

Development of PVC-free Mastic Sealer

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ABSTRACT

A PVC-free mastic sealer has been developed as a recyclable, environmentally friendlier material. Core-shell structure type acrylic resin was selected to replace PVC resin due to its compatibility with the plasticizer in the formulation. The required mechanical properties could not be achieved by simple replacement of the PVC resin with the equivalent amount of acrylic resin. Therefore, we investigated a change in the synthetic rubber component of the sealer to increase strength. As a result, we found that the addition of an SBR rubber with high tearing strength provided the mastic sealer with high strength and high elasticity properties. The fluidity and contamination properties were improved by changing 42% of the calcium carbonate to a surface-treated calcium carbonate and using an inorganic vulcanization catalyst. This provided the PVC-free mastic sealer with the same performance properties as the conventional mastic sealer. Improving the adhesion to aluminum was required due to the increasing application of aluminum for automobile body panels. We focused on the adhesion performance of the sealer by evaluating its absorption of the aluminum stamping oil in the development. Improved adhesion properties to the aluminum was achieved with a solvent that had a low molecular weight of 170. Due to this study, we achieved a PVC-free mastic sealer that is approximately 30% lower in cost than the conventional PVC sealer, which can be used on both aluminum and steel body panels.

1. Introduction

With the enactment of the Automobile Recycling Act in Japan, automobile manufacturers are faced with demands to develop technology to reduce the environmental load with automobile designs that use recyclable materials. As a result, it has become necessary to make further efforts for automobile recycling⁽¹⁾. Conventional automobile centers for material recycling consists of breaking down automobiles into components as much as possible and then reusing components or recycling metals, resins and other materials into reusable raw materials⁽²⁾. Thus far, an effective recycling

rate of 85% has been achieved. However, in order to raise the effective recycling to 95% by 2015 as mandated by EU and Japanese regulations, it will be necessary to recycle shredder dust (hereafter “ASR”) into energy by incineration. The main components of ASR include metal, resin, rubber, adhesive, and sealers used in the vehicle. Polyvinyl chloride (hereafter “PVC”) has conventionally been used in the mastic sealer, which is a body sealer. However, when incinerating ASR that contains PVC, a dioxin is produced causing chlorine gas-induced corrosion of the incineration facilities, which is a concern⁽³⁾. This makes it necessary to reduce the amount of PVC in order to lower the chlorine concentration in the ASR

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as much as possible.

Low-strength and high-strength types of mastic sealer are used according to requirements of the outer panel stiffness and deformation of the part. The low-strength type can be substituted with NBR type rubber spot sealer. However, it is necessary to develop a new formulation for the high-strength type.

2. Development Goals

Mastic sealer is mainly applied between the skin and the stiffener in the doors, trunk, hood, roof and other parts. This mastic sealer is cured by baking in the paint process. It is applied to prevent interference between the skin and the stiffener to ensure sufficient skin panel stiffness. High-strength type mastic sealer is used when the outer panel stiffness is especially required (Fig. 1). The shear strength of a conventional high-strength mastic sealer is approximately 0.7 to 0.8 MPa. This strength is provided by the PVC component. A key point in developing PVC-free materials

Table 1 Main ingredients of mastic sealer

Main ingredients	Form	Role
Rubber	SBR/NBR	Elongation; Modulus
Vulcanization aid	Organic	Vulcanization for rubber
Resin	PVC	Strength
Filler	CaCo3	Workability
Plasticizer	DINP	PVC plasticizer; Viscosity adjustment
Solvent	High molecular weight	Viscosity adjustment

was to increase the mastic sealer strength that was set at 0.8 MPa.

In addition, the application of aluminum to the hood and other parts are increasing in order to reduce the vehicle weight. Aluminum has a lower adhesion adaptability, so conventional low-cost mastic sealer for steel sheets cannot be applied. Therefore, the goal for the development of a PVC-free mastic sealer was a low-cost sealer that can be used on both steel and aluminum sheets.

PVC resin is a low cost material that has superior physical properties such as strength and adhesion adaptability. In order to replace PVC resin, components other than the resin were changed in order to maintain these physical properties. The goal was set at maintaining the same performance as the current PVC materials at an equal or lower cost.

The key points when developing a high-strength, high elasticity PVC-free mastic sealer were set as follows:

- (1) Technology for maintaining high strength with a PVC-free formulation
- (2) Bonding to aluminum sheet
- (3) Reducing the cost

3. Material Formulation

3.1. PVC Replacement and Improvement of Physical Properties

Table 1 shows the main components of the current mastic sealer and the roles of each component.

D-isononylphthalate (hereafter “DINP”) has conventionally been used as the plasticizer in the mastic sealer. DINP is a low cost, general-purpose plasticizer that is a large percentage of the formulation and was used as the plasticizer in this development.

In developing a PVC-free mastic sealer, the formulation was studied as follows in order to satisfy the mastic sealer performance requirements.

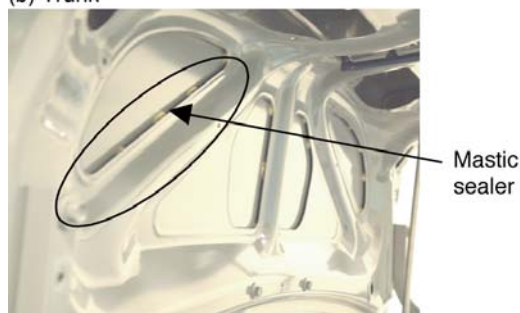
3.1.1. Selection of the PVC replacement resin

Acrylic resin was selected to replace the PVC resin material. Acrylic resin has an excellent compatibility with the general-purpose plasticizer DINP, so it is an appropriate replacement resin for PVC resin. The high-strength type mastic sealer has a PVC resin content of approximately 10%, so replacement with the same amount of acrylic resin was attempted. Figure 2 shows the change in the viscosity of a sealer that had the same amount of general-purpose acrylic resin polybutylmethacrylate (hereafter “PBuMA”) as PVC. The viscosity increased after storage (40 °C, 168 hours)

(a) Applied parts



(b) Trunk



(c) Door

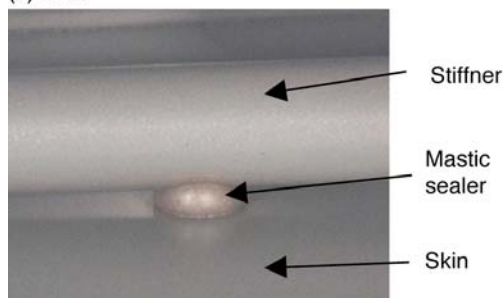


Fig. 1 Examples of application of mastic sealer

compared to the initial viscosity. The results showed that simply changing to PBUA causes a decrease in storage stability. Therefore, an acrylic resin formulation with a core-shell structure that uses polymethylmethacrylate (PMMA) that is known to have an excellent stability with DINP as the outer shell in combination with the general-purpose acrylic resin PBUA as the core was investigated. This formulation achieved the target storage stability as shown in Fig. 2. Based on these results, the decision was made to use acrylic resin with a core-shell structure as the replacement for PVC in the formulation.

Figure 3 shows the shear strength with the equivalent amount of core-shell structure acrylic resin as PVC resin. The results showed that replacement with the same amount of core-shell structure acrylic resin causes the shear strength to drop. Therefore, the decision was made to replace the PVC with the same amount of core-shell structure acrylic resin and to adjust the strength by some other formulation change.

3.1.2. Synthetic rubber formulation

An attempt was made to improve the mechanical characteristics with the synthetic rubber. NBR or SBR type synthetic rubber compounds have conventionally been used as the synthetic rubber. NBR has a high polarity, which makes it suitable for use in combination with PVC resin that has a high polarity. However, phase separation occurred and the strength dropped as shown in Fig. 3, when used together with acrylic resin that has a low polarity. Therefore, a SBR type synthetic rubber compound with a low polarity was used. There are different grades of SBR type synthetic rubber compounds each having different mechanical characteristics such as strength and hardness. Therefore, the change in shear strength of the mastic sealer when changing the strength

Table 2 Properties of rubber compound

Grade (strength)	Low	Middle	High
Tearing strength (kN/m)	45	65	75
Hardness (JISA)	65	80	90

grade of the synthetic rubber compound was investigated. Table 2 shows the tearing strength and hardness of the synthetic rubber compounds used in this study.

Figure 4 shows the relationship of the tearing strength of the synthetic rubber compound versus the shear strength of the mastic sealer containing the synthetic rubber compound.

This figure showed that the tearing strength of the SBR type synthetic rubber compound has a direct relation to the shear strength of the mastic sealer. Therefore, the target shear strength can be obtained by formulating a SBR type synthetic rubber compound with a tearing strength of 75 kN/m or more. In addition, the rubber content can be reduced and with the low cost of SBR type synthetic rubber compounds it provides a cost effective way to improve the shear strength and other mechanical characteristics.

Based on these results, DINP was selected as the plasticizer, acrylic resin with a core-shell structure was selected to replace the PVC resin, and a high-strength type SBR synthetic rubber compound was selected as the rubber component.

3.1.3. Pretreatment contamination

In order to obtain high strength by cross-linking the rubber in the curing process, it was necessary to increase the amount of vulcanization catalyst used for SBR type synthetic rubber compounds. However, increasing the vulcanization catalyst amount contaminated the alkali degreasing solution in the pretreatment process.

In the pretreatment process, the mastic sealer is sent through the pretreatment tank before curing, so care must be taken to prevent solution contamination by the extracts from the sealer. Within the pretreatment process, the alkali degreasing solution is particularly susceptible to solution contamination. Yellowing of the solution due to the mastic sealer formulation was a concern. Therefore, an investigation of each component in the formulation was immersed in a

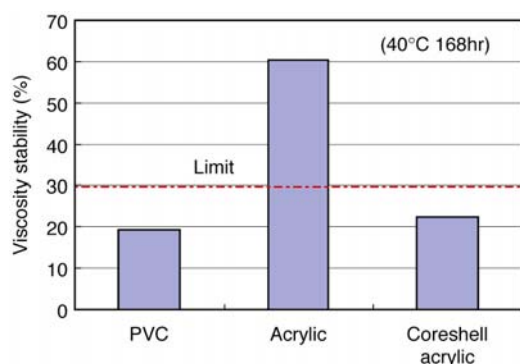


Fig. 2 Influence of different resins on viscosity stability

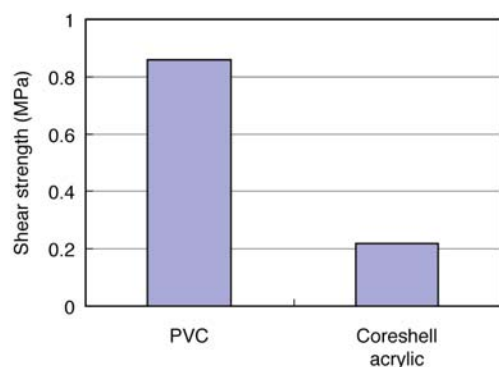


Fig. 3 Influence of different resins on share strength

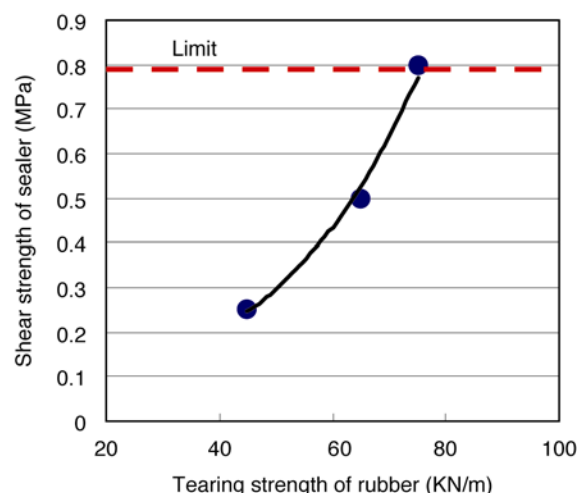


Fig. 4 Relationship of tearing strength of rubber compound and strength of sealer

45 °C degreasing solution for two minutes and the solution was checked for color change. Figure 5 showed the change in color when the vulcanization catalysts were immersed in an alkali degreasing solution and the results when the mastic sealer containing the vulcanization catalyst were immersed in the alkali degreasing solution. The vulcanization catalysts generally used thus far have been organic. The immersion test using only the vulcanization catalyst showed that the organic vulcanization catalyst dissolved and yellowed the alkali degreasing solution. Therefore, the formulation was changed from an organic catalyst that dissolved in the alkali degreasing solution to a chemically stable inorganic vulcanization catalyst.

3.1.4. Surface-treated calcium carbonate formulation

Using a high-strength synthetic rubber compound provided sufficient strength even when the synthetic rubber compound content was reduced. However, reducing the rubber compound amount increased the overall liquid component content of the sealer, which was found to increase the fluidity (sagging) when the temperature increased during the curing process. Sagging occurred because the overall liquid component content of the sealer increased, making the sealer more susceptible to drops in viscosity at higher temperatures. Therefore, improvement was attempted by changing the calcium carbonate, which is used in the formulation to adjust the viscosity. Calcium carbonate is included in particle condition as a solid within the mastic sealer paste. The viscosity of the sealer can be increased by the interaction of the liquid components with the solids. It is known that the intermolecular force within the sealer can be raised to further increase the viscosity by altering the surface condition of the calcium carbonate with the particle size and the surface functional group. In this development, the fluidity of the sealer was improved by replacing part of the conventional calcium carbonate with organically surface-treated calcium carbonate in order to increase the intermolecular force with the liquid components that would ultimately increase the viscosity at high temperatures.

	Conventional	Newly developed
Vulcanization aid only	Organic vulcanization aid 	Inorganic vulcanization aid 
Mastic sealer	Mastic sealer with organic vulcanization aid 	Mastic sealer with inorganic vulcanization aid 

Fig. 5 Pretreatment test

Fluidity was evaluated according to ASTM D2202 and the results are shown in Fig. 6.

When the high-strength synthetic rubber compound was used with conventional non-surface-treated calcium carbonate it resulted in sagging of 8 mm. However, increasing the ratio of surface-treated calcium carbonate to 42% of total calcium carbonate reduced the sagging amount to 0 mm; while still maintaining the same workability as the conventional mastic sealer.

As a result, the decision was made to use a filler formulation fortified with 42% surface-treated calcium carbonate.

3.2. Adhesion Performance

Tests were conducted to confirm the adhesion performance to steel sheet with the PVC-free mastic sealer formulation. Figure 7 shows the shear strength test results. The SPCC material and GA material both resulted in cohesive failure, indicating that sufficient adhesion performance was obtained.

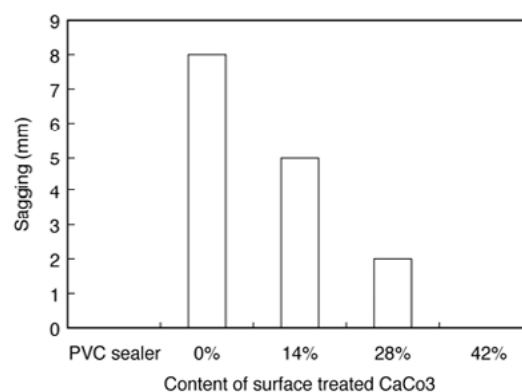


Fig. 6 Influence of surface treatment CaCO₃

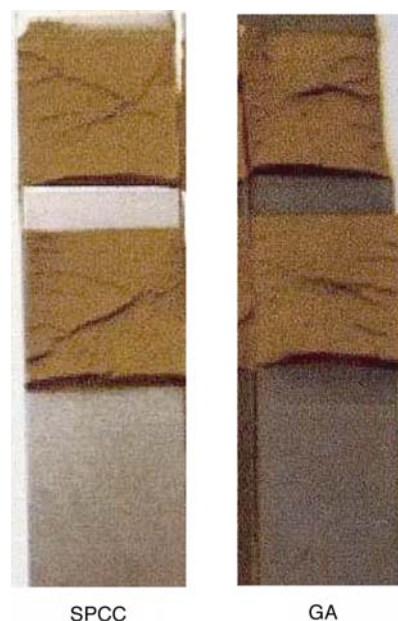
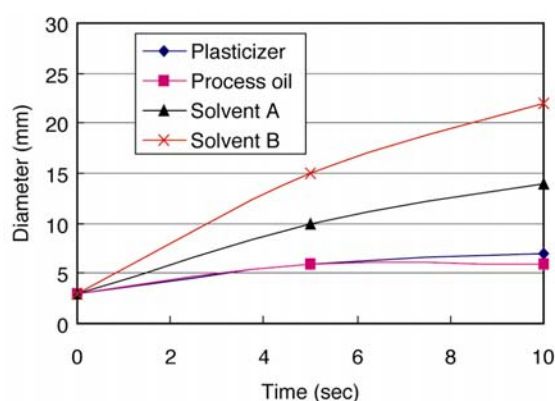


Fig. 7 Shear strength test for steel

4. Adhesion to Aluminum

Sealers in the welding process are used on oily surfaces. The conventional mastic sealer was designed to obtain adhesion by absorbing the stamping oil on the steel sheet surface so that the adhesive component inside the sealer contacts the material surface. Different stamping oils are used for aluminum than for steel sheets. The stamping oil for aluminum is not sufficiently absorbed by the mastic sealer developed for steel sheets, so adhesion cannot be obtained. Therefore, the goal of the development of a PVC-free mastic sealer was to improve adhesion by absorbing the aluminum stamping oil. First, improving the wettability between the



		Plasticizer	Process oil	Solvent	
Drop diameter (mm)	5sec	6	6	A	B
	10sec	7	6	14	22
Molecular weight		400	500	250	170
Adhesion to Al		No good	No good	No good	OK

Fig. 8 Wettability test



Fig. 9 Shear strength test for Al

Table 3 Ingredients

	PVC	PVC-free
Rubber	SBR/NBR	High strength SBR
Resin	PVC	Acrylic
Filler	CaCo3	Surface treatmented CaCo3
Plasticizer	DINP	DINP
Vulcanization aid	Organic	Inorganic
Solvent	High molecular weight	Low molecular weight

Table 4 Properties

	Conventional	Newly developed
Hardness	27	27
Shear strength (MPa)	0.69	0.8
Elongation (%)	210	160
Density	1.41	1.4
Stability (40°C, 168hr)	○	○
Workability (170°C cure)	○	○
Adhesiveness (Fe)	○	○
Adhesiveness (Al)	×	○

liquid components of the mastic sealer and the stamping oil was investigated as a means of increasing the amount of stamping oil absorbed by the sealer. Investigation of the wettability of the plasticizer, process oil and solvents are the liquid components conventionally included in the mastic sealer formulation. Measurements were performed by dropping each component onto an aluminum sheet coated with stamping oil and then measuring the increase in the diameter of the drop after 5 seconds and 10 seconds. Figure 8 shows the results.

The solvents exhibited better wettability than the plasticizers and process oils, which have high molecular weights. The solvent with the lower molecular weight had the best wettability. The results indicated that using a solvent with a lower molecular weight that has a better wettability increases the amount of stamping oil absorbed into the sealer, which can improve the adhesion performance to aluminum. Figure 9 shows the shear strength test results for mastic sealer using a solvent with a molecular weight of 170. Cohesive failure resulted for each type of aluminum material that used a solvent with a higher than 170 molecular weight. Therefore, using a solvent with a molecular weight of 170 ensured sufficient adhesion to aluminum body panels.

5. Formulation Specifications

5.1. Formulation Specifications

The following specifications were determined as a result of the above formulation studies. The newly developed formulation achieved a cost reduction of 30% compared to the conventional PVC type mastic sealer.

5.2. Physical Property Values

Table 4 shows the various properties of the newly developed sealer. This shows that the newly developed PVC-free mastic sealer has the same performance as the conventional sealer.

6. Conclusion

The formulation was adjusted to develop an inexpensive, high-strength PVC free mastic sealer based on acrylic resin. The following results were obtained:

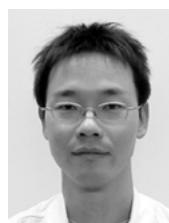
- (1) Acrylic resin with a core-shell structure was found to be suitable for developing a high-strength PVC-free mastic sealer.
- (2) The sealer strength was improved at a low cost by using a SBR type synthetic rubber compound with a high tearing strength in the formulation.
- (3) The vulcanizing catalyst had the greatest effect on contamination of the degreasing solution and was improved by changing from an organic to an inorganic vulcanizing catalyst.
- (4) Changing 42% of the calcium carbonate filler to a surface-treated calcium carbonate made it possible to increase the intermolecular force within the system, which improved the fluidity.
- (5) Adhesion performance to aluminum sheets were ensured by selecting a solvent with a molecular weight of 170, which has excellent compatibility with the aluminum stamping oil.

This newly developed high-strength PVC-free mastic sealer for both steel and aluminum sheets was first applied to the S2000 released in 2003, making it the first such environmentally friendlier, PVC-free material technology to be applied to the mass production of an automobile.

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