

Comparison between dismantlability and thermal behavior of adhesives containing various inorganic/organic salts

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Abstract

The authors previously showed that epoxy adhesives containing various salts such as ammonium perchlorate were dismantled at lower temperature than filler-free epoxy adhesives. These adhesives are expected to be used as dismantlable adhesives. In this fundamental study on dismantlable adhesives, we conducted differential scanning calorimetry (DSC) for 13 types of filler-containing adhesives, and compared the observed thermal behaviors and dismantlabilities. In the DSC results for filler/adhesive mixtures with comparatively high dismantlabilities, which completely lose adhesion strength at lower than 280°C (dismantlement temperature $\leq 280^\circ\text{C}$), the exothermic peak temperatures (T_{exo}) and/or the endothermic peak temperatures (T_{endo}) tended to shift to lower values compared with the temperatures for the unmixed adhesive and individual fillers. In contrast, no such shifts in T_{exo} and T_{endo} were observed in mixtures with low dismantlabilities (dismantlement temperature $>280^\circ\text{C}$). Thus, the thermal behaviors differ depending on the dismantlability, so we consider that the dismantlabilities of adhesives as a result of chemical reactions can be qualitatively discriminated using DSC.

Keywords : dismantlable adhesive, epoxy adhesive, construction adhesive, ammonium perchlorate, DSC.

1. Introduction

Adhesives that do not lose much adhesivity under a high load for a long time, or construction adhesives, are used in various applications, for example, to join construction materials or automobile and airplane components. Carbon fiber reinforced plastics (CFRPs) have recently been considered as a constituent material of automobile bodies. However, welding cannot be used to join CFRPs and metallic materials; therefore, they are joined using construction adhesives. One of the drawbacks of joining with adhesives is the difficulty in dismantlement, which poses a problem when recycling. Hence, there might be an increasing demand for adhesives that have high strength but that can be easily dismantled under the

application of external stimuli such as heat.

Previously proposed dismantlable adhesives contain thermally expandable graphite^{1),2)} or thermally expandable microcapsules^{3),4)} as fillers. These adhesives are designed to physically lose adhesivity when the fillers expand on heating. On the other hand, in the authors' past studies⁵⁾⁻⁷⁾, metal plates joined with adhesive containing various salts were heated and retained at various temperatures, and the dismantlement temperature at which the plates peeled off was determined by visual inspection. The results showed that adhesives that contain salts such as ammonium perchlorate have lower dismantlement temperatures than do adhesives with no salt added. Since ammonium perchlorate is a highly

chemically-reactive material used as a feedstock of rocket propellants^{8)–10)}, the adhesive will have been dismantled by its reaction. This type of adhesive is a new category of adhesives that have dismantlability originating from chemical reactions with the filler, and such adhesives are different from those containing thermally expandable materials. These adhesives are expected to have new applications in energetic materials.

In the present fundamental study on dismantlable adhesives containing chemically reactive salts, differential scanning calorimetry (DSC) was performed on mixtures of an adhesive and various salts, and the correlations between thermal behavior and dismantlability were investigated.

2. Experimental

2.1 DSC measurements

An epoxy resin (bisphenol A epoxy resin, Epicoat 828, Japan Epoxy Resins Co., Ltd.) and a curing agent (modified aliphatic polyamine, Adeka Hardener, Adeka Corp.) were mixed, maintained under low pressure at room temperature for 24 h, and then heat-cured for 1 h at 80°C. The heat-cured adhesive and one of 13 fillers were finely ground and mixed at a ratio of 1 mg of adhesive to 2.1×10^{-6} mol of filler in a nitrogen glove box (oxygen concentration less than 0.05 vol% and humidity of 5 RH% or less) to prevent absorption of moisture by the samples.

The following fillers were used in this study: methylamine hydrochloride (Tokyo Chemical Industry Co., Ltd.), anilinium hydrochloride (Sigma-Aldrich Japan K. K., 98%), 4-aminophenol hydrochloride (Tokyo Chemical Industry Co., Ltd.), m-aminobenzoic acid hydrochloride (Wako Pure Chemical Industries, Ltd., 95%), *trans*-4-aminocyclohexanol hydrochloride (Sigma-Aldrich Japan K. K., 97%), cyclohexylamine hydrochloride (Tokyo Chemical Industry Co., Ltd.), cyclohexylamine nitrate (Showa Chemical Co., Ltd., 98.5%), cyclohexylamine hydrobromate (Wako Pure Chemical Industries, Ltd., 98%), cyclohexylamine sulfate (Showa Chemical Corp., Ltd., 98.5%), ammonium chloride (Wako Pure Chemical Industries, Ltd., 99.5%), ammonium perchlorate (Wako Pure Chemical Industries, Ltd., 98.0%), potassium perchlorate (Wako Pure Chemical Industries, Ltd., 99.5%), and potassium nitrate (Wako Pure Chemical Industries, Ltd., 99.0%).

The samples were placed in a closed pressure-resistant capsule (P/N560–006 SUS15–Capsule, Seiko Instruments), sealed, and then the thermal behavior was investigated using DSC (DSC3100, Mac Science Corp.) at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ over the temperature range of 70 to 500°C. DSC measurements of unmixed adhesive and fillers as reference samples were performed under similar conditions.

2.2 Heating test (measurement of dismantlement temperature)

Mixtures of epoxy resin, curing agent, and filler were prepared in mass ratios of 7.7 : 2.3 : 1.0. The edges (25 mm \times 12.5 mm) of aluminum plates (width 25 mm, length 100

mm, thickness 1.6 mm) surface treated according to JIS K 6850¹¹⁾ were bound together with the adhesive. The bound aluminum plates were maintained under low pressure at room temperature for 24 h, and then heat-cured for 1 h at 80°C.

The bound aluminum plates were placed in an electric furnace and heated at various constant temperatures. The dismantlement temperature is defined as the temperature at which an aluminum plate drops under its own weight within 30 min from the start of heating and is used as a measure of the dismantlability of adhesives. The dismantlement temperatures in Table 1 were measured in a previous study, which was the origin of the patent applications^{12,13)}.

3. Results and discussion

Table 1 shows the exothermic peak temperatures (T_{exo}) and the endothermic peak temperatures (T_{endo}) of various adhesives examined using DSC.

3.1 DSC measurements of adhesives with high dismantlability

The thermal behavior of ammonium perchlorate/adhesive, which was determined to have high dismantlability (dismantlement temperature $\leq 280^\circ\text{C}$) in a previous study, is shown in Figure 1A. T_{exo} of the adhesive is observed at 347°C ; however, it is observed at 307°C when the adhesive is mixed with ammonium perchlorate. This indicates that exothermic decomposition of the adhesive progresses by the addition of ammonium perchlorate.

A similar result was obtained with methylamine hydrochloride, where T_{exo} of the mixture was observed at 323°C , which is lower than that without the filler (Figure 1 B). In addition, T_{endo} of methylamine hydrochloride was observed at 228°C , and T_{endo} of the mixture shifted toward a lower value (209°C).

Also in the case of the other filler/adhesive mixtures with dismantlement temperatures lower than 280°C , T_{exo} and/or T_{endo} tended to be lower than those for the individual adhesive or filler (Table 1).

3.2 DSC measurements of adhesives with low dismantlability

The thermal behavior of potassium perchlorate/adhesive, which was determined to have low dismantlability (dismantlement temperature $> 280^\circ\text{C}$) in a previous study, is shown in Figure 2A. This figure shows that T_{exo} and T_{endo} of potassium perchlorate/adhesive are 349°C and 301°C respectively, and are unchanged from those of the adhesive ($T_{\text{exo}} = 347^\circ\text{C}$) and potassium perchlorate ($T_{\text{endo}} = 301^\circ\text{C}$). A similar trend was observed with potassium nitrate (Table 1).

In the case of the cyclohexylamine sulfate/adhesive mixture (Figure 2B), the endothermic peak originating from cyclohexylamine sulfate shifted to a lower temperature, but no change in the thermal behavior was observed at temperatures below T_{exo} of the pure adhesive.

Combining these results with the results in section 3.1,

Table 1 Results of heating tests and differential scanning calorimetry measurements

Additive	Heating test results ^{5)–7)}		DSC results	
	Dismantlement temp. [°C]	T_{endo}^* [°C]	T_{exo} [°C]	T_r^{**} [°C]
Adhesive alone (additive free)	340	–	347	347
Methylamine hydrochloride	270	209 (228)	323	209
Anilinium hydrochloride	190	165 (183)	327	165
4-Aminophenol hydrochloride	250	235 (264)	319	235
<i>m</i> -Aminobenzoic acid hydrochloride	290	– (264)	320	320
<i>trans</i> -4-Aminocyclohexanol hydrochloride	270	219 (228)	330	219
Cyclohexylamine hydrochloride	240	194 (210)	320	194
Cyclohexylamine nitrate	240	147 (157)	301	147
Cyclohexylamine hydrobromate	260	219 (228)	332	219
Cyclohexylamine sulfate	>290	344 (347)	386	386
Ammonium chloride	280	191 (193)	328	328
Ammonium perchlorate	280	244 (244)	307	307
Potassium perchlorate	>290	301 (301)	347	347
Potassium nitrate	>290	130 (130)	361, 405	361

*Numbers shown in parentheses are the endothermic peak temperatures of additives alone.

**The lowest T_{exo} or T_{endo} that shifted to a lower temperature was defined as the thermal reaction temperature T_r .

However, when both T_{exo} and T_{endo} do not shift, the lowest T_{exo} is used as T_r .

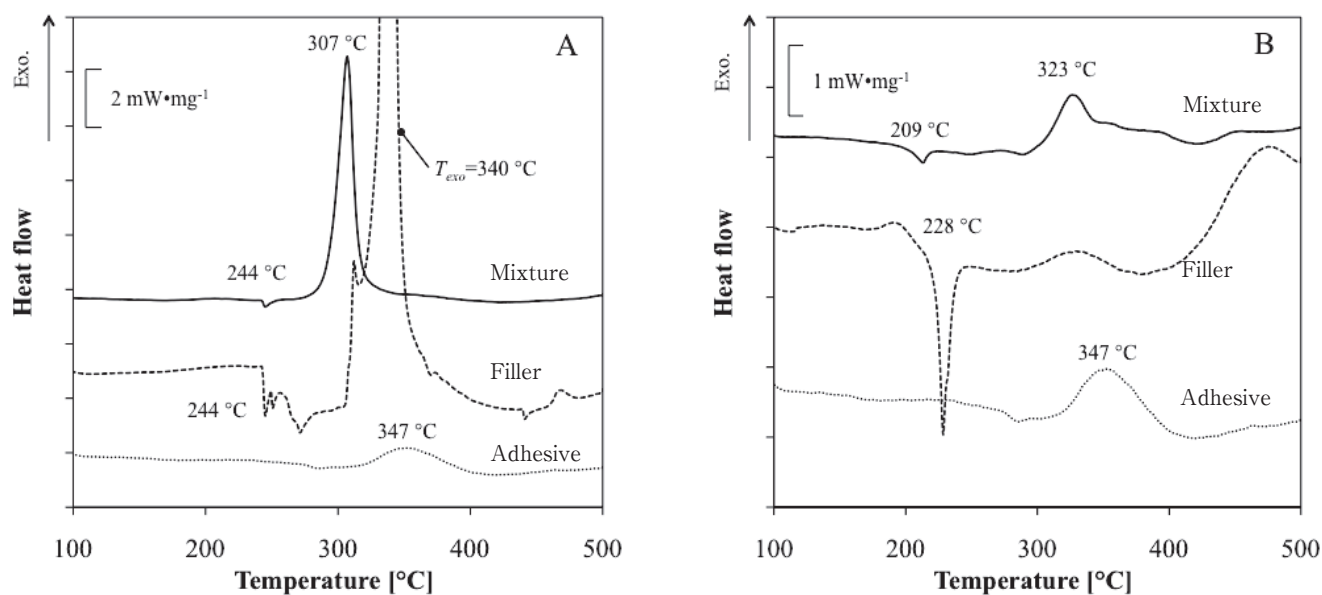


Figure 1 Thermal behavior of adhesives having dismantlability.
A: Ammonium perchlorate and B: methylamine hydrochloride

T_{exo} and/or T_{endo} of filler/adhesive mixtures with high dismantlability would tend to shift to lower values as compared to those for the individual adhesive or filler, but T_{exo} and T_{endo} do not change for mixtures with low dismantlability.

3.3 Correlation between dismantlement temperature and DSC results

The correlation between the dismantlement temperatures in Table 1 and the T_{exo} and T_{endo} values observed in the DSC measurements was investigated. The T_{exo} or T_{endo} values at the lowest temperatures in the DSC measurements are plotted against the respective

dismantlement temperatures in Figure 3A. The plots for both T_{exo} and T_{endo} had low correlation ($R^2 \approx 0.3$).

In sections 3.1 and 3.2, it is shown that T_{exo} and T_{endo} in filler/adhesive mixtures with high dismantlability tend to shift to lower values as compared to those for the filler and adhesive alone. Reactions between the adhesive and the filler that contribute to the dismantlability may be occurring at temperatures near the shifted exothermic or endothermic peaks for these adhesives. Therefore, the lowest T_{exo} or T_{endo} that shifted to a lower temperature was defined as the thermal reaction temperature T_r (the lowest T_{exo} is used as T_r in adhesives where both T_{exo} and T_{endo} do not shift), and the correlation with the

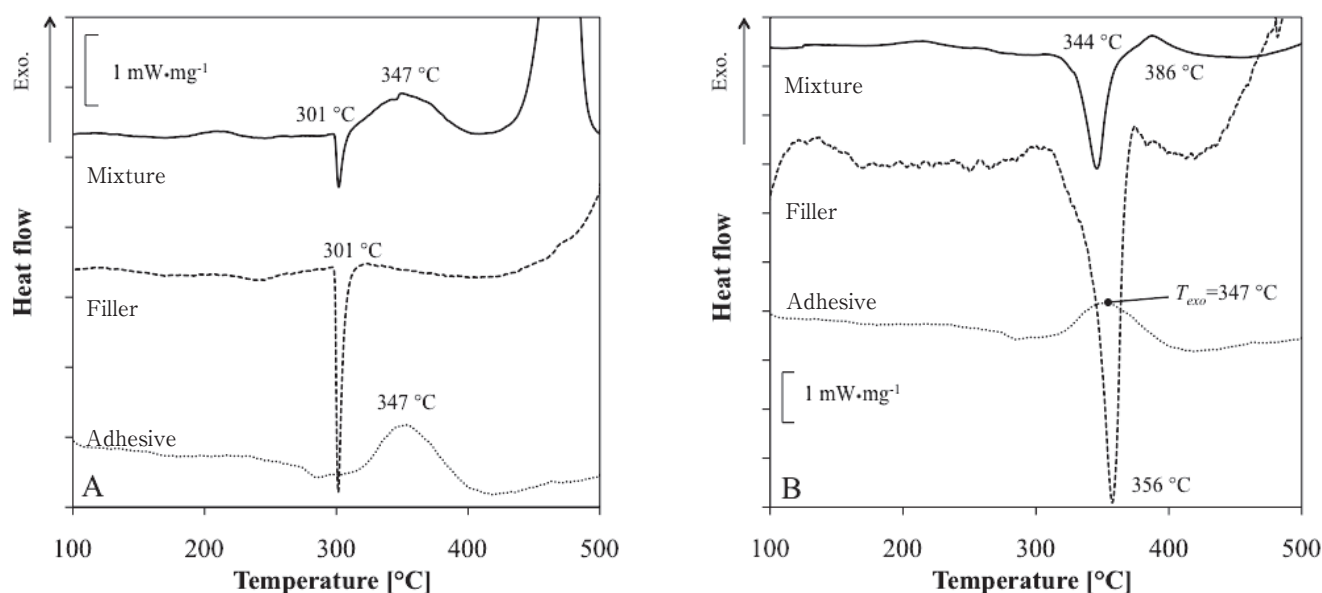


Figure 2 Thermal behavior of adhesives having no dismantlability.
A : Potassium perchlorate and B : cyclohexylamine sulfate

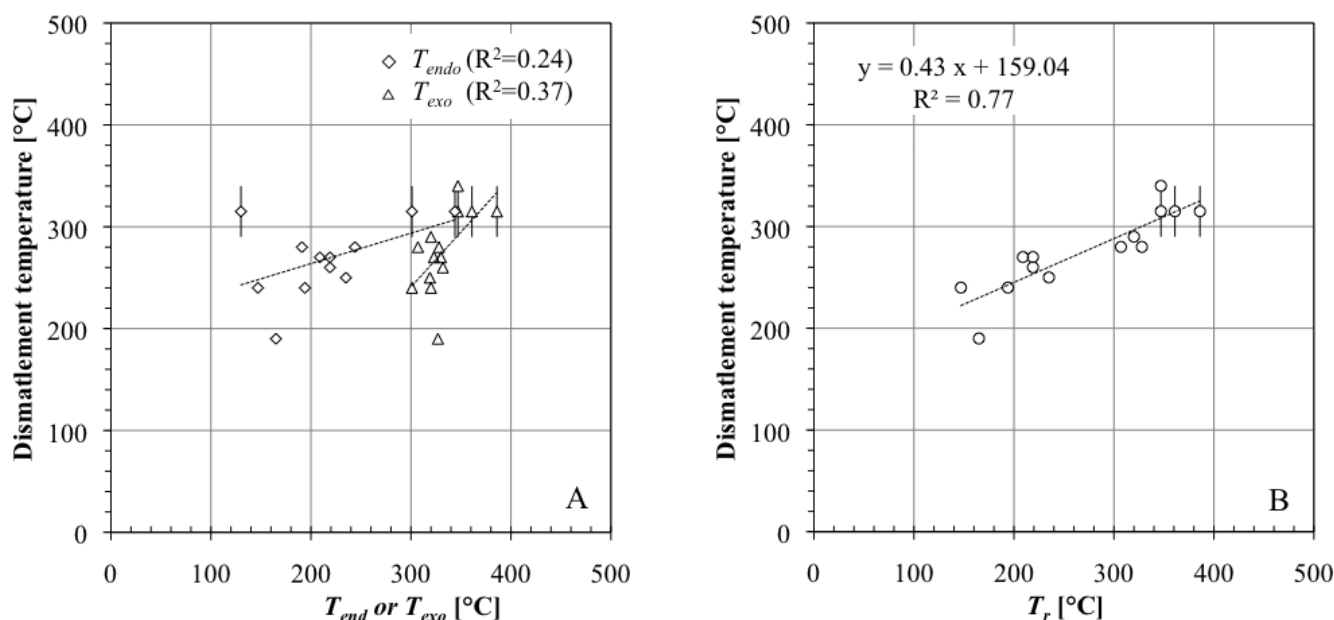


Figure 3 Relationship between dismantlement temperature and differential scanning calorimetry results.
A : $T_{\text{endo}}/T_{\text{exo}}$ vs. dismantlement temperature and B : T_r vs. dismantlement temperature

dismantlement temperature was evaluated. Figure 3B shows that there is a relatively high correlation ($R^2 = 0.8$). Therefore, it is considered possible to qualitatively determine, on the basis of the DSC results, the dismantlabilities of adhesives in which chemical reactions contribute to the dismantlement.

4. Conclusions

As a fundamental study on dismantlable adhesives, this research investigated the correlation between DSC measurement results and dismantlability for mixtures of an adhesive and various salts. We arrived at the following conclusions.

- (1) T_{exo} and/or T_{endo} shifted to lower values for filler/adhesive mixtures with high dismantlability as compared to those for the adhesives or fillers alone. In

contrast, no shifts in T_{exo} and T_{endo} were observed in adhesives with low dismantlability.

- (2) A relatively high correlation was found between T_r and the dismantlement temperature. It is therefore possible that the dismantlability of adhesives could be screened using DSC results.

5. References

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種々の有機／無機塩類を含有した接着剤の解体性と 熱的挙動の比較

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著者らの既往の研究において、過塩素酸アンモニウム等を含むエポキシ系接着剤は、無添加の接着剤と比較して低温で剥離解体することが明らかになった。このような接着剤は、解体性接着剤としての利用が期待される。本研究では、新規解体性接着剤の開発に係る基礎研究として、13種類の有機／無機塩類をそれぞれ含有した接着剤に対しDSC測定を実施し、得られた熱挙動と解体性を比較した。280°C以下の温度で接着強度が完全に喪失する（解体温度 $\leq 280^{\circ}\text{C}$ ）、解体性が高い添加剤／接着剤のDSC結果では、発熱ピーク温度（ T_{exo} ）あるいは吸熱ピーク温度（ T_{endo} ）が接着剤単独およびフィラー単独と比較して低温側へシフトする傾向があった。一方、解体性が低い添加剤／接着剤（解体温度 $> 280^{\circ}\text{C}$ ）の場合、このような T_{exo} あるいは T_{endo} の変化は認められなかった。このように、熱的挙動は解体性により異なっていることから、化学反応を伴う接着剤の解体性をDSC結果から予測できる可能性がある。

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