Immersion Behavior of Automobile Shredded Residue in Surfactant Solutions and Detachment of Particulate Matter

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This study investigated the effect of the addition of wetting agents on automobile shredded residue (ASR) wettability, and found that the surfactants diisooctyl sodium sulfosuccinate (AOT) and sodium dodecyl sulfate (SDS) were effective to improve immersion of the ASR, due to their ability to reduce the solution surface tension and the contact angle of ASR. Urethane foam is a bulky compound in ASR and its immersion and wetting behavior showed similar changes as those of the ASR samples. With SDS the surface wettability of urethane was improved. The surfactant solutions were also effective in the detachment of the entrapped particles from the agglomerate of entangling fiber like materials. The effects of the surfactant concentrations on ASR wettability and the amount of detached particles are described.


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1. Introduction

In Japan, the automobile recycling law enacted in January 2005 obligates the proper disposal of automobile shredded residue (ASR), and improvement in the ASR recycling ratio is necessary to meet the automobile recycling ratio set by the Ministry of Economy Trade and Industry, and to conserve landfill sites.

This ASR, containing burnable materials like urethane, cloth fibers, plastics, and wood chips, is a potential source of solid fuel when unburnable metals and polyvinyl chloride (PVC) are removed. The TACUB jig is widely used for coal cleaning and Tsunekawa et al. have reported that this jig is very useful to separate relatively low density particles such as plastics1) and have demonstrated that highly efficient jig separation by type of plastic component in waste office automation equipment recycling is possible in pilot-scale tests.2) The authors are now investigating the recovery of valuable materials from ASR using this jig. The jig would be able to separate metals of heavy density, plastics of light density, and PVC of middle density. Jig treatment is a wet gravity separation method but the crushed ASR does not immerse well into water due to its strong hydrophobic properties. Further, plastic and metal particles are entrapped in agglomerates of entangling fiber like materials derived from components such as seat covers. Therefore, the control of the ASR wettability and detachment of the entrapped components are needed prior to the ASR jig treatment. This study describes the effect of the addition of wetting agents on ASR wettability and detachment of the entrapped particles.

2. Materials and Reagents

2.1 Materials

End-of-life automobiles are dismantled to recover valuable parts such as handles, engines, and metals and after dismantling the rest is shredded to reduce the volume. After removing valuable metals such as iron, copper, and aluminum from the shredded product the residue is called ASR. Figure 1 shows the material compositions of ASR samples obtained from one dismantling facility. In this company ASR is gathered from several recovering points on the waste automobile treatment line, samples one to four, and the compositions vary. The material compositions were measured by hand picking. The ASR samples are composed of plastics as a major component and metals, sand, and glass as minor components; PVC is measured separately from the other plastics as PVC must be removed from the burnable components before it can be used as solid fuel because of chlorine-containing polymers. In the plastic component, the volume ratio of urethane foam used as seat cushions is high.

The ASR sample, No. 3 of Fig. 1, was crushed by a turbo mill, Georgens G-130, and used in this study since the size of the ASR components ranged from several mm to a few dozen cm and the samples contain un-liberated particles. The
most of the crushed product was less than 1 cm and liberation of materials, e.g. metal wire and covering material from electric wiring harness, was confirmed. The turbo mill crushes materials by vortex flow of extremely high speeds and turbo mill crushing was selected since this machine can crush both brittle and elastic substances containing thermoplastic resin. Crushed sample contains entangling fiber like materials derived from components such as seat cover cloth. Plastic and metal particles are entrapped in agglomerates of entangling fiber like materials.

Further, cubes of 1 cm on a side of urethane foam, Inoac Corp., were used for immersion experiments; and urethane plate, Nisshinbo industries Inc., urethane elastomer (0.5 mm thick), was used for contact angle measurements.

2.2 Reagents
Acetone, ethanol, and methanol solutions, Wako pure chemical industries Ltd., diluted by water were used in this study. The organic solvent content shows the volume ratio of the organic solvent before the mixing of the organic solvent and water e.g. with 80 cm$^3$ of organic solvent and 20 cm$^3$ of water mixed is shown as 80%.

Tannic acid (TA), dioisooctyl sodium sulfosuccinate (aerosol OT, AOT), polyvinyl alcohol (PVA), poly-oxethylene dodecyl ether (POEDE), and sodium dodecyl sulfate (SDS), Wako pure chemical industries Ltd., which are wetting agents for plastic flotation, diluted with water in 100 ppm, 250 ppm, 500 ppm, and 1000 ppm concentrations were also tested.

3. Experimental Method

3.1 Surface tension measurements of solutions
Surface tensions of solutions were measured by Kuruss K100 at 25°C using a Pt plate method.

3.2 Immersion experiments with crushed ASR and urethane foam
Crushed ASR (weight 0.15 g) and 1 cm$^3$ of urethane foam were placed on the solution surface of a 50 cm$^3$ beaker, solution volume 50 cm$^3$, and immersion states after 10 minutes and 24 hours were observed.

3.3 Contact angle measurements of crushed ASR and urethane plate
The contact angle of crushed ASR was calculated using the results of sorption measurements, one of the contact angle measurement methods for powder samples, using Kuruss K100, and the contact angle of a urethane plate was measured by a captive bubble method. The crushed ASR after drying, at 40°C and for 24 hours, was used for the sorption method as described below. Crushed ASR, 0.5 g, was filled into a test column having mesh bottom and 2 mm from the bottom of column was immersed into the solution within one second and pulled up until where the bottom of the column contacts the solution surface. This operation was carried out automatically by the equipment. Changes in suction weight of the solution by the samples from the bottom mesh of the column with time were measured. This experiment was carried out at 25°C.

For powder samples and where the penetration pathways of solution in the powder of the column are regarded as bundles of capillaries with a mean capillary radius $r$, a modified Washburn equation$^5$ can be used as follows.

$$M^2/t = (c \cdot r)(S \cdot \varepsilon)^2 \cdot \rho_L^2 \cdot \gamma_L \cdot \cos \theta)/2\eta_L$$ (1)

$M$: suction weight of the solution
t: time of flow$c$: constant to estimate the tortuous path in the capillaries$S$: cross-sectional area of the column$\varepsilon$: porosity of the powder in the column$\rho_L$: density of the solution$\gamma_L$: surface tension of the solution$\theta$: advancing contact angle$\eta_L$: viscosity of the solution

The term $(c \cdot r)$ is a constant which depend on packing property of the solid powder with the dimension of length; $S$ is the cross-sectional area of the column; and $\varepsilon$ is the porosity of the powder in the column and these values are assumed to be constant. Densities and viscosities of organic solutions use data as reported in literature. The values of the density and viscosity of water (25°C) were used as the values of surfactant solutions since the measured values of surfactant solutions were very similar to those of water. Equation (1) can be rewritten as eq. (2) and numerical values of the left-hand side of eq. (2) can be calculated using experimental and literature data. As the terms $(c \cdot r)$ and $(S \cdot \varepsilon)$ do not change when the packing conditions of the powder are similar, the values of the left-hand side changes with the variations in $\cos \theta$ and this value is shown as $\cos \theta$, arbitrary units (a. u.), in this paper.

$$M^2/2\eta_L/(t \cdot \rho_L^2 \cdot \gamma_L) = (c \cdot r)(S \cdot \varepsilon)^2 \cdot \cos \theta$$ (2)

The contact angle of urethane plate (0.5 mm x 10 mm x 20 mm) was measured by a captive bubble method. An air bubble generated from a syringe needle was adhered to the undersurface of urethane plate which was held in the solution. An photo of the bubble adhering to the urethane plate was taken by a digital microscope and the mean contact angle of the left and right sides of the bubble was calculated by an Dataphysics OCA15 plus.

3.4 Measurements of detachment ratios of particulate matter from crushed ASR sample and urethane foam
Easily detaching particles were removed from crushed ASR using a vibrating 5.6 mm sieve, amplitude 3 mm and for 3 minutes. The over 5.6 mm fraction contains entangling fiber like materials derived from components such as seat covers, and also contains plastic and metal particles being entrapped in agglomerates of entangling fiber like materials. The sample was dried at 40°C for 24 hours and 1.5 g was put on the solution surface of 50 cm$^3$ beaker filled with 50 cm$^3$ solution. After 40 minutes, including mechanical stirring for 5 minutes, the floating and sunk products were recovered and the weight was measured after drying; 1000 ppm of wetting agent solutions were used in this experiment.

Urethane foam piece, with adhering dark fine particulate matter, was selected by hand picking from the ASR before
crushing and used in this experiment. Urethane foam having 1 cm$^2$ of unclean surface, with adhering dark fine particulate matter, was put on the solution surface. After 40 minutes, including mechanical stirring for 5 minutes, the color of the urethane foam facing the solution surface was observed.

4. Results and Discussion

4.1 Immersion experiments of crushed ASR and urethane foam

Immersion experiments with crushed ASR samples were carried out, and urethane foam, which is a major component of ASR, was also tested. Figure 2 shows a photo when (a) the sample floats on the solution surface (water, 10 min) and (b) the sample has immersed into the solution (acetone 100%, 10 min). Figure 3(a) and 3(b) show the situation of crushed ASR samples after 10 minutes and 24 hours. In Fig. 3 the open circles and triangles show that the sample has immersed into the solution within 10 minutes and 24 hours (Fig. 2(b)) and crosses show that the sample floats on the solution surface after 24 hours (Fig. 2(a)). In Fig. 3, the horizontal and vertical axes show the concentrations of reagents and solution surface tension. The organic solvents mixed with water at various ratios to change the solution surface tension were used in the immersion experiments as typical solutions having low surface tension. It was found that the immersion behaviors in organic solvent solutions, in Fig. 3(a), were similar and immersion occurred rapidly when the surface tension was low; the surface tension decreased with increasing solvent concentration. Rapid immersion, within 10 minutes, was observed in solutions where the surface tension was below 35 mN/m. These results indicate that a reduction in surface tension is effective to immerse the sample rapidly. Figure 3(b) shows the results with wetting agent solutions. With TA and PVA, the surface tension changed little from 0 to 1000 ppm and the samples did not immerse. With AOT and POEDE, the surface tension decreased with increasing agent concentration and samples immersed rapidly at low surface tensions (below 40 mN/m). With SDS, samples immersed within 10 minutes when the surface tension was 60 mN/m. The immersion behaviors of AOT 100 ppm (47.60 mN/m) and SDS 1000 ppm (49.25 mN/m) were different although the

Fig. 2 Photos of immersion tests of crushed ASR of (a) sample floats on the solution surface (water, 10 min), and (b) sample is immersed into the solution (acetone 100%, 10 min).

Fig. 3 Immersion behavior of ASR. (a) Crushed ASR with organic solvent solutions, (b) crushed ASR with wetting agent solutions, (c) urethane foam with organic solvent solutions, (d) urethane foam with wetting agent solutions.
surface tension values were similar. This shows that the immersion behavior of samples cannot be predicted by solution surface tension alone.

Figure 3(c) and 3(d) show the situation of urethane foam after 10 minutes and 24 hours and the results show similar behaviors to that of crushed ASR. Urethane foam was immersed below the surface tension of 30 mN/m with organic solvent solutions.

4.2 Contact angle measurements of crushed ASR and urethane plate

The contact angles with various solutions of crushed ASR and urethane plate were measured. Figure 4 shows the relationship between surface tension of solution and the cosine $\theta$, where $\theta$ represents the contact angle of the sample. Figure 4(a) and 4(b) are the results for crushed ASR samples and urethane plate, respectively. The cosine $\theta$ value increased with decreasing solution surface tension indicating that the contact angle decreased with decreasing surface tension and that the wettability of the sample increased. This behavior was observed in both the crushed ASR and urethane samples. In Fig. 4(a), the behaviors of cosine $\theta$ for ethanol, methanol, and AOT are also similar. With SDS, the value of the surface tension where cosine $\theta$ begins to increase was different from that of the other solutions. Similar trends are observed in Fig. 4(b).

Zisman$^6$ investigated the surface wettability of hydrophobic solids such as polytetrafluoroethylene using solutions which are a homologous series of organic liquids, e.g. n-alkane solutions. Zisman defined the critical surface tension, $\gamma_c$, as the value of the surface tension where the cosine $\theta$ reaches one, $\theta$ is zero, and suggested that $\gamma_c$ represents an innate value correlating with sample wettability. In coal flotation studies, $\gamma_c$ measurements using ethanol-water mixtures rather than pure organic solvent are common and this is used as an index for evaluating particle floatability.$^7$ The $\gamma_c$ of urethane plate can be determined and the $\gamma_c$ obtained with ethanol and AOT are expected to show similar values, with the value of SDS higher than of ethanol and AOT in Fig. 4(b). Since solutions such as ethanol and methanol would not change the urethane surface properties drastically, it is considered that the increase in cosine $\theta$ is caused by a decrease in solution surface tension, and this would also apply for AOT. For SDS, it is assumed that the SDS changes the solid surface properties by surface modification and the solid surface becomes relatively more hydrophilic than in the native state. It is considered that the critical surface tension of SDS is affected by both solution surface tension and specific absorption of SDS to the solid. It is assumed that this specific absorption causes the increase in wettability by adsorbing hydrophobic groups on the solid phase and orienting hydrophilic groups to the liquid phase. The authors are presently investigating the SDS adsorption mechanism of urethane.

Immersion wetting occurs when the contact angle is below 90 degrees, a cosine of $\theta$ is larger than zero, and this is explained by Young’s equation. The contact angle of ASR cannot be calculated because the capillary radius is unknown and all contact angle values of urethane plate in various solutions are below 90 degrees. This shows that urethane plate is subject to immersion wetting. Urethane components contained in ASR is the very porous urethane foam and the agglomerates of entangling fiber like materials which also contain many voids. The apparent contact angle of complex substances can be calculated by a summation of the values obtained by multiplying the area ratio of each component such as air, urethane, and metals by the contact angle of the component.$^9$ The apparent contact angle increases with increasing void ratio and it is considered that the difficulty of immersion of crushed ASR in water may arise due to the porous characteristics.

4.3 Detachment of the particulate matter from the agglomerate of entangling fiber like materials of crushed ASR or urethane foam

A urethane foam with adhering dark fine particulate matter was put on the solution surface with the dirty surface attaching to the solution surface. After 40 minutes, including mechanical stirring for 5 minutes, the colors of the urethane foam facing the solution surface were observed. Figure 5 shows photos of the samples after the experiments. The color when treated with water did not change while the color
with ethanol 100% solution became lighter since the dark particles detached. Color changes were observed for samples where the sample was immersed into the solution. This result shows that the fine particles adhering to urethane foam can be removed when samples are immersed into the solution.

Crushed ASR was put on the solution surfaces and after 40 minutes, including mechanical stirring for 5 minutes, the floating and sunk products were recovered and the weight was measured after drying. Floating products contain light components and consist of mainly fiber like materials derived from components such as seat covers and urethane foam used in seat cushions, and sunk products were composed of small particles of plastics, metal, sand, and glass. Table 1 shows the results of the tests, an increase in the sunk product ratio means improved detachment of particulate matter from the aggregate. The results are average values of 3 tests and the maximum deference in the values was less than 10%. Sink ratios in water and PVA were very low and the wettability of crushed ASR in these solutions was also low. High sink ratios were achieved with POEDE, AOT, SDS, ethanol, and acetone. It was found that detachment of particulate matter from aggregate was possible if crushed ASR is immersed rapidly into the solution.

Crushed ASR sample, cloth and plastics collected from ASR samples, and the floating and sunk products of the above experiments, treated with AOT and ethanol, were ashed at 815°C for 2 hours, JIS Z7302-4 (Densified refuse derived fuel Part 4: Test method for ash). There were 71% and 29% of burnable and un-burnable matter (ash) respectively in crushed ASR sample. The un-burnable matter (ash) contents of burnable materials such as cloth, covering of electric wiring harness, and ridged and non-ridged plastic particles were 10 to 18% since these materials contain additives, like thermostabilizer, which are cause of ash. Table 2 shows the analytical results of floating and sunk products, and un-burnable contents for ethanol and AOT show similar values, about 13% for floating products and 53 to 56% for sunk products, it is suggested that the burnable material content in the floating product is very high. This suggests that the particle detachment method here can separate the source materials for solid fuels such as fiber like materials and urethane foam as floating product and particulate matter as sunk product.

5. Conclusions

Automobile Shredded Residue (ASR) is composed of plastics as the major component and also metal, glass, and sand. Plastics include the voluminous urethane foam. It was found that the immersion behaviors of crushed ASR and urethane foam are improved by decreasing the solution surface tension and surface modification also influences the immersion behavior.

The immersion behavior of crushed ASR is associated with the changes in cosine of θ and the behavior of urethane is similar to that of crushed ASR. These results show that wettability predictions are possible using urethane samples instead of crushed ASR and that the immersion behavior is greatly affected by the wettability of the urethane component. Detachment of particulate matter from aggregate was possible when crushed ASR is rapidly immersed into the solution.

Acknowledgment

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![Fig. 5 Changes in color of dirty urethane surface. (a) water, (b) 60% ethanol, (c) 80% ethanol, (d) 100% ethanol.](a) (b) (c) (d)

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<th>Table 1</th>
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