Review

Material Recycling Technology of Crosslinked Rubber Waste

Kenzo Fukumori and Mitsumasa Matsushita

架橋ゴム廃材のマテリアルリサイクル技術

福森健三，松下光正

Abstract

A new material recycling technology for crosslinked rubber was developed using the continuous reactive processing method. In this process of producing reclaimed rubber, breakage of crosslinking points in the crosslinked rubber occurs selectively under the controls of shear stress, reaction temperature, and internal pressure in a modular screw type reactor. Deodorization during the process has also become possible by a newly developed method. The reclaimed rubber obtained from rubber waste generated from both manufacturing products and post-consumer products shows excellent mechanical properties applicable to new rubber compounds. Furthermore, an enhanced rubber recycling process for producing thermoplastic elastomer (TPE) based on rubber waste has been established. The TPE obtained exhibits highly recoverable rubber elasticity and mechanical properties comparable to commercial TPE. It is expected that the rubber recycling technology developed during this study will contribute to protecting the environment and also saving resources.

Keywords
Crosslinked rubber, Waste, Recycle, Reclaimed rubber, Devulcanization, Deodorization, Automotive product, Tire, Thermoplastic elastomer

要　旨

連続再生法に基づく新規ゴムリサイクル技術を開発した。スクリュー回転方式の連続再生装置を用いて，架橋ゴムに適切な温度，圧力およびせん断力を負荷することにより架橋結合点の選択的切断を可能とし高品質の再生ゴムを製造する方法を確立した。またゴム再生過程で再生ゴム特有の臭気を同時に除去することも可能にした。ゴム製品生産工程や使用済みゴム製品から発生する各種ゴム廃材について，本技術で得られる再生ゴムは新ゴムに近い物性を示し，実用上再びゴム製品の原料ゴムとして活用できることが確認された。さらに本技術を発展させ，廃ゴムを原料として，製品成形時の架橋工程が不要，かつリサイクル性に優れる熱可塑性エラストマを製造する方法を確立した。得られる熱可塑性エラストマは市販品と同等の物性を示した。本研究で開発した新規ゴムリサイクル技術は，国内外で発生するゴム廃棄物を対象に，今後の埋立て処分量の削減や再資源化促進に大いに貢献するものと期待される。

キーワード
架橋ゴム，廃棄物，リサイクル，再生ゴム，脱硫，脱臭，自動車部品，タイヤ，熱可塑性エラストマ

1. Introduction

Recently, the importance of recycling waste materials has been increasing for all industries worldwide. For rubber products, the automotive and transportation industries are the biggest consumers of raw rubber. Rubber waste is usually generated during the manufacturing process of products for these industries and by disposal of post-consumer (retired) products, mainly including scrap tires. For example, in Japan, about one million tons of scrap tires are generated annually.

The oldest and simplest reclaiming method in the rubber recycling industry is called the “pan method”. The reclaimed rubber obtained by this method is far inferior in physical properties to virgin rubber, however. From the viewpoint of energy balance, material recycling of rubber waste is preferable to other recycling techniques.1) In spite of this, material recycling in the form of crumb rubber and reclaimed rubber accounted for only about 11% of total scrap tires in 1998.2) New material recycling technologies such as the microwave method3) and the ultrasonic method4) have been developed with the aim of shorter reaction times. However, here also the reclaimed rubber from these methods are not so excellent in quality as to be widely applicable to practical rubber products. Finally, technological development of new types of tires, such as steel belted and radial ones, has led to some limitations in the amount of recycled rubber that can be included in higher quality rubber compounds for new tires.1)

In this study, a new continuous rubber recycling technology has been developed for crosslinked rubber waste for the purpose of obtaining recycled materials of high quality, as reclaimed raw rubber and thermoplastic elastomer (TPE).

2. Rubber recycling technology

2. 1 Automotive rubber waste

For motor vehicles, many crosslinked rubber products are used as weather strips, hoses, vibration insulators and miscellaneous parts, except for tires, as shown in **Fig. 1**.5) The sum of their weights corresponds to about 3% of the total weight of the vehicle. Among the rubber polymers used for these automotive rubber products, ethylene-propylene-diene rubber (EPDM) makes up about one half of the rubber by weight as shown in Fig. 1. Thus, in this study, a continuous rubber recycling technology has been developed mainly for crosslinked EPDM waste. The rubber waste was roughly crushed into small pieces to a size of about 5 mm for the following recycling process.

2. 2 Recycling process for producting reclaimed rubber

2. 2. 1 Principle of producing reclaimed rubber

Material recycling of crosslinked polymers, including rubber, is generally thought to be difficult using a simple heating procedure, because of the three-dimensional network structure restricting the material from melting. In the rubber recycling process by the conventional pan method, finely ground rubber powder mixed with oils and reagents is heated with steam in a pressure vessel at a temperature of ~200°C for more than 5 hours. Moreover, usually this process has to be followed by several procedures (refining and straining) before obtaining the final reclaimed rubber. As noted above, the reclaimed rubber obtained by this method is inferior in quality to virgin rubber. This is due to the occurrence of unselective breakage of both the crosslinking points and main chain (C-C) bonds in the rubber.

In the newly developed continuous recycling process,6) various chemical reactions corresponding to selective breakage of crosslinking points (so-called, devulcanization) can be efficiently controlled

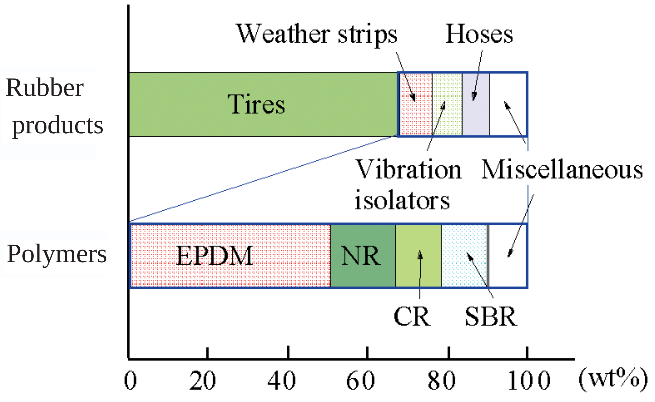

Fig. 1 Rubber products for motor vehicles.

by optimizing the parameters in the reactor such as shear stress, temperature, and internal pressure. The continuous recycling process for crosslinked rubber waste is performed in a modular screw type reactor as schematically shown in **Fig. 2**. The screw configuration with the modular screw elements (right-handed screw, kneading disk, etc.) is suitably designed to be applicable to a continuous recycling process. In the first pulverizing zone of this process, roughly crushed rubber material is converted into fine particles by high shear stress, and heated to the devulcanization reaction temperature quickly. The residence time is assured to be long enough to complete the devulcanization reaction under shear flow in the next devulcanizing zone. In this reaction zone, fine particles of crosslinked rubber become highly elongated by filling and shearing with the kneading disk elements, and are thus eventually plasticized.

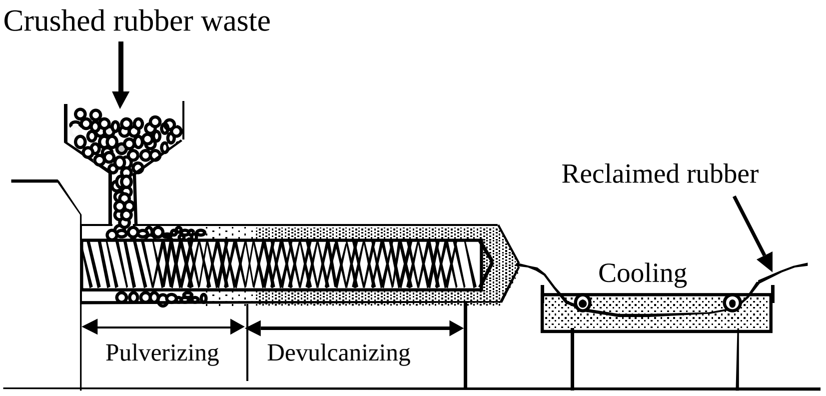

Fig. 2 Schematic illustration of the reactor for the product of reclained rubber.

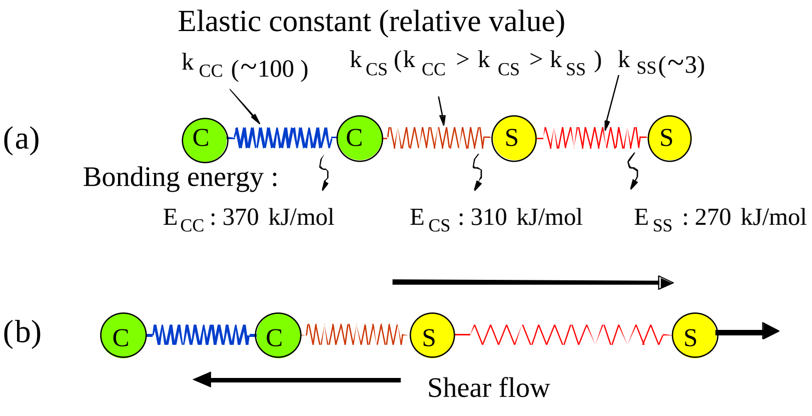

Fig. 3 Breakages of crosslinking points in high shear flow : (a) model for the network chain; (b) deformation of the network chain (particularly, S-S bonds) by shearing.

A basic understanding of the cleavage of crosslinking bonds under high shear stress is suggested as follows. As shown in **Fig. 3**, there appears to be only a small difference in the bond energy between C-C bonds and C-S or S-S bonds. Hence, by simple heating in a pressure vessel, cleavage of both C-C and C-S or S-S bonds may occur unselectively. This leads to the lowering of the physical properties of reclaimed rubber by the conventional method. On the other hand, with regard to the elastic constant k for these bonds (estimated approximately on the basis of the values for crystals), the k-value for the S-S bonds can be estimated to be about 1/30th that for the C-C bonds, as shown in Fig. 3(a). Generally, it is understood that the mechanical behavior of crosslinked rubber may be mainly controlled by the entropic term in the strain energy. In contrast with this entropic deformation behavior, at extremely higher shear stresses induced by filling and kneading in the reactor, most of the rubber molecules may become fully elongated to their limited extensibility. Under these conditions, the bonds having lower elastic constant (the S-S bonds) may become more extended in comparison with bonds having higher elastic constant (the C-C bonds), in an elastic manner as shown in Fig. 3(b). That is, the elastic energy induced by high shearing may be particularly effective on the S-S bonds, causing the selective breakage of crosslinking points.

2. 2. 2 Change in the network structure during the recycling process

Under suitable process conditions (i.e., screw configuration, reaction temperature, screw rotation speed, etc.), reclaimed EPDM with good surface appearance can be continuously obtained from the head of the reactor, as shown in **Fig. 4**. This was closely connected with the values of the Mooney viscosity for the rubber polymer. **Figure 5** shows the changes in the appearance and Mooney viscosity of the EPDM sampled from various positions along the axial length of the screw in the reactor. As explained above, in the first pulverizing zone, roughly crushed rubber material is turned into fine particles by high shearing. In the next devulcanizing zone, the fine particles of crosslinked EPDM become plasticized. The Mooney viscosity of the EPDM samples decreases along the axial length of the screw, corresponding to the progress of devulcanization.

Figure 6 shows the changes in the average

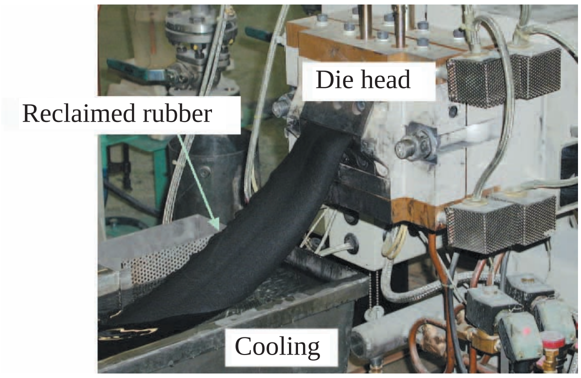

Fig. 4 Continuous recycling process for the product of reclaimed rubber.

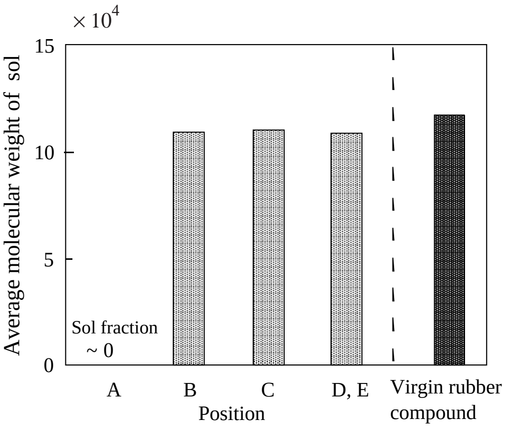

Fig. 6 Changes in the average molecular weight of sol component in rubbers sampled from positions A-E.

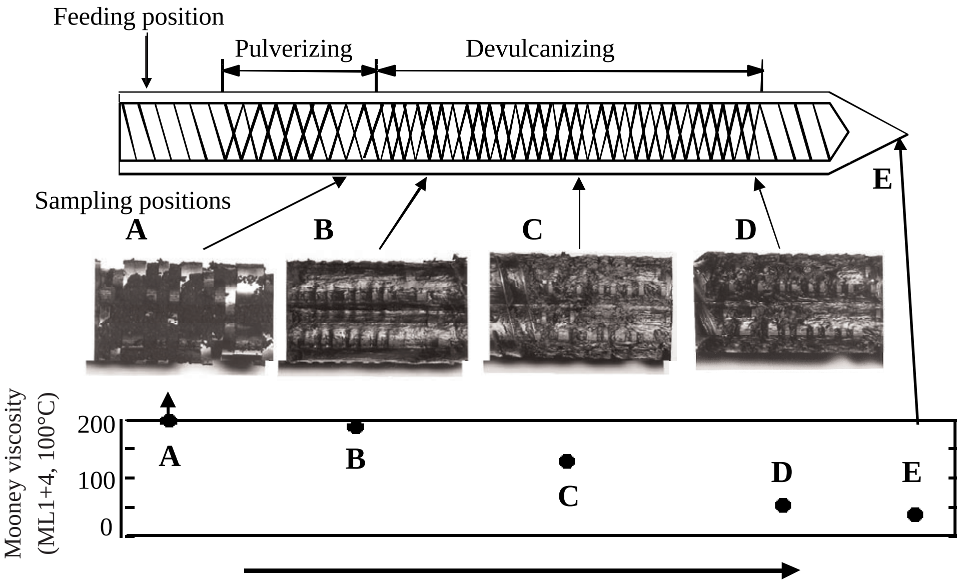

Fig. 5 Appearances and Mooney viscosity of rubbers sampled from the positions A-E.

molecular weight of the sol component during the process. The average molecular weight of the sol component in the reclaimed EPDM is nearly constant, comparable to that of virgin EPDM, from position B to position D. This result supports the occurrence of selective breakage of crosslinking points in the EPDM during the continuous recycling process.

2. 2. 3 Deodorization of reclaimed rubber

A characteristic odor arising from reclaimed rubber sometimes limits its practical application. Hence, a deodorization procedure is also included in the continuous recycling process using a newly developed method,$^{7)}$ in which high-pressure water is injected into the barrel during the devulcanization. The deodorization mechanism during the continuous process is schematically shown in **Fig. 7** as follows. Components in the rubber compound causing the odor are trapped in the high-pressure water vapor and removed efficiently through vents with vacuum pumps. The barrel temperature and screw elements around the positions for water injection are suitably adjusted to avoid inadequate progress of the devulcanization caused by the decreased temperature through the diffusion of water molecules. **Figure 8** shows gas chromatography signals of the odorous components in reclaimed rubbers (both untreated and treated) and virgin rubber compound. For the reclaimed rubbers, the odorous components in the treated rubber are barely detected, similar to the virgin rubber compound, while there are many odorous components detected in the untreated rubber. Thus, the deodorization procedure appears to be quite effective.

2. 2. 4 Properties of reclaimed rubber and its practical uses for automotive rubber products

The reclaimed EPDM was compounded and crosslinked with an accelerated sulfur vulcanization system according to the conventional recipe. **Figure 9** shows stress-strain curves for a reclaimed rubber from the developed method and for a virgin rubber. The reclaimed rubber exhibits an excellent tensile stress-strain property, almost comparable to the virgin rubber.

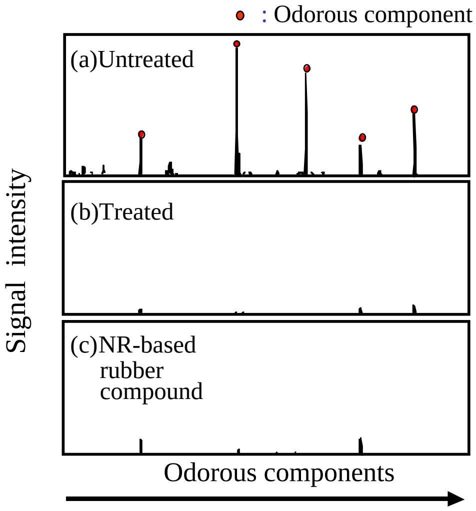

Fig. 8 Signals from odorous components in rubbers.

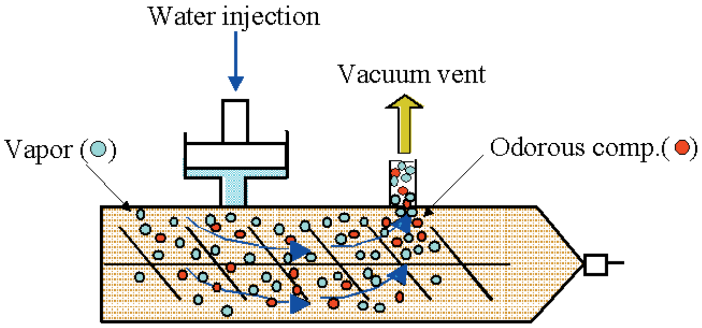

Fig. 7 Schematic illustration of the deodorization mechanism during the devulcanization.

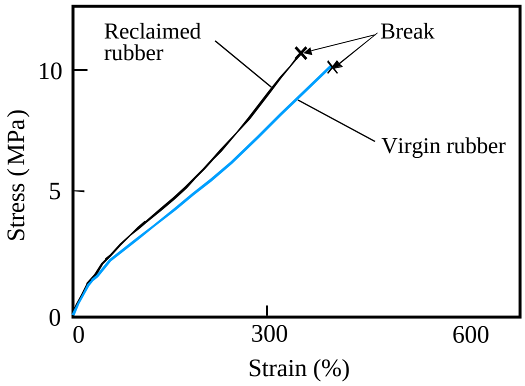

Fig. 9 Stress-strain curves of crosslinked rubbers.

In 1997, this technology was put to practical application in the material recycling of EPDM waste generated in manufacturing processes of automotive weather strips in a plant having production capacity of 500 tons/year for reclaimed rubber^5)^. The reclaimed EPDM is currently being utilized for producing various automotive rubber products, as shown in **Fig. 10**.

2. 2. 5 Application of continuous recycling technology to tire rubber waste

The amount of various rubbers, such as natural rubber (NR), styrene-butadiene rubber (SBR) and butyl rubber (IIR), consumed for the production of new tires correspond to about 70% of the total weight of raw rubber materials annually consumed in Japan. This results in one million tons of scrap tires generated per year. Hence, the continuous rubber recycling technology in this study was also applied to tire rubber waste, generated from both manufacturing products and scrap tires,[7)] to investigate its application potential here.

Test truck tires were prepared by mixing NR-based reclaimed rubber (10 wt%) from manufacturing products treated by the continuous recycling process with NR-based virgin rubber (90 wt%) for the tread rubber compound. Standard truck tires using only NR-based virgin rubber were also prepared for comparison. Actual road tests were carried out at mileages up to 200,000 km. During the road tests, the changes in the tread depth for both the test tire and the standard tire were examined against the mileage driven. The changes in the tread depth for the test and standard truck tires are shown in **Fig. 11**, along with the positions of the tires on the vehicle. The tread depths were measured against mileage for the tires on the rear positions. Based on the results, the tread wear behavior of the test truck tire is estimated to be similar to that of the standard tire for mileages up to 200,000 km. These results confirmed that the reclaimed tire rubber obtained by the continuous recycling technology can be applied to new tire rubber compounds with appropriate content, suitable for practical engineering. This recycling technology of tire rubber waste was licensed out to Yokohama Rubber Co., Ltd. in 2001.

2. 3 Recycling process of producting TPE

2. 3. 1 Principle of producing TPE

Thermoplastic elastomer (TPE) possesses highly recoverable properties similar to conventional crosslinked rubber, and can be processed with the moldability and efficiency of thermoplastics. In addition to simpler processing, the principal advantages of using TPE compared to crosslinked rubber include easier recycling of waste, design flexibility, product quality and dimensional consistency. Hence, owing to these excellent characteristics, TPE is now widely used in a variety of applications, including automotive products, as substitute material for rubbers and soft plastics. In this study, as the next step in the development of

< Typical applications >
Head lamp seal, Radiator support seal
Hose protector, etc.

Fig. 10 Applications of reclaimed rubber for automotive products.

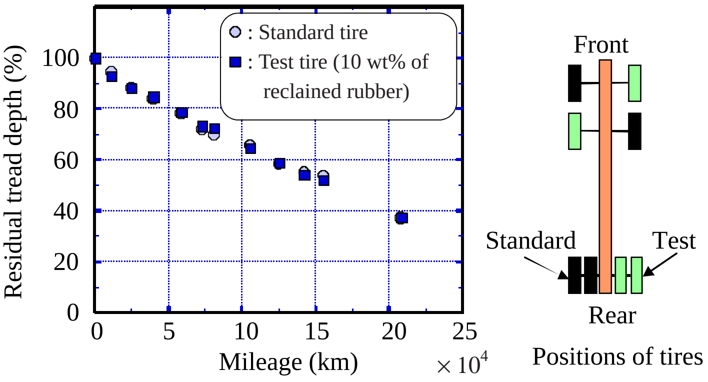

Fig. 11 Changes in tread depth for standard and test truck tires during actual road tests.

rubber recycling technology, a more enhanced recycling process of producing a dynamically crosslinked TPE based on EPDM waste has been established.[8)]

The enhanced recycling process of producing TPE is composed of pulverizing, devulcanizing, blending, and dynamically crosslinking procedures. **Figure 12** shows a schematic illustration of the recycling of EPDM waste to produce the TPE. In the first zone, crushed EPDM is pulverized by shearing. In the following zones, the devulcanization (selective breakage of crosslinking points in the EPDM), blending of the reclaimed EPDM with polypropylene (PP, ca. 20 wt% to ca. 80 wt% EPDM), and the dynamic crosslinking of the EPDM component in the blend proceed continuously and result finally in the formation of a product with desirable domain structure.

2. 3. 2 Change in the phase structure during the recycling process

In order to obtain TPE showing preferable physical properties, the screw geometry and configuration of the reactor and the reaction conditions during the continuous recycling process have to be suitably adjusted to form the desirable domain structure in the product. The target morphology of the TPE corresponds to formation of a phase structure with the chemically crosslinked EPDM phase (major component) dispersed in a PP matrix (minor component). **Figure 13** shows the

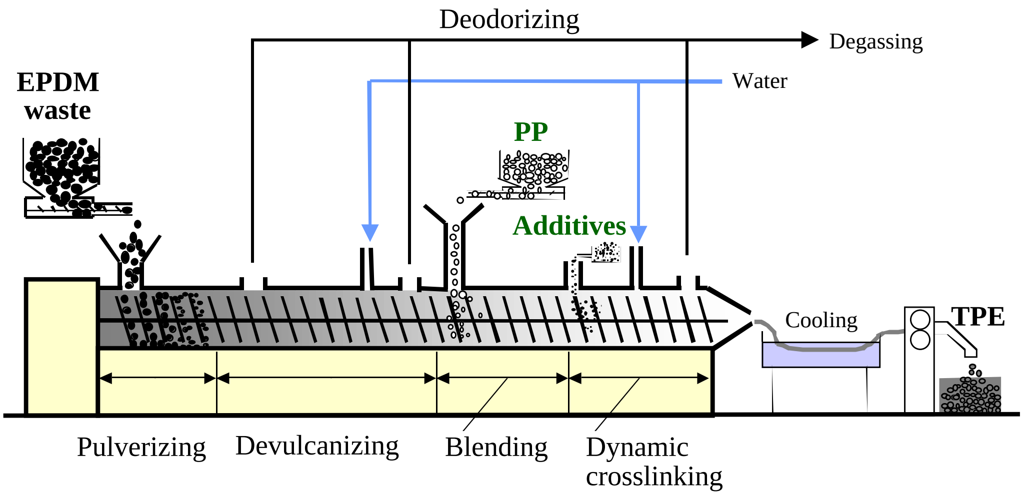

Fig. 12 Continuous recycling process for the product of TPE based on EPDM waste.

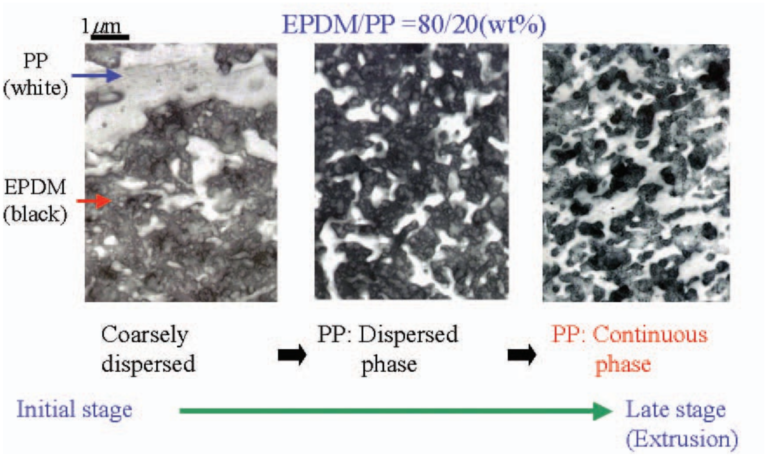

Fig. 13 Temporal changes in the phase structure of the EPDM/PP blend during the continuous recycling process.

temporal changes in the phase structure of the EPDM/PP blend during the continuous recycling process. At the early stage of the process, the EPDM component forms the continuous phase, depending on its volume amount in the blend. At the following intermediate and late stages of the process and under suitable reaction conditions, inversion of the phase structure occurs. The desired TPE domain structure, in which a re-crosslinked EPDM phase of less than 1 μm is finely dispersed in the continuous PP phase, is then formed.

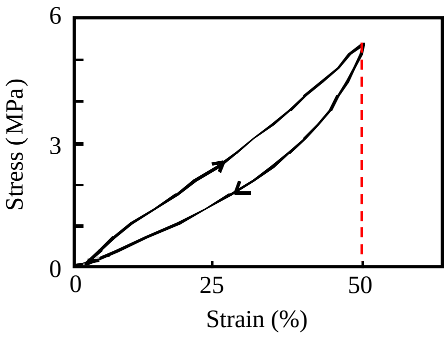

Fig. 14 Elongation-retraction property of TPE based on EPDM waste.

2. 3. 3 Properties of TPE based on EPDM waste and its applications for automotive products

The obtained TPE pellets can be molded by extrusion molding or injection molding methods, like conventional thermoplastics. Injection molded TPE specimens showed good tensile properties and recovered its original length after elongation in an elongation-retraction experiment, as shown in **Fig. 14**. In engineering practice, this TPE based on waste EPDM is comparable to commercial TPE in various properties, including tensile property, processability, and surface appearance.

Mass production of TPE based on foamed EPDM waste, which is generated in the manufacturing process of automotive weather strips, was started in July 2002 at a new plant having production capacity of 350 tons/year for TPE. The development of automotive products made with the TPE, as shown in **Fig. 15**, is presently being worked on to explore its practical uses.$^{9)}$

3. Conclusion

In this study, a new material recycling technology for automotive rubber waste was developed utilizing a modular screw type reactor. In the reactor with optimized screw geometry and configuration,

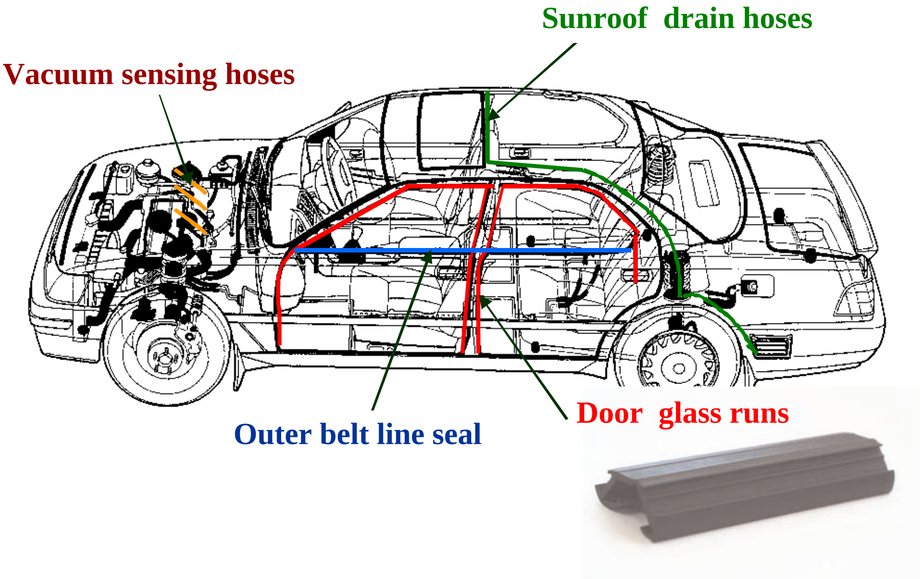

Fig. 15 Applications of TPE for automotive products.

selective breakage of crosslinking points in the waste rubber can occur predominantly under suitable conditions of temperature, shear stress and internal pressure. Reclaimed rubber produced from EPDM waste generated in the manufacturing process of weather strips exhibits excellent physical properties, almost equal to those of virgin rubber. The reclaimed rubber is currently being mass produced and has been used for manufacturing automotive rubber products since 1997. It was also confirmed that this technology can be applied to the recycling of tire rubber waste, including scrap tires. Furthermore, as a next phase of development, an enhanced rubber recycling process for producing TPE based on rubber waste has been established. The TPE also shows good physical properties, comparable to commercial TPE. Mass production of TPE based on EPDM waste was started in July 2002.

It is expected that the newly developed rubber recycling technology described in this study will contribute to both protecting the environment and saving resources with regard to rubber waste generated throughout the world.

Acknowledgements

This work was carried out jointly during research and development with Toyoda Gosei Co., Ltd. and Toyota Motor Corp., and partly in cooperation with the International Center for Environmental Technology Transfer in 1999-2001, commissioned by the Japanese Ministry of Economy Trade and Industry.

References

1) "Recycling of Rubber", RAPRA Rep. 99(1997), 9
2) TIRE INDUSTRY OF JAPAN, JATMA, 1999
3) Goodyear Tire & Rubber Co. Ltd., Plast. Rubb. News, Sept. 9(1979)
4) Isayev, A. I., Chen, J. and Tukachinsky, A. : Rubber Chem. Technol., **68**(1995), 267
5) Otsuka, S., Owaki, M., Suzuki, Y., Honda, H., Nakashima, K., Mouri, M. and Sato, N. : SAE Tech. Pap. Ser., No. 2000-01-0015 (2000)
6) Fukumori, K., Mouri, M., Sato, N., Okamoto, H., Matsushita, M., Honda, H., Nakashima, K., Suzuki, Y. and Owaki, M. : Gummi FASERN Kunststoffe, **54**(2001), 48
7) Fukumori, K., Matsushita, M., Okamoto, H., Sato, N., Suzuki, Y. and Takeuchi, K. : JSAE Rev., **23**(2002), 259
8) Okamoto, H., Fukumori, K., Matsushita, M., Sato, N., Tanaka, Y., Okita, T., Takeuchi, K., Suzuki, N. and Suzuki, Y. : Prepr. of IUPAC-PC2002, Dec. 2-5, 2002, 638
9) Tanaka, N., Watanabe. T., Okita, Y., Matsushita, M., Okamoto, H., Fukumori, K., Suzuki, N. and Suzuki, Y. : SAE Tech. Pap. Ser., No. 2003-01-0941 (2003)

(Report received on Jan. 31, 2003)

Kenzo Fukumori 福森健三
Year of birth : 1954
Division : Organic Materials. Lab.
Research fields : Physical properties of rubber Polymers, Reactive processing of polymer blends and composites, Polymer recycling
Academic degree : Dr. Engng.
Academic society : The Soc. of Polym. Sci., Jpn., The Soc. of Rubber Ind., Jpn., The Soc. of Rheol., Jpn., Mater. Life Soc.

Mitsumasa Matsushita 松下光正
Year of birth : 1958
Division : Organic Materials. Lab.
Research fields : Reactive processing of polymer blends and composites, Polymer recycling
Academic society : The Soc. of Polym. Sci., Jpn.