

Characteristics and Applications of Sumitomo® Easy Processing Polyethylene

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Polyethylene (PE) is a commodity plastic that is widely used in products such as films, foams, containers, and pipes.

Polyethylene that is manufactured by the metallocene catalyst system (m-PE) and has a narrow molecular structural distribution has been penetrating the market mainly because of its high mechanical strength. On the other hand, this m-PE generally exhibits poor processability, so R&D has recently been focused on the development of m-PE with good processability.

Sumitomo Chemical has succeeded in the development of a new type of Easy Processing Polyethylene (EPPE) that exhibits a good balance of processability and toughness. The main features of EPPE are easy processability similar to that of high pressure-low density polyethylene (HP-LDPE) and considerably high mechanical strength. These features are mainly the result of EPPE's unique molecular structure based on long chain branching.

EPPE can be processed at low temperatures or under high output conditions because EPPE has a low kneading torque and high melt tension. In this review, we will introduce the viscoelastic features of EPPE and some applications such as high quality film, energy saving processing and high productivity which are possible because of its easy processability.

This paper is translated from R&D Report, "SUMITOMO KAGAKU", vol. 2006-II.

Introduction

Both universities and industry have been carrying out unrelenting research and development worldwide to find polyethylene materials with higher quality and higher productivity than existing materials. As a result, polyethylene materials with many different characteristics have been industrialized using various catalysts and polymerization processes, and they have been used in a wide range of applications, such as films, foams, containers, pipes and filaments. Particularly in the area of low density polyethylene technology there have been technical innovations since the discovery of high-pressure polyethylene, such as the development of tubular processes, the discovery of Ziegler-Natta catalysts, the development of gas phase processes and the discovery of metallocene catalysts. These have been industrialized and are widely used for the key resins that we currently cannot live without.^{1)–3)}

Low density polyethylene is roughly classified into high-pressure low density polyethylene (HP-LDPE)

manufactured by a high pressure polymerization process using a radical initiator, and linear low density polyethylene produced by ionic polymerization using a transitional metal catalyst. Because of its long chain branched structure, the most typical characteristic of HP-LDPE is its superior processability. Therefore, it is still being used in a wide range of applications worldwide even after more than 70 years since its discovery in 1933, and it accounts for about half of the low density polyethylene produced in the world.

On the other hand, LLDPE is a low density polyethylene that can be obtained by co-polymerization of ethylene and α -olefin using a Ziegler-Natta catalyst or a metallocene catalyst, and the variations in the primary structure typified by the comonomer short chain branching and the compositional distribution (the distribution of the comonomer among the molecules) make for variations in the higher order structure. This structure determines the mechanical strength and other physical properties in the end products.^{5)–14)} The production capacity of LLDPE has been

expanded due to its advantages of high mechanical strength and application to downsizing of films since the 1980s. Large expansions in production capacity are planned for the future, focusing on LLDPE manufactured by gas phase processes¹⁵⁾, which are superior in terms of energy costs.^{4), 16)}

Sumitomo Chemical Co., Ltd. has succeeded in developing a new Easy Processing Polyethylene (EPPE) which has superior processability. In this paper, we will introduce the basic properties and typical applications of EPPE.

Conventional Low Density Polyethylene

The relationship between mechanical strength and processability is shown in Fig. 1. HP-LDPE has greatly superior processability, but it is inferior in terms of mechanical strength. On the other hand, Ziegler-Natta catalyst-based and metallocene catalyst-based LLDPE are characterized by their superior mechanical strength.

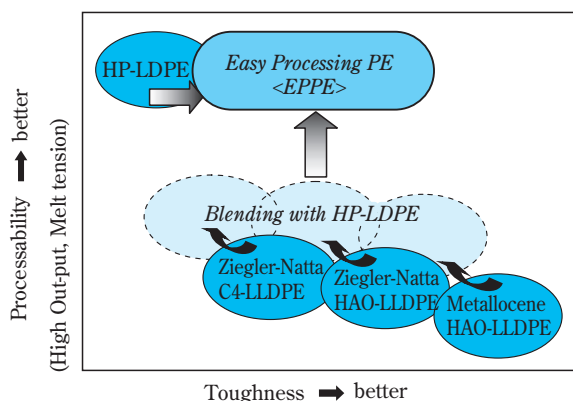


Fig. 1 Position of EPPE in various polyethylenes

Sumitomo Chemical Co., Ltd. has also made improvements in mechanical strength and film blocking properties of polyethylene in response to market needs. Of the various polyethylenes, metallocene catalyst-based LLDPE (m-LL) has a narrower molecular distribution and composition distribution than Ziegler-Natta catalyst-based LLDPE (ZN-LL). As a result, m-LL has higher mechanical strength, and it has permeated the plastics market for its merits in improving strength of films and allowing them to be made thinner.¹⁴⁾

However, since LLDPE has inferior processability, it is typically used in blends with HP-LDPE, sacrificing

the high mechanical strength of the LLDPE. When processing LLDPE alone, not only it is impossible to obtain a practical level of processability in blown film processing, which is the most typical film processing method for low density polyethylene, but also a film with good transparency cannot be obtained. Therefore, HP-LDPE must be blended to achieve good processability and high transparency.

As a consequence of this, a polyethylene material with both good processability and high mechanical strength has been desirable.

Sumitomo Chemical Co., Ltd. EPPE

EPPE is polyethylene based on new metallocene catalyst technology which Sumitomo Chemical has developed, and it has both superior processability and higher mechanical strength compared to LLDPE.^{17)–20)}

The typical structural feature of EPPE is its long branches. Because of this characteristic structure, EPPE is a polyethylene which has both extremely superior processability on a level rivaling HP-LDPE and high mechanical strength which is equivalent to ZN-LL as is shown in Fig. 1. Furthermore, EPPE can be designed over a wider density range than conventional HP-LDPE, and we expect that it will be suitable for use in developing of new applications.

Basic Properties of EPPE

We will describe the characteristics of EPPE in comparison with various other polyethylenes from the standpoint of molten viscoelasticity, melt tension and melt elongation.

1. Melt Rheological Properties

(1) Kneading Torque

The molten viscosity and the torque correspond to the load during kneading of the molten polymer are properties common to many processing methods. The lower these values are, the easier the extrusion of the molten resin is.

Fig. 2 shows the torque during melt kneading of various types of polyethylene at 60 rpm. The higher the molecular weight of the polyethylene (the lower the MFR) is, the more the torque increases. One can see that EPPE has a much lower torque than m-LL and ZN-LL with the same MFR. The torque of EPPE is lower

than HP-LDPE with the same MFR, and the extrusion properties of EPPE are very good.

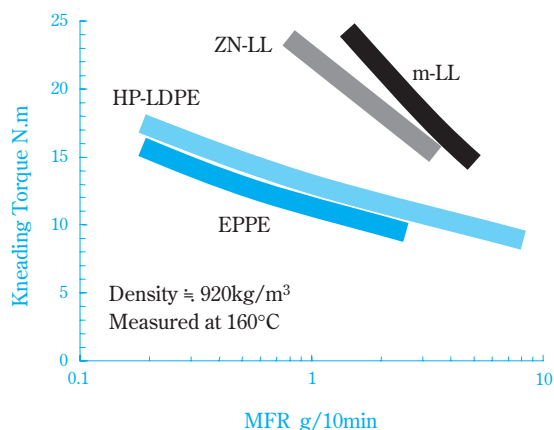


Fig. 2 Kneading torque of EPPE

(2) Dynamic Viscoelasticity

The relationship between frequency and melt viscosity η^* for dynamic viscosity measurements is shown in Fig. 3. Characteristically, the frequency dependence of η^* for HP-LDPE is high, and it is small for LLDPE.

On the other hand, EPPE greatly resembles the behavior for HP-LDPE, and its η^* changes remarkably according to frequency, and it is low in the high frequency range and high in the low frequency range. This behavior is a characteristic behavior of polymers with wide absolute molecular weight distribution.

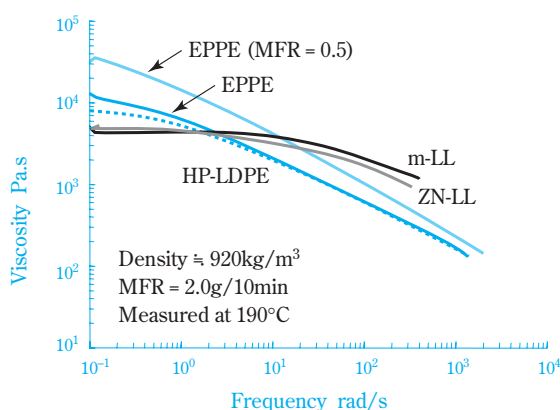


Fig. 3 Shear viscosity of EPPE

Fig. 4 shows the relationship between the dynamic storage modulus G' and the dynamic loss modulus G'' for dynamic molten viscosity measurements. A similar relationship was also obtained for static measure-

ments (first normal stress differential vs. shear stress). In the case of shearing, the ratio of the energy stored in the molecules and the energy lost depends on the molecular structure, and it shows the stress state of the molten polymer. In Fig. 4, HP-LDPE and EPPE are almost on the same line and differ from the lines for ZN-LL and m-LL. From these results, it can be seen that the molecules that constitute EPPE exhibit a response that is very similar to that of HP-LDPE under stress.

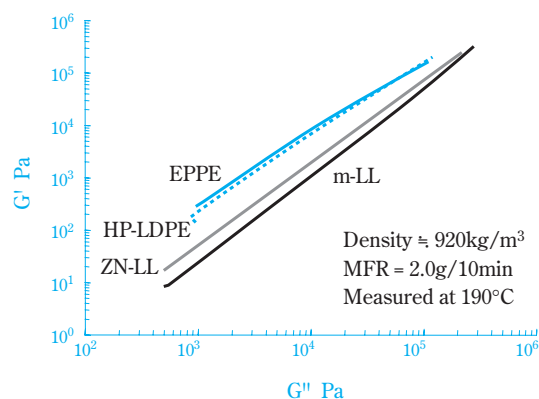


Fig. 4 Storage modulus vs. loss modulus for various polyethylenes

(3) Melt Tension

The melt tension of polyethylene is one of the melt rheological properties which indicates the ability of polyethylene to be melted and molded into films, sheets and containers or tube and pipe shapes. For example, in brown film molding, which is a typical processing method for polyethylene films, a high melt tension is necessary for carrying out stable processing. If the melt tension is small, the molten film will not

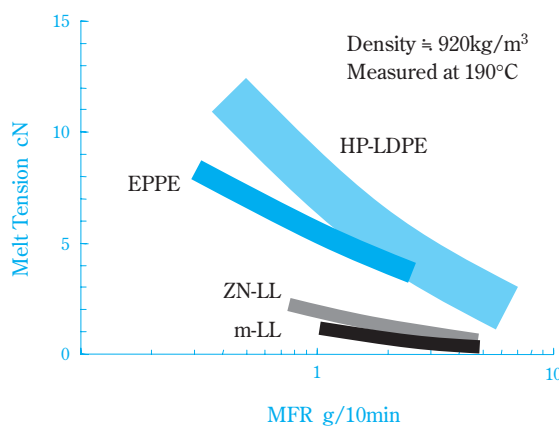


Fig. 5 Melt tension of EPPE

be drawn up properly during the drawing-up process while air is being blown into the tube-shaped molten polyethylene film, or vibration of the molten film will result, which will prevent stable processing from being carried out or will result in a film product without a uniform thickness. The melt tension of various types of polyethylene at 190°C is shown in Fig. 5. HP-LDPE exhibits a high melt tension, but on the other hand ZN-LL and m-LL exhibit extremely low melt tension values. The melt tension of EPPE is near that of HP-LDPE and is clearly higher than for these LLDPE materials.

(4) Melt Elongation

The melt elongation of polyethylene materials is a physical property that mainly determines the high-speed processability. The melt elongation is measured as the maximum take-up velocity (MTV) when a molten strand extruded from an orifice is taken up at high speed when the thread fractures. The higher the MTV value is, the better is the melt elongation.

Fig. 6 shows the relationship between temperature and MTV for various types of polyethylene. In general, polyethylene tends to have a higher melt elongation for higher temperatures. On the other hand, it is extremely interesting that EPPE exhibits a completely opposite temperature dependence to LLDPE and HP-LDPE. These results are scientifically interesting results, and they must be investigated further from various viewpoints. As can be seen from this figure, the MTV of EPPE exhibits higher values than HP-LDPE in the low temperature range. From this, it can be expected that high-speed molding at low temperatures that were difficult for conventional polyethylene materials will be possible with EPPE.

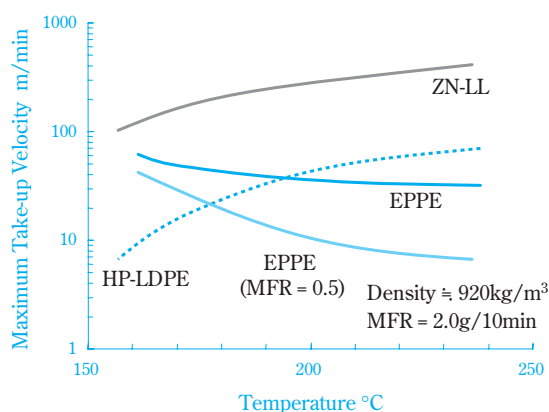


Fig. 6 Drawdown property of EPPE

2. Practical Physical Properties

(1) Impact Resistance

Fig. 7 shows the relationship between the density and the dart drop impact strength of various polyethylene films. EPPE exhibits higher impact strength than HP-LDPE, and it has an impact strength that is almost the same as ZN-LL that has a higher α -olefin (HAO), such as hexane or octene for a comonomer.

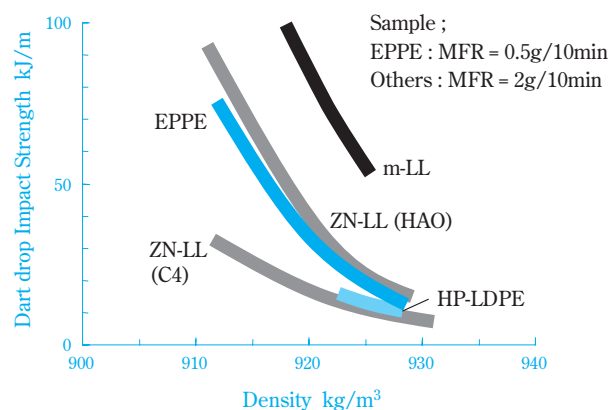


Fig. 7 Impact strength of EPPE blown film (50μm thickness)

(2) Heat Seal Property

Fig. 8 shows the heat seal properties for various types of polyethylene film. EPPE has a heat seal strength which is higher than HP-LDPE and equivalent to ZN-LL (HAO). Furthermore, there are limits for production when lowering the density of HP-LDPE, and when low temperature sealing and flexibility are necessary while maintaining processability, ethylene-vinyl acetate copolymers have been used. EPPE, with its density of 912 kg/m³, exhibits heat seal properties which are equivalent to EVA with a VA content of 5%.

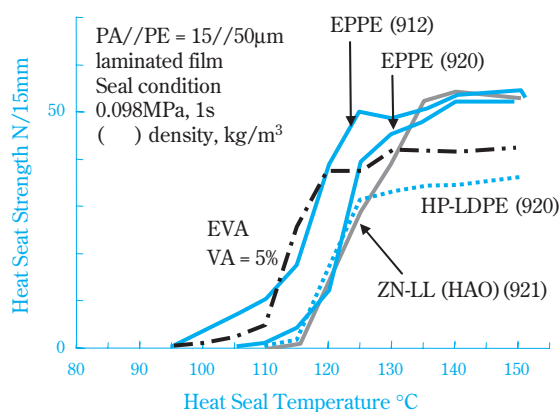


Fig. 8 Heat seal property of various polyethylenes

and the seal strength is superior to EVA.

Thus, with EPPE, it is possible to expand the density range, which was difficult with HP-LDPE, and it is possible to obtain products with superior low temperature sealing properties, superior flexibility and high strength.

(3) Environmental Stress Cracking Resistance (ESCR)

ESCR is an important physical property required mainly for containers, caps and pipes. Cracks may arise in such molded products when they are in contact with surface active agents and similar chemicals for long periods of time under a fixed stress. Under conditions of exposure to a surface active agent (IGEPAL) at a temperature of 50°C, occurrence of cracks was seen in HP-LDPE at the longest in 10 hours, but EPPE exhibited higher strength where cracks were not seen in 1000 hours or more.

These various physical properties are of a performance standard not obtained with conventional HP-LDPE, and while EPPE has a processability equivalent to HP-LDPE, it has shown itself to be a polyethylene based material with superior strength at a level not seen before.

Processability of EPPE

As has been discussed up to this point, EPPE is a superior material with a good balance between processability and strength. **Fig. 9** shows the basic concepts for development of applications using this superior processability.

Typical problems in the processing of LLDPE are high motor loads and high resin pressures. Bad appearance in the film surface and bubble stability

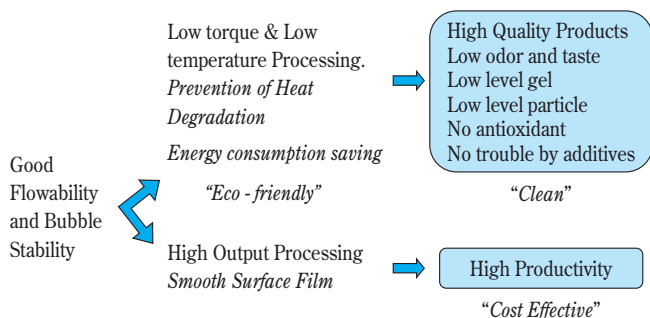


Fig. 9 Advantages of EPPE based on easy processability

failures are problems which may be caused by heat generation as a result of high shear levels and resin deterioration because of high molding temperatures. EPPE is a material that overcomes these problems because of its superior melting flow characteristics and bubble stability, and thus low temperature molding and a high output extrusion molding are possible.

1. Low Temperature Molding

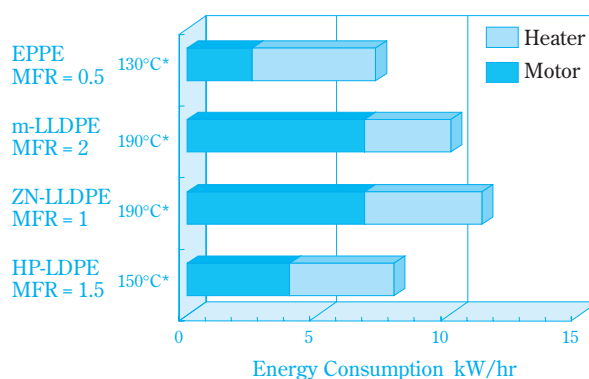
Table 1 gives the low temperature molding characteristics of EPPE in comparison with m-LL. Under conditions of a molding temperature of 150°C and a die lip gap of 0.8mm, the resin pressure and motor load with EPPE was held to approximately 1/2 that of m-LL. In terms of the appearance of the film, it was possible to mold the EPPE without the occurrence of surface roughness. In this manner, EPPE can be easily processed at low temperatures, so along with holding down resin deterioration, it is possible to reduce the amount of energy consumed.

Fig. 10 shows amount of energy consumed during

Table 1 Processability of EPPE at low temperature

		EPPE	m-LL
MFR	g/10min	0.5	2.0
Density	kg/m ³	912	912
Motor Load	Ampere	27	56
Resin Pressure	MPa	14	28
Resin Temperature	°C	153	158
Film surface		smooth	melt-fractured

Processing Conditions: 50mmφ extruder, die 125mmφ, lip gap 0.8mm, Temperature 150°C, BUR 1.8, Out put 24kg/hr, Film thickness 80μm



Condition : 55mmφ Extruder, Die 125mm, Lip gap 2mm, BUR 2.0, Output 25kg/hr, Processing temperature*

Fig. 10 Energy consumption in blown film processing

the molding of various types of polyethylene. All of the energy consumed for driving the motor and using the heater of the molding machine for heating was measured for the energy consumed during the molding process. By carrying out low temperature molding at 130°C, it was found that a 30–40% reduction in the energy consumed overall was possible with EPPE compared to LLDPE.

2. High Output Extrusion Molding (High-speed molding)

Even with high output extrusion conditions, it is possible to obtain molded products with little surface roughness using EPPE. **Fig. 11** shows the results of surface observations of strands extruded with a comparatively high shear rate range (100s^{-1}). While surface roughness was observed with m-LL, it absolutely could not be seen, and an extremely smooth surface was given with EPPE. In addition, this level is also better than that of HP-LDPE.

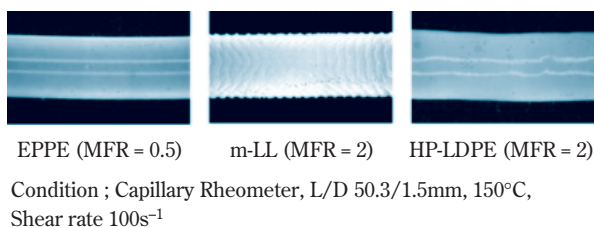


Fig. 11 Strand surface of various polyethylenes at high output condition

In the case of blown film molding, not only are the extrusion characteristics good, but also the same typical characteristics of EPPE are shown as for high-speed molding. In blown film molding, causes that can be cited for preventing increased speeds include (1) high load on the motor during extrusion, (2) the bubble becoming unstable and (3) fracturing of the molten film.

Table 2 gives the high-speed molding characteristics of various types of polyethylene. When blown film molding is carried out using LLDPE, it is typically used as a blend with HP-LDPE. Because of the molten film becoming unstable and the extrusion load increasing excessively, the molding speed limit is 80m/min with LLDPE, and with HP-LDPE, the melt elongation is small, so the limit is 70m/min because of molten film breakage. With EPPE, it is possible to raise the mold-

ing speed to 150m/min (limit value for the test apparatus) as a result of its having superior melt characteristics.

Table 2 Processability of EPPE at high output condition

	Temp. °C	Lip gap mm	Max. speed m/min	Cause of processing limit
EPPE (MFR = 1)	150	2	100	drawdown
		0.8	> 150	—
ZN-LL (MFR = 1) + HP-LDPE 20%	190	2	80	bubble stability
		0.8	< 10	motor load
HP-LDPE (MFR = 2)	170	2	40	drawdown
		0.8	70	drawdown

Processing Conditions : 55mmφ extruder, die 125mmφ, BUR 2.0,
Out put 125kg/hr (max)
Film thickness 20μm

Development of EPPE Applications

Because of its superior low temperature molding characteristics, EPPE can be expected to provide high quality products for films without additives and which do not contain antioxidants, and also for low odor and low taste films, gel free films and other similar products. In addition, for blow bottles, sheets and pipes that have conventionally used HP-LDPE because of its processability, it will be possible to increase strength and increase flexibility or rigidity while maintaining good processability by using EPPE.

In the next section, we will introduce several examples of specific applications that make use of the typical characteristics of EPPE.

1. Low Odor Films and Containers

In food packaging applications, films and containers which have little odor that is transferred from the packaging material to the food (namely the polyethylene odor and the foreign odors of additives and materials that have undergone thermal deterioration) are used to maintain the quality of the food products as much as possible. In addition, it is not only food products but also a variety of other fields that have required a reduction in odors from packaging in recent times.

Typically, the packaging materials employed in these fields have made use of HP-LDPE without any additives. With recent trends in making packaging films thinner, it has been desirable to reduce the odor of LLDPE, which has higher strength than HP-LDPE.

In most cases, antioxidants are added to LLDPE and molding at comparatively high temperatures is necessary, and this has placed limits on the level of reduced odor that can be reached.

With EPPE, low temperature molding is possible, so the addition of antioxidants is not normally necessary for the purpose of preventing thermal deterioration. Fig. 12 shows the results of an analysis using an odor discriminating sensor of the odor level for films formed at low temperatures from EPPE without additives.

It can be seen that the odor level of EPPE is good compared to that of an LLDPE film to which an antioxidant has been added and an LLDPE film without additives.

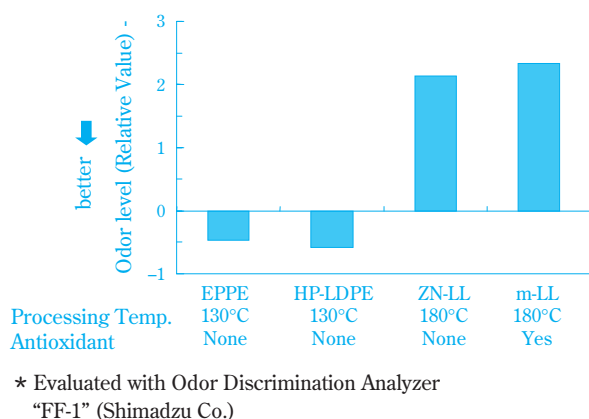
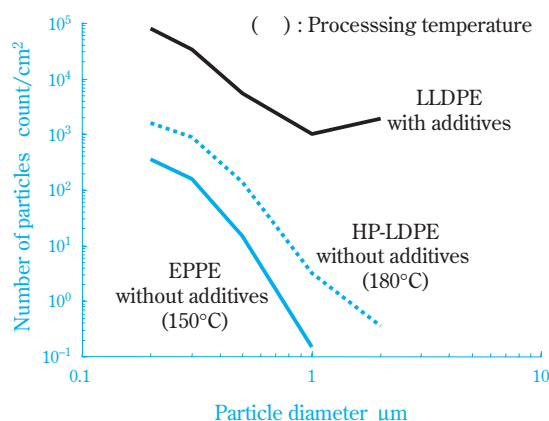


Fig. 12 Odor level of various polyethylene films

2. Clean Films and Containers

In fields where precision products such as electronic components and optical components are handled, there are requirements for clean packaging materials that do not have foreign matter mixed in. In this field also, there have been limits to the use of LLDPE similar to those discussed above. Since low temperature molding is possible with EPPE without additives, it also exhibits merits for creating clean materials.

Fig. 13 shows the cleanliness for various types of polyethylene film. The cleanliness was a measurement of the number of particles with a diameter of 0.2μm or greater which were recovered from the washing liquid using a particle counter when the film surface was washed with ultra pure water. It can be seen that the EPPE film without additives had a large reduction in the number of particles compared to the LLDPE film containing an antioxidant, and in addition, it was superior to HP-LDPE film.

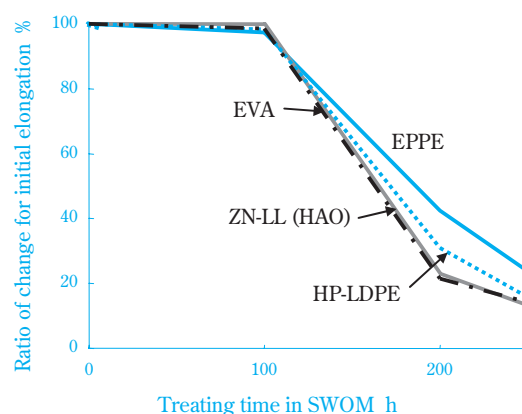


* Particles in the rinse water were counted with Particle Counter "KL-22" (Rion Co.)

Fig. 13 Cleanliness of EPPE film

3. Weather Resistant Films and Sheets

Fig. 14 shows the weather resistance of various types of polyethylene evaluated using a sunshine weather meter. EPPE has a smaller reduction over time in the tensile elongation than EVA, HP-LDPE and ZN-LL (HAO), and it can be seen that the weather resistance is superior. Therefore, it can be said that EPPE is a material that is suitable for applications such as mulching films and greenhouses for agriculture, and waterproof sheeting for construction. In general, weather resisting agents, such as hindered amine based stabilizers (HALS) and ultraviolet absorbing agents (UVA) are usually added to increase the weather resistance in such applications. It is thought that these additives can be reduced if EPPE is used.



* SWOM conditions : Temperature 83°C, with water spray

Fig. 14 Weatherability of various polyethylenes

4. Modifier for LLDPE s

In most cases, LLDPE is blended with HP-LDPE

for the purpose of improving the processability. However, when LLDPE is blended with HP-LDPE, there is generally a large reduction in the resulting mechanical strength. Table 3 gives the physical film properties when ZN-LL is blended with EPPE. In addition to improvements in the processability, the transparency of the film is improved, and furthermore, it was found that the drop in the mechanical strengths, such as tensile strength and impact strength, is smaller than with the HP-LDPE blend used for comparison.

Table 3 Film properties of ZN-LL (HAO) modified by blending EPPE

Modifier		EPPE	HP-LDPE	None
MFR	g/10min	0.5	2	—
Density	kg/m ³	920	923	—
Blending Ratio	%	25	25	—
Haze	%	13	10	22
Dart drop Impact Strength	MPa	39	31	43
Ultimate Strength (MD/TD)	MPa	43/41	34/35	44/44
Tear Strength (MD/TD)	kN/m	79/256	71/260	144/143

Processing Conditions : 55mmφ extruder, die 125mmφ, lip gap 2.0mm, Temperature 170°C, BUR 2.0, Out put 25kg/hr, Film thickness 80μm

Base resin : C8LL, MFR 1g/10min, Density 920kg/m³

Thus, by using EPPE as a modifier it is possible to create a new film with a superior balance of properties such as processability, transparency and strength.

Conclusion

In this paper, we have given an explanation of the typical characteristics and applications of the new easy processing polyethylene (EPPE) from Sumitomo Chemical Co., Ltd. while comparing it to conventional polyethylene materials such as HP-LDPE and LLDPE. While EPPE has superior processability which is equivalent to that of HP-LDPE, it is a unique material that has high mechanical strength. For the most part, we have discussed the three typical characteristics of low energy consumption, increased quality through low temperature processing and high productivity, but since it is a new material, we can assume that it still hides further unknown possibilities.

In the future, we want to make further progress with EPPE in response to the needs of customers, and we want to draw out the features of EPPE for many applications. Furthermore, we expect that through these

characteristics, this material will be used widely throughout the world as a high quality, high productivity material.

References

- 1) Yuki Iseki, Tatsuhiro Nagamatsu, Kenichiro Yada, *Plastics age encyclopedia* (2006).
- 2) Satoru Hosoda, *Transparent Plastics of Optical Access Generation*, 149 (2004) CMC Publishing Co., Ltd.
- 3) Satoru Hosoda, *Plastics · Functional plastics Encyclopedia*, 2 (2004), Industrial Research Center of Japan, Inc.
- 4) Konrad Scheid, *POLYETHYLENE 2006 11th WORLD CONGRESS*, MBS (Feb.1-3, 2005, Zurich Switzerland.).
- 5) S. Hosoda, M. Furuta, *Makromol. Chem., Rapid Commun.*, **2**, 577 (1981).
- 6) S. Hosoda, *Makromol. Chem.*, **185**, 787 (1984).
- 7) S. Hosoda, K. Kojima, M. Furuta, *Makromol. Chem.*, **187**, 1501 (1986).
- 8) S. Hosoda, *Polymer J.*, **20**, 383 (1988).
- 9) Satoru Hosoda, Shigeo Tanaka, Takayuki Okada, *Sumitomo Chemical R&D Reports*, Vol .**1988-I**, 4 (1988).
- 10) S. Hosoda, H. Nomura, Y. Gotoh, H. Kihara, *Polymer*, **31**, 1999 (1990).
- 11) S. Hosoda, A. Uemura, *Polymer J.*, **24**, 939 (1992).
- 12) S. Hosoda, *Trends in Polymer Science*, **3**, 265 (1993).
- 13) S. Hosoda, A. Uemura, Y. Shigematsu, I. Yamamoto, K. Kojima, in "Catalyst Design for Tailor-made Polyolefins", Ed. by K. Soga, M.Terano, Kodansha (Tokyo) (1994), p.365.
- 14) Kenzo Chikanari, Yasuro Suzuki, *Sumitomo Chemical R&D Reports*, Vol .**1999-I**, 42 (1999).
- 15) Kohzoh Miyazaki, Masashi Hamba, Hikaru Nagashima, Tsutomu Konaka, *Sumitomo Chemical R&D Reports*, Vol .**1994-I**, 23 (1994).
- 16) "Supply and demand trend of petrochemicals in the world", Ministry of Economy, Trade and Industry, (2006).
- 17) S. Hosoda, Y. Iseki, T. Nagamatsu, S. Shiromoto, K. Chikanari, K. Yanase, T. Kasahara, T. Konaka, *Advances in Polyolefin 2005*, ACS (Sept., 2005, California, USA).
- 18) K. Chikanari, T. Nagamatsu, K. Yanase, T. Mitsuno, S. Hosoda, *Specialty Plastic Films 2005*, MBS (Oct., 2005, Zurich Switzerland).

- 19) Yasuro Suzuki, CONVERTECH, **12**, 65 (2005).
20) T. Nagamatsu, Y. Iseki, K. Chikanari, T. Mitsuno,
K. Yamada, Y. Nozue, S. Shiromoto, K. Yanase,

T. Kasahara, S. Hosoda, *ANTEC 2006*, SPE (May, 2006, USA).

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