報　　告

新ゴムリサイクル技術
ゴム端材を原料とする熱可塑性エラストマーの開発

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New Rubber Recycling Technology: Development of Thermoplastic Elastomer Based on Waste Rubber

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要　　旨

EPDMゴム端材から熱可塑性エラストマー（TPE）を製造する新しいゴムリサイクル技術を開発した．本技術では，EPDM端材の脱硫，脱硫EPDMとポリプロピレン（PP）とのブレンド，ゴム成分の動的架橋が連続的に行われ，目的とするTPE（以下，Recycled Rubber based Thermoplastic Elastomer；RR-TPEと表記する）が得られる．

得られたRR-TPEは市販のオレフィン系熱可塑性エラストマー（TPO）と同等のゴム弾性，機械物性を示す．これらの特性は適切に形成された相構造に起因する．この新技術により製造されたRR-TPE材料を使って自動車用シール部品が開発中であり，製造される予定である．

本技術により，環境保全・省資源を推進することができる．

Abstract

A new rubber recycling technology to produce a thermoplastic elastomer (TPE) based on ethylene-propylene-diene rubber (EPDM) waste was developed. In this technology, the developed process consists of devulcanization of EPDM waste, blending of the devulcanized EPDM and polypropylene (PP), and dynamic vulcanization of the rubber component. All three are set up in as a continuous process in which the Recycled Rubber based Thermoplastic Elastomer (which is indicated as “RR-TPE” henceforth) is finally obtained.

The RR-TPE exhibits elasticity and mechanical properties similar to those of commercial Thermoplastic olefins (TPO). These properties may be due to a suitably formed phase structure. Automotive sealing parts are being developed and are going to be produced with the RR-TPE manufactured by this new technology.

This technology will contribute to both protecting the environment and saving resources.

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1. INTRODUCTION

Waste rubber generated from in-process or scrap products has now risen to more than 30 million tons in the world and more than one million tons in Japan. From the viewpoint of protecting the environment and saving resources, recycling of waste rubber has become an important issue in recent years.

Currently various rubber materials are applied to automotive parts due to their high elasticity. For example, tires, hoses, bodysealing parts, functional parts, etc., are produced with rubber materials. In Japan about 5 million vehicles are scrapped annually, causing a large amount of waste rubber.

When the rubber material is processed into a product, the three-dimensional network structure called “crosslinking” is constructed which contributes to rubbery elasticity. But due to the network structure, it is difficult to recycle as a raw material. In fact the method mainly used for recycling of rubber is incineration (energy recycling). Material recycling, which is thought to be the most desirable method, is used in only about 10% of all treatment of waste rubber[1]. As for material recycling of waste rubber, the application of powdered rubber that is produced by grinding is a mainstream in and out of Japan. It is extremely rare to devulcanize waste rubber (breaking of sulfur crosslinking bonds). In Japan the general production method of devulcanized or reclaimed rubber is called “pan reclaiming process”[2]. The reclaimed rubber according to this conventional method is poor in quality and its productivity is very low. Similar results were found in other various rubber reclaiming methods[3, 4].

Recently, a continuous rubber recycling technology has been developed for EPDM waste[5]. In this process, the breakage of crosslinking bonds occurs selectively under the control of shear stress, reaction temperature and internal pressure. The devulcanized rubber exhibits excellent mechanical properties nearly equal to those of neat rubber. This recycling technology has been utilized industrially and the reclaimed rubber has been used as materials for automotive parts since 1997 in TG.

Based on this technology, we have developed a new rubber recycling technology to produce a thermoplastic elastomer based on EPDM waste.

TPE’s are polymers, which have plasticity at high temperature and rubbery elasticity at room temperature. TPE can be substituted for rubber and this demand has been increased. There are various types of TPE’s such as styrenic based (SBC), olefinic based (TPO), polyurethane based (TPU), copolyesters (COPE), copolyamides (COPA), and so on. Thermoplastic olefin (TPO) is generally made by melt-blending of EPDM (70-80wt%) with thermoplastics (20-30wt%) such as PP or polyethylene (PE). It consists of the continuous thermoplastic matrix and dispersed EPDM domains that are usually vulcanized (TPO is also called “thermoplastic vulcanizate: TPV”). Therefore, though TPO has similar properties to those of EPDM, it also has reprocessability by heating like general thermoplastics. Due to these properties TPO has recently been applied to various products as substitute material for EPDM.

Using this new technology, it is possible to produce TPE with one continuous process that consists of devulcanizing waste rubber, blending with PP, and re-vulcanizing (dynamic vulcanizing) of the rubber component. Also, automotive parts are being developed and are going to be produced with the RR-TPE manufactured by this technology.

This paper outlines the developed production process for the RR-TPE, reports on the technical points of processing, and provides material properties and part performance results.

2. DEVELOPMENT OF AUTOMOTIVE PART WITH ENHANCED RECYCLING TECHNOLOGY

DEVELOPMENT OF ENHANCED RECYCLING TECHNOLOGY

Rubber material to apply for development of the recycling technology

In the primary technology for rubber reclamation described previously, sulfur crosslinked EPDM was chosen for development. EPDM occupies more than 50% of rubber components that are used in vehicles except tires. Also in the development of this technology, on the extension of the basic technology, it was decided to apply EPDM rubber. It is one of the reasons that TPO is generally made of EPDM and PP. The EPDM waste was collected from in-process scrap weatherstrip generated in a manufacturing plant.

Principle and processing system for RR-TPE

The RR-TPE is produced with the "Shear Flow Reactor" based on a twin screw extruder. A schematic diagram is shown in Fig.1. This processing system consists of pulverizing zone, devulcanizing zone, blending zone, and dynamic vulcanizing zone, designed in appropriate screw configuration and position of side-feeders.

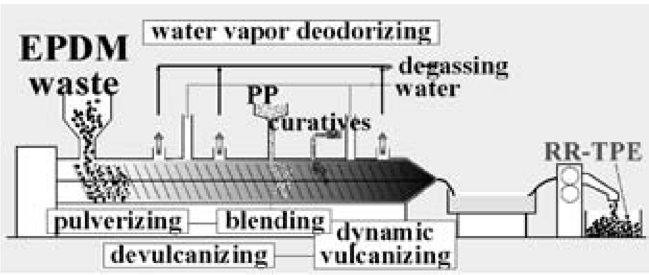

Fig.1 Outline of the processing system for RR-TPE based on waste EPDM

Pulverizing zone

In this zone, roughly crushed rubber fed from a hopper is pulverized into fine particles, and heated to devulcanizing reaction temperature quickly.

Devulcanizing zone

In this zone, due to addition of high shearing distortion and heat to the pulverized rubber, crosslinking bonds of the rubber are broken selectively and the sulfur crosslinked EPDM is devulcanized.

The bond energies of the crosslinking bonds (S-S: 237kJ/mol, C-S: 269kJ/mol) are lower than that of the main chain (C-C: 354kJ/mol) in sulfur crosslinked EPDM. On the other hand, the elastic constant (approximately estimated on the basis of the values for crystals) for the S-S bonds can be evaluated to be about one thirtieth in comparison with that for the C-C bonds. High shearing distortion is added to the sulfur crosslinked EPDM in the extruder, and the energy induced by the distortion is concentrated to the crosslinking bonds whose elastic constants are lower. Consequently, only crosslinking bonds are highly elongated. By addition of heat to EPDM in this condition, crosslinking bonds are broken selectively (Fig.2). These are the primary procedures for rubber reclamation[5-8].

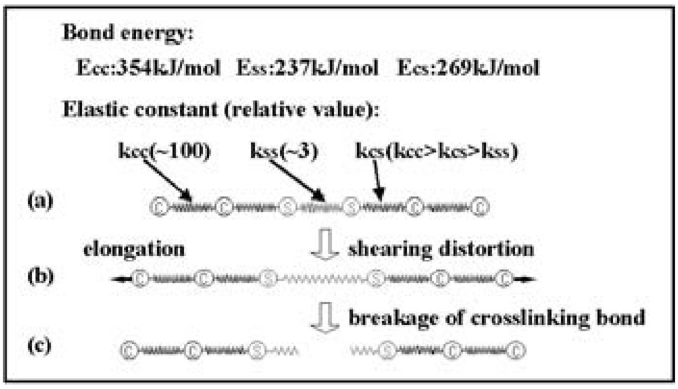

Fig.2 Breakage of the crosslinking bonds in high shear flow
(a) Model for the network chain
(b) Deformation of the network chain (particularly, S-S bonds) by shearing
(c) Breakage of crosslinking bonds

Blending zone

In this zone, to convert devulcanized rubber into thermoplastic elastomer, blending the devulcanized rubber with thermoplastic resin (PP) and mixing are carried out. The PP is fed from side-feeder at a rate to attain 20wt% for the RR-TPE.

Dynamic vulcanizing zone

In this zone, to assure its "rubbery" properties, the devulcanized rubber component is dynamically vulcanized by metering in curatives. Since the viscosity of rubber component becomes much higher than PP due to the dynamic vulcanization, the rubber component forms in a dispersed phase. Finally the targeted phase structure corresponding to the morphology of continuous PP matrix and dispersed EPDM domain can be attained.

In addition, a deodorizing treatment[8] is carried out within the reactor. During devulcanization of sulfur crosslinked EPDM, odor components are generated. In this deodorizing process a small amount of water is injected into the extruder, then the odor components are dissolved in vapor and removed from the compound by degassing with vapor.

After these processes in each zone in the extruder, the RR-TPE is extruded in the form of strands from the extruding head, cooled in the water bath, and pelletized continuously. The total time required for these processes is about seven minutes.

Technical points

In order to obtain desirable RR-TPE continuously in a short time, there are some important parameters that need to be controlled. Those are shear stress and pressure in the extruder, reaction temperature of devulcanization and dynamic vulcanization, dwell time of material, and compound design. Factors that should be adjusted in practical process to control above parameters are corresponding to screw configuration, screw rotation speed, cylinder temperature, feed rate of material, and compounding ingredient and recipe. Particularly the screw configuration is the most important factor in the ability to produce RR-TPE continuously. Similarly to the primary technology, segment type screws are used for this technology, and the screw shape can be designed at the request of the application. In order to pulverize, devulcanize, blend with PP, dynamically vulcanize, and construct morphology in each zone continuously, the screw shape and the position of side-feeders to feed PP and curatives were designed appropriately and suitable conditions (temperature, screw rotation speed, etc.) to obtain desirable RR-TPE were decided.

<u>Properties of the RR-TPE based on waste EPDM rubber</u>

The RR-TPE obtained in this technology can be extrusion molded or injection molded similarly to commercial TPO. Properties of the RR-TPE depend on degree of devulcanization of the EPDM, degree of cure of the devulcanized rubber component in the RR-TPE, and its phase structure. Fig.3 shows the relationship between compression set or extruded surface roughness of the RR-TPE samples and the added amount of curatives during dynamic vulcanization process. Compression set is one of the tests to evaluate rubber-like elasticity. Sulfur is preferable to organic peroxide as vulcanizing agent, because sulfur has comparative higher reactivity with the devulcanized EPDM than organic peroxide. Compression set becomes lower with the increase in the added amount of sulfur. Accordingly rubbery elasticity of the RR-TPE depends on the degree of cure of the EPDM component. On the contrary, extruded surface roughness of the RR-TPE becomes rougher with the increase in the added amount of sulfur. It is thought that the surface roughness might depend on the phase structure. In case the degree of cure of the EPDM is low, the EPDM phase may form the matrix phase. As the degree of cure of the EPDM is increased and the viscosity of the EPDM phase becomes higher, phase inversion between EPDM and PP might occur and the PP might form the matrix phase. As the degree of cure of the EPDM is increased, the domain formation might be disturbed by higher viscosity of the EPDM.

The extruded surface roughness of the RR-

TPE after dynamic vulcanization became smoother with the decrease in Mooney viscosity of the devulcanized EPDM before blending with PP as shown in Fig.4. In other words, the degree of devulcanization of the EPDM may influence the phase formation of the RR-TPE. In case Mooney viscosity of the EPDM is too high, i.e., there are large amounts of crosslinking in the devulcanized EPDM, the phase inversion might not occur completely. In addition, the shear stress and pressure in blending and dynamic vulcanizing zone contributes to the phase formation, consequently to the extruded surface roughness as shown in Fig.5. In Fig.5, the shear pressure in dynamic vulcanizing zone could be changed by different screw configurations. By mixing with higher shear pressure in dynamic vulcanizing zone, surface roughness becomes smoother; the re-vulcanized EPDM phase may be finely dispersed.

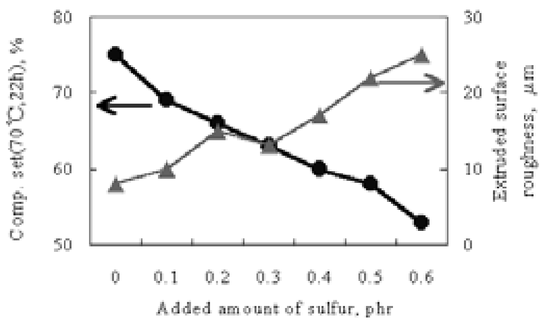

Fig.3 Relationship between compression set or extruded surface roughness of RR-TPE samples and added amount of sulfur

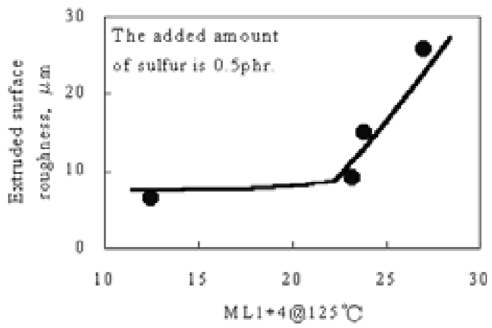

Fig.4 Relationship between extruded surface roughness of RR-TPE and Mooney Viscosity of devulcanized EPDM

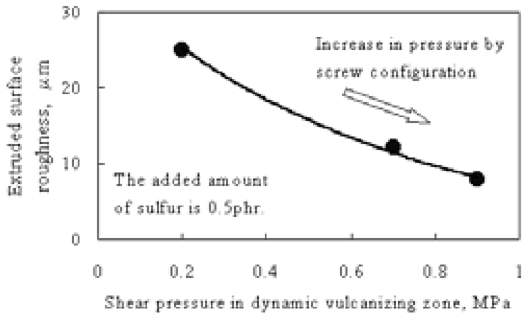

Fig.5 Influence of shear pressure in dynamic vulcanizing zone on extruded surface roughness

Fig.6 shows transmission electron microscope (TEM) images of the RR-TPE obtained by this technology in comparison with that of the commercial TPO (TPV) applied for weatherstrip part of automobile. In the RR-TPE obtained under optimized conditions, EPDM phase was dispersed with a size of 1-micrometer order in the continuous PP phase. On the contrary under inappropriate conditions, EPDM formed a continuous phase. It is shown that the appropriate controls of the devulcanization and dynamic vulcanization reaction for EPDM and of the mixing conditions in the blending and dynamic vulcanizing zone are important to form the suitable morphology for the RR-TPE. As shown in Table 1, the RR-TPE obtained under optimized condition exhibits rubber-like mechanical properties comparable to the commercial TPO described above. It is thought that suitable control of the phase structure contributes to the production of the RR-TPE showing good properties.

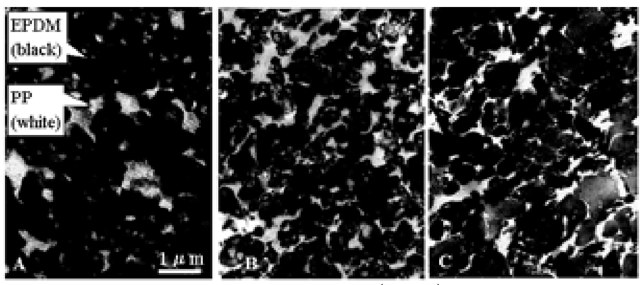

Fig.6 TEM images of RR-TPE's(A, B) and commercial TPO(C)

A: RR-TPE obtained under inappropriate conditions
B: RR-TPE obtained under optimized conditions (EPDM/PP=80/20wt%)
C: Commercial TPO

Table 1. Mechanical properties of RR-TPE in comparison with commercial TPO

Property	unit	RR-TPE	Commercial
Specific gravity		1.10	0.90
Hardness (IRHD)		80	76
Tensile strength	MPa	6.7	6.9
Modulus at 100%	MPa	3.9	4.3
Elongation at break	%	380	440
Tear strength	N/cm	430	420
Compression set 70℃*22h,25%comp.	%	53	50

DEVELOPMENT OF AUTOMOTIVE PARTS WITH RR-TPE

To study the development of automotive parts, parts were selected which do not require higher function or excellent quality appearance. The produced amount of the RR-TPE, the material characteristics, and the processability of parts are used to determine the process condition and ratio of the RR-TPE.

Weatherstrip door glass run (channel portion)

Fig.7 shows the cross-section of weatherstrip door glass run. The roles of door glass run are to seal door glass against wind or rain and to guide the ups and downs of door glass. The compression set performance is required of the lip portion in order to seal glass. On the other hand, the function of the channel portion is to fix itself on window sash therefore higher compression set performance is not as critical as compared with the lip portion. Therefore, the application of the RR-TPE was investigated for the channel portion. In this case, possibilities were confirmed that the RR-TPE could be substituted for virgin TPO and that the part's performance is similar to the part using virgin TPO. However, in consideration of the performance of glass run and the produced amount of the RR-TPE, the application of the RR-TPE in the way of blending with the current TPO is being investigated.

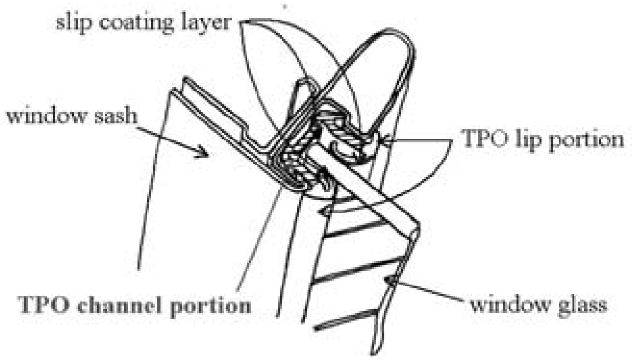

Fig.7 Schematic cross section of weatherstrip door glass run

Others

Other applications of the RR-TPE to replace virgin TPO parts will be investigated in the near future (Fig.8). The properties such as compression set, hardness, extruded surface roughness, etc. are important in most cases, so that the compounding recipes of the RR-TPE and added ratios to virgin TPO must be examined.

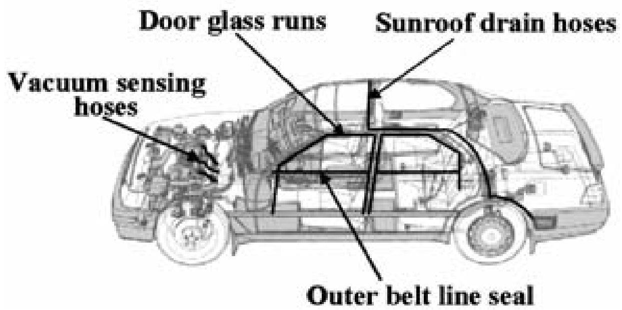

Fig.8 Applications of the RR-TPE to automotive parts

3. CONCLUSION

A new rubber recycling technology to produce a thermoplastic elastomer based on sulfur crosslinked EPDM waste was developed using a shear flow stage reactor. Automotive parts are being developed and are going to be produced with the RR-TPE by this new technology.

1. It is possible to produce TPE based on sulfur crosslinked EPDM waste by continuous devulcanizing, blending with PP, and dynamic vulcanizing processes in a short time.

2. The RR-TPE obtained under optimized conditions exhibits good material properties comparable to those of the commercial TPO. These properties are due to a suitably formed phase structure (i.e., re-vulcanized EPDM domains dispersed in PP matrix).
3. The RR-TPE can be applied to automotive parts similarly to virgin TPO, and part performance requirements are achieved.
4. This recycling technology is very useful in point of converting waste rubber with a limited range of uses into general-purpose materials such as thermoplastic elastomer or rubber toughened plastics. Little profit can be made on this technology in the present situation, but this technology can contribute to both protecting environment and saving resources toward zero emission society forecasted in the near future.

Areas for future improvement of the RR-TPE based on sulfur crosslinked EPDM are the following.

1. Further improvement of mechanical properties. (Aim at high flow characteristics, lower hardness, lower compression set, and so on)
2. Further improvement of surface appearance and application to design surfaces. (Solution of surface spots caused by roughly dispersion of EPDM and PP or material degradation)

Further expansion of applications to investigate use of this recycling technology includes the following.

1. Production of RR-TPE or rubber toughened thermoplastics from various types of vulcanized rubbers has been confirmed experimentally other than EPDM including sulfur crosslinked natural rubber (NR), styrene-butadiene rubber (SBR), and acrylonitrile- butadiene rubber (NBR). Modification of the RR-TPE 's for applying to products should be investigated.
2. Application to waste thermoplastics: sprue or runner waste can be blended with rubber to produce RR-TPE's.
3. Application to materials removed from end-of life vehicles (ELV).

4. ACKOWLEDGMENTS

This work was partly carried out by joint research and development with Toyota Central Research and Development Labs. Inc., Toyota Motor Corp., and International Center for Environmental Technology Transfer in 1999-2001, commissioned by the Ministry of Economy, Trade and Industry of Japan.

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