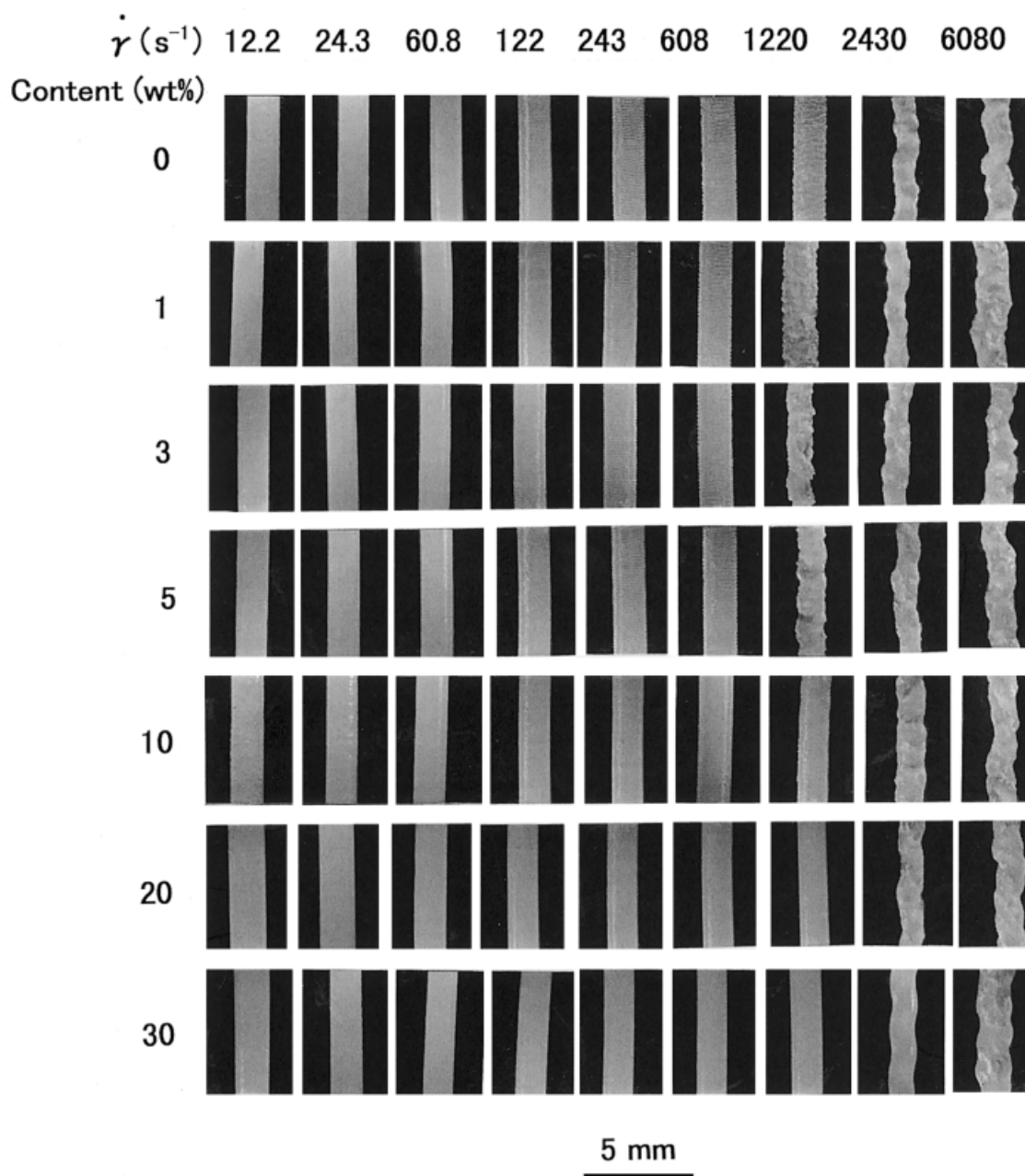
(a)

Figure 1   (a) Effect of MPP-1 content and shear rate on surface state of PER extrudate. (b) Effect of SMAH content and shear rate on surface state of PER extrudate. (c) Effect of MPP-1 content and shear rate on surface state of CRPP extrudate.

with soap water;[21] (5) broadening the molecular weight distribution of the resin;[9,13,23,26,27] (6) decreasing the molecular weight of the resin;[23,26] and (7) adding to the resin external lubricants such as fluorocarbon elastomer,[5,28–30] silicone,[29,31] hyperbranched poly-mer,[32] and boron nitride[33,34] to promote the slip of the resin at the die wall. For the method of adding the resin external lubricants such as fluorocarbon elastomer, there are drawbacks that an incubation time of up to 1 h is needed until the effect appears after the start of extru-
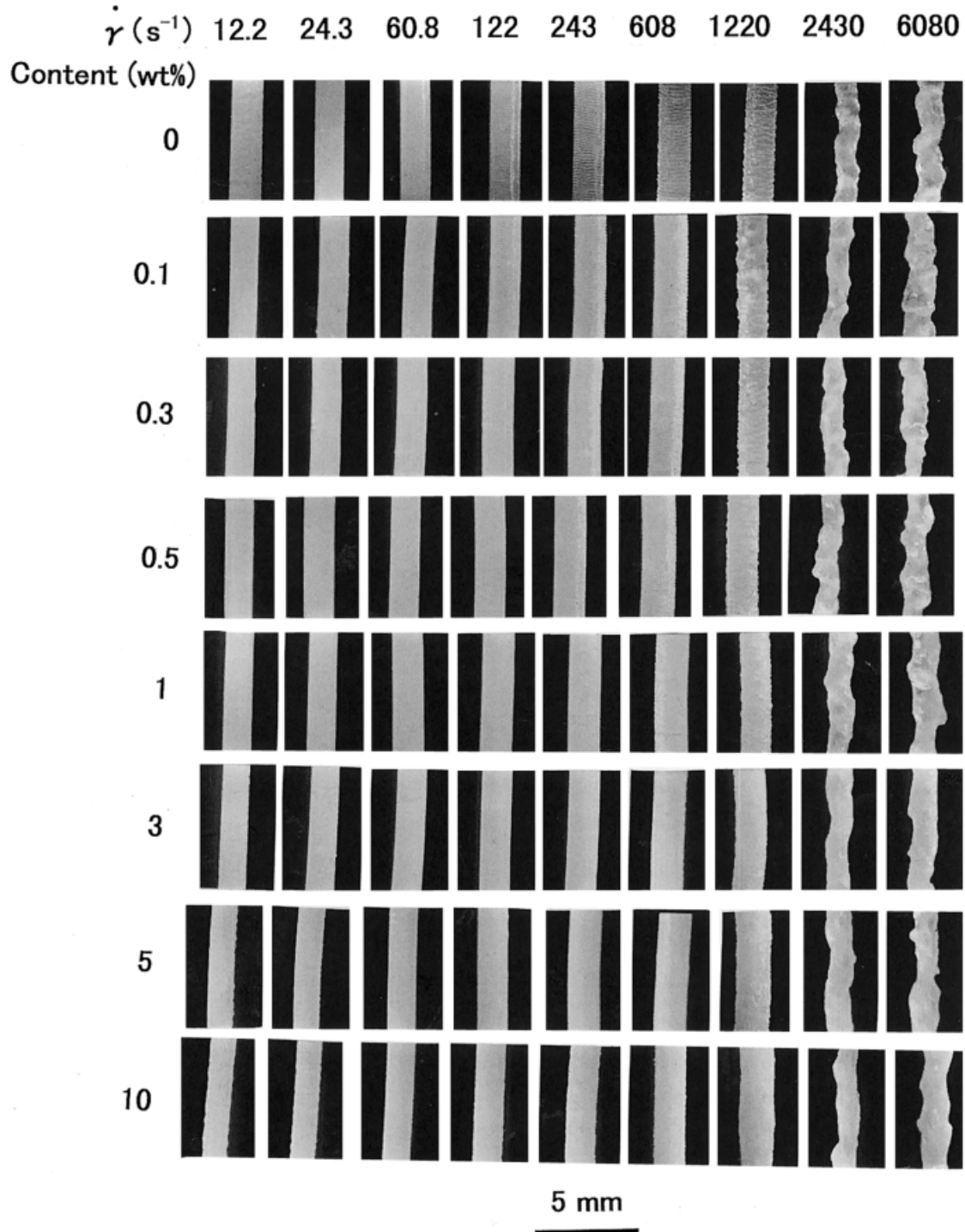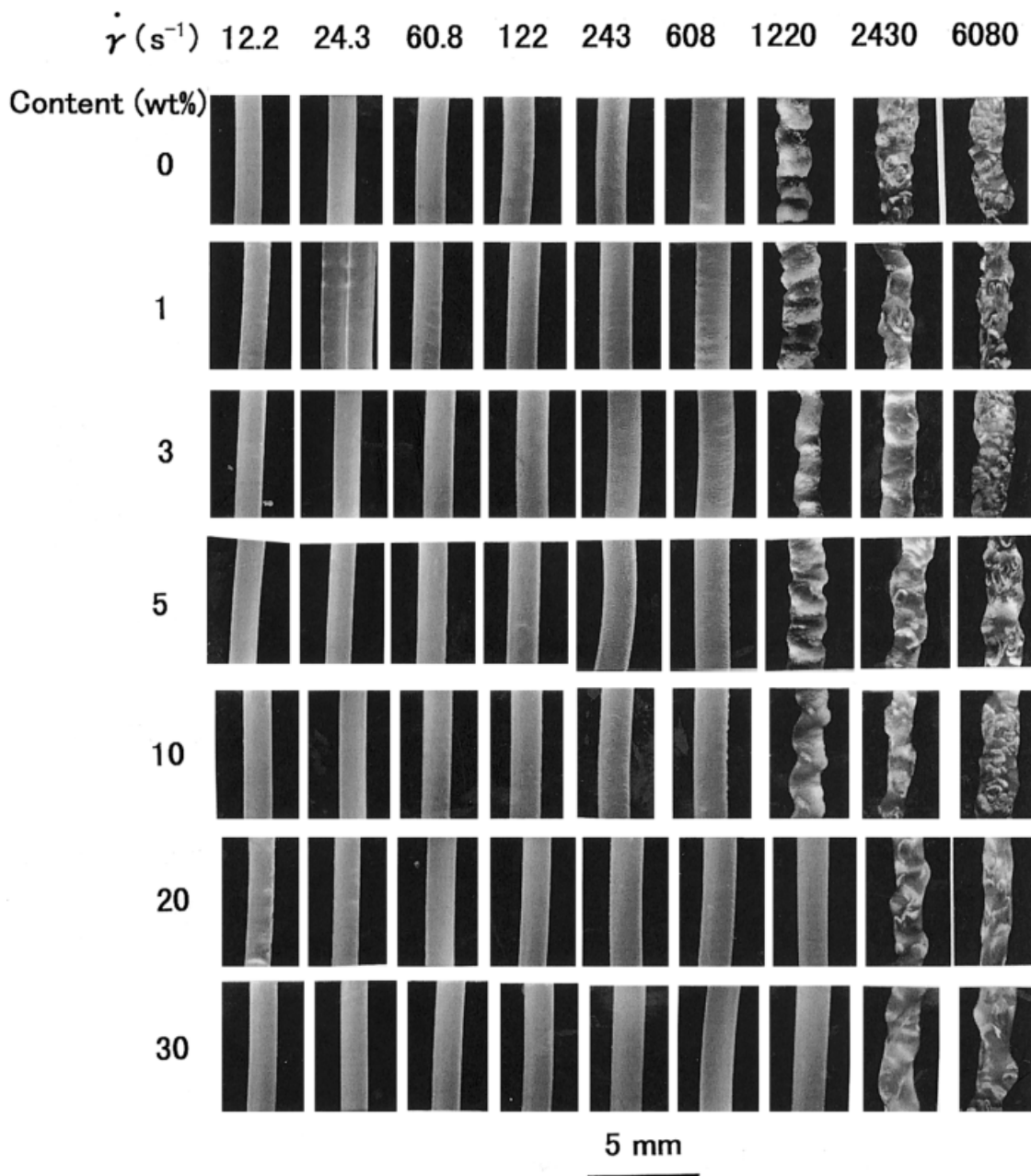
Figure 1   (*Continued from the previous page*)

sion and that a time to exchange the resin in the extruder after extrusion is needed.[5,30] Furthermore, there are also drawbacks of whitening of the extrudate and of bleeding of the lubricant on the extrudate surface. The methods of adding external lubricants such as fluorocarbon

Figure 1   (*Continued from the previous page*)

elastomer to the resin and of coating the die wall with lubricant materials such as fluorocarbon elastomer and Teflon are based on the hypothesis of stick-slip and positively make the resin slip at the die wall. The authors inversely considered that the sharkskin may also be suppressed by stopping the slip and studied the addition of adhesives.

EXPERIMENTAL

Samples

PER used was a transparent extrusion grade P.E.R. T310E manufactured by Tokuyama Corp. For comparison, a controlled rheology PP (CRPP) was used. It was prepared by degrading an ultra
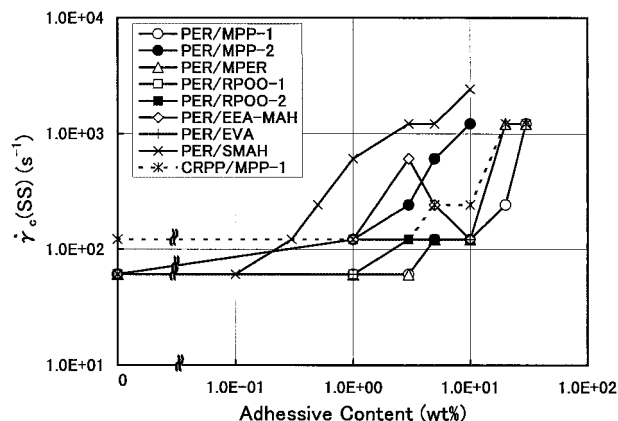
Figure 2 Dependence of critical shear rate at which sharkskin begins to occur, $\dot{\gamma}_c(SS)$, on adhesive content.

high molecular weight PP with a peroxide to form a low molecular weight and a narrow molecular weight distribution. The characteristics of these samples were described in the previous article.[4]

Eight adhesives shown in Table I were studied. Almost all of them are resins modified with maleic anhydride (MAH).

PER or CRPP was melt-mixed with the adhesives at 200°C for 5 min by use of a Brabender Plastograph (Germany).

Extrusion

Extrusion was carried out with a capillary rheometer (Capirograph 1B Type, Toyo Measurement Instruments Co. Ltd., Japan) at 240°C by use of a die with capillary length L = 10 mm, capillary diameter D = 1 mm, and L/D = 10. Extrudates were taken at shear rates of 12.2, 24.3, 60.8, 122, 243, 608, 1220, 2430, and 6080 s^{-1}.

Observation of Extrudates

The extrudates were observed with a real image optical microscope (Olympus SZH Type, Japan) under a magnification of 30× and the photographs were taken.

RESULTS AND DISCUSSION

Figure 1(a)–(c) exemplifies changes of surface state of the extrudate with adhesive content and shear rate for MPP-1-added PER, SMAH-added PER, and MPP-1-added CRPP, respectively.

Figure 1(a), which is for PER added with maleated PP (MPP-1), shows that MPP-1 takes effect

of suppressing the sharkskin from around 10 wt % and almost completely eliminates it at 30 wt %.

In the case of MPP-2, whose MAH content is about 10 times that of MPP-1, it takes effect from around 3 wt % and almost completely eliminates the sharkskin at 10 wt %. In cases of high MPP-2 contents, a skin roughness other than the sharkskin appears at low shear rates, which is supposed to originate from bubbling by moisture adsorption. Such phenomenon was observed also for MPER, RPOO-1, RPOO-2, EEA-MAH, and SMAH systems.

In the case of MPER, which is maleated PER with an MAH content of about three times that of MPP-1, takes effect from around 5 wt % and almost completely eliminates the sharkskin at 20 wt %.

Reactive polyolefin oligomers, RPOO-1 and RPOO-2, show only weak effects of suppressing the sharkskin.

Ethylene/ethylacrylate/MAH copolymer, EEA-MAH, shows a maximum effect at 3–5 wt %. It improves the clarity of PER as well.

Ethylene/vinyl acetate copolymer, EVA, shows little effect of suppressing the sharkskin below 10 wt %.

Figure 1(b), which is for PER added with a styrene/MAH copolymer, SMAH, shows that SMAH takes effect of suppressing the sharkskin from around 0.3 wt % and almost completely eliminates it at 3–5 wt %. Although SMAH takes effect of suppressing the sharkskin at low contents, it shows a drawback that the whitening of extrudate occurs at contents above 1 wt % and the bleeding of SMAH occurs at contents above 5 wt %.
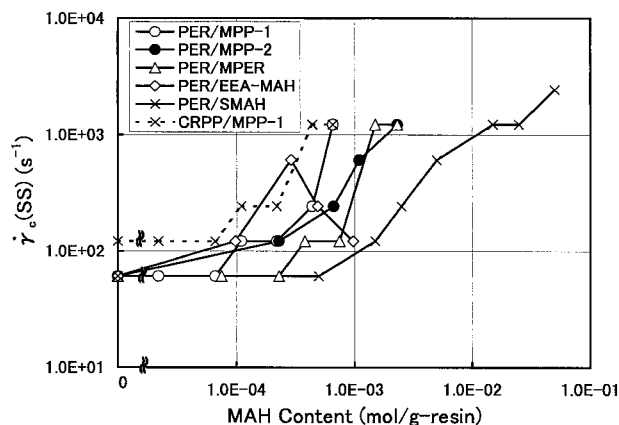

Figure 3 Dependence of critical shear rate at which sharkskin begins to occur, $\dot{\gamma}_c(SS)$, on maleic anhydride (MAH) content.

Figure 1(c), which is for CRPP added with MPP-1, shows that MPP-1 takes effect of suppressing the sharkskin from around 5 wt % and eliminates it almost completely at 20–30 wt %. Accordingly, it may be assumed that the adhesives suppress the sharkskin not only for PER but also for PP and maybe other polyolefins.

Figure 2 shows the dependence of the critical shear rate at which the sharkskin begins to occurs, $\dot{\gamma}_c$(SS), on adhesive content. Although EVA and RPOOs do not show the effect of suppressing the sharkskin, the effect is the more notable for the adhesives with the more MAH content among the adhesives that have the effect. EEA-MAH shows a maximum effect of suppressing the sharkskin at around 3 wt %, and has the effect of improving the clarity as well as the effect of suppressing the sharkskin.

Figure 3 shows the dependence of the critical shear rate $\dot{\gamma}_c$(SS) on MAH content for adhesives with remarkable effect of suppressing the sharkskin. The adhesives take effect from around 1 $\times 10^{-4}$ mol/g-resin and increase the effect with increasing MAH content except for EEA-MAH. However, the plots of $\dot{\gamma}_c$(SS) vs. MAH content do not unify into a master curve but the individual characters of adhesives remain. Generally, an adhesive with the higher MAH content locates at the higher MAH content side and its effect of suppressing the sharkskin is the smaller for its MAH content.

From experimental results above, it was found that the addition of small amount of adhesive resins with good adhesion to metal to PP-type resins with narrow molecular weight distributions suppresses the sharkskin. The suppressive effect of the sharkskin was generally the more remarkable by the higher loading of the adhesives with the higher MAH content. This is the direction of increasing adhesion. Accordingly, the sharkskin of the PP-type resins with narrow molecular weight distributions should not be regarded as to originate from a periodic growth and relaxation of tensile stress at the extrudate surface but from a stick-slip at the die wall. Based on this mechanism, it may be said that the sharkskin can be suppressed by both ways of directions of promoting and suppressing the slip at the die wall.

CONCLUSIONS

Standing on a hypothesis that the sharkskin of a polymer with a narrow molecular weight distri-bution at extrusion processing originates from a stick-slip of the polymer at the die wall, the suppression of the sharkskin was tried by means of suppressing the slip by the addition of adhesives. The following results were obtained:

1. For the maleated PP or maleated PER system, one with the more MAH content takes effect of suppressing the sharkskin of PER from the lower addition content.
2. The styrene/MAH copolymer takes the effect of suppressing the sharkskin from around 0.3 wt % and almost completely eliminates it at 3–5 wt %. However, it shows a drawback that the whitening of extrudate occurs above 1 wt % and the bleeding occurs above 5 wt %.
3. Ethylene/ethylacrylate/MAH copolymer, EEA-MAH, shows a maximum effect at 3–5 wt %. It improves the clarity of PER as well.
4. Ethylene/vinyl acetate copolymer and reactive polyolefin oligomers do not show remarkable effect.
5. Maleated PP also suppresses the sharkskin of controlled rheology PP.

From experimental results above, it is assumed that the sharkskin of PP-type resins with narrow molecular weight distribution originates from a stick-slip of the resin at the die wall.

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