Estimation of the Compatibility of Blend Composites of Resins by Measuring the Fluorescent Spectra

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The effects of adding desipramine-containing fluorescence polymer (poly(10,11-dihydro-5-[3-(N-methylamino)propyl]-dibenzo[b,f]azepine-2,8-diyl-alt-9,9-didodecylfluorene-2,7-diyl, PAzep-Fl) to resins were investigated. When composites were prepared by a reactive blend of poly(lactic acid) (PLA), PAzep-Fl, and disiocyanate, the molecular weight of the obtained composite was larger than that of the composite, which was blended without PAzep-Fl. This suggested that a chemical bonding occurred between PLA and PAzep-Fl via disiocyanate. The effects of adding PAzep-Fl in two kinds of resins/lysine trisocyanate (LTI) blend were also investigated. The addition of LTI to resins/PAzep-Fl blend composites afforded a shorter wavelength shift of the fluorescence λmax due to the release of the aggregation of PAzep-Fl by LTI. This suggested that the compatibility of two kinds of resins could be estimated by this simple method. The addition of PAzep-Fl to PLA/poly(ε-caprolactone) (PCL)/LTI blends improved the impact strength because of chemical bond formation between PAzep-Fl and the resins (PLA and PCL) via LTI.

Keywords Desipramine, fluorescent additive, multifunctional isocyanate, reactive blend, compatibility

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Introduction

Usually, virgin resins are functionalized by additives. Therefore, many additives for resins have been widely researched. We have improved the mechanical properties of resins by the reactive blend (RB), which is a method of adding multifunctional isocyanates (MFI, such as lysine trisocyanate (LTI), Fig. 1) as a reagent to the terminal hydroxyl group of polyesters, such as poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL), and poly(butylenc succinate) (PBS) (Fig. 1). PLA is a synthetic biopolymer derived from biomass through bioconversion and polymerization; therefore, the modification and functionalization of PLA have been widely researched.

Our group developed additives for PLA, such as a nucleating agent, and a layered silicate for improving the impact strength. On the other hand, to make PLA with a fluorescence function, we added polymers containing diphenylamine with a bridged structure, whose bridge units were monosilane (phenazasiline: Phenaz, Fig. 2)24–26 and ethylene (dibenzazepine: PAzep, Fig. 2).27 These polymers were expected to have good thermal stability because of their bridged structure on the polymer main chain.28 We focused on the fluorescence properties of additives. In the present work, poly(10,11-dihydro-5-[3-(N-methylamino)propyl]-dibenzo[b,f]azepine-2,8-diyl-alt-9,9-didodecylfluorene-2,7-diyl) (PAzep-Fl)29 was used for fluorescent functional additives. Desipramine is a dibenazepine derivative with a reactive secondary alkylamine on the N atom of its diphenylamine unit, and has pharmaceutical applications, such as an antidepressant.30 When desipramine homopolymer (poly(desipramine) (PAzep-a, Fig. 2)) was blended with MDI (methylene diphenyl 4,4’-disiocyanate) and PLA, a chemical bond was formed between PAzep-a and PLA through MDI. We tried to prepare blend composites by the RB of fluorescence additive, PLA and MFI (Fig. 3). We also investigated the effect of MFI to blend composites of two kinds of resins (PLA and PCL) and PAzep-Fl.

Experimental

Reagents and chemicals

PAzep-Fl was prepared by the Suzuki coupling reaction between dibromodesipramine hydrochloride and 9,9-didodecylfluorene diboronic acid (Aldrich) by reported method.29 MFI (multifunctional isocyanates; LTI (Kyowa Hakko Kogyo), MDI (Tokyo Chemical Industry), methyl 2,6-disiocyanatohexanoate (LDI, Kyowa Hakko Kogyo), 1,6-disiocyanatohexane (HMDI, Tokyo Chemical Industry), and 1,1’-methylenebis(4-isocyanatocyclohexane) (H2MDI, Tokyo Chemical Industry)) were commercial products. The other chemicals were also commercial products.

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Measurement

Fluorescence spectra were measured with a Hitachi F-4010 spectrometer. Molecular weights and molecular weight distributions were determined by using a JASCO (PU-2080, CO-2065 and RI-2031) operating with CHCl₃. The GPC was calibrated using polystyrene standards.

Addition of PAzep-Fl to resin

Preparation of PAzep-Fl-containing PLA. PAzep-Fl (3 mg, 0.01 phr (per hundred resin, detailed explanation of phr is written in Supporting Information)) and PLA (30 g) were mixed and put into an extruder. Kneading the mixture at 190°C gave a PAzep-Fl-containing pellet. Kneading the pellet at 190°C and injection-molding gave a tensile specimen, PLA-1 (dumbbell).

Preparation of reactive blend composite of PAzep-Fl, PLA, and diisocyanate. PAzep-Fl (3 mg, 0.01 phr), MDI (15 mg, 0.05 phr), and PLA (30 g) were mixed and put into an extruder. Kneading the mixture at 190°C gave a MDI and a PAzep-Fl-containing pellet. Kneading the pellet at 190°C and injection-molding gave a tensile specimen, PLA-M1 (dumbbell). Other diisocyanate-containing reactive blend composites were prepared, as listed in Table 1.

Preparation of PAzep-Fl-containing PCL. PAzep-Fl (3 mg, 0.01 phr) and PCL (30 g) were mixed and put into an extruder. Kneading the mixture at 190°C gave a PAzep-Fl-containing pellet. Kneading the pellet at 190°C and injection-molding gave a tensile specimen, PCL-1 (dumbbell).

Preparation of reactive blend composite of PAzep-Fl, LTI, and one kind of resin. PAzep-Fl (3 mg, 0.01 phr), LTI (150 mg, 0.5 phr), and PLA (30 g) were mixed and put into an extruder. Kneading the mixture at 190°C gave a blended pellet. Kneading the pellet at 190°C and injection-molding gave a tensile specimen, PLA-T1 (dumbbell). Blending with PAzep-Fl (3 mg, 0.01 phr), LTI (150 mg, 0.5 phr), and PCL (30 g) afforded PCL-T1.

Preparation of reactive blend composite of PAzep-Fl, PLA, PCL, and LTI. PAzep-Fl (3 mg, 0.01 phr), LTI (150 mg, 0.5 phr), and PLA (27 g) and PCL (3 g) were mixed and put into an extruder. Kneading the mixture at 190°C gave a blended pellet. Kneading the pellet at 190°C and injection-molding gave a tensile specimen, Blend-T1 (dumbbell). Other blend composites were prepared as listed in Tables 2 and 3.

Measurement of impact strength

Charpy impact tests were performed by using a CEAST impact pendulum and a pendulum of 2 J or 4 J adapted to the standard ISO 179-1993 (E) at 23°C and 50%RH. Testing was done on notched specimens of 80 × 10 × 4 mm².

Results and Discussion

Use of PAzep-Fl as functional additives for resins

Chemical bond formation between PLA and PAzep-Fl via diisocyanates. First, we checked whether PAzep-Fl is useful for a fluorescence additive. The fluorescence λ_max of PLA-1
(Table 1) was almost the same as that of PAzep-Fl in CHCl3. This suggests that PAzep-Fl has good dispersibility in PLA, similar to that of PPhenaz. Next, RB by using PAzep-Fl, PLA, and diisocyanate was carried out. The blend ratios of PAzep-Fl, PLA, and diisocyanate are given in Table 1. We expected the formation of a chemical bond between the resins and PAzep-Fl via not only aryl diisocyanate, but also alkyl diisocyanate, because we have already reported that the reaction between desipramine and MFI gave the corresponding urea compound. The chemical bond formation in PLA was evaluated by a change of its molecular weight. As shown in Table 1, $M_n$ of PAzep-Fl-containing composites were larger than that of the composites without PAzep-Fl. This result was explained as shown in Fig. 4. In the absence of PAzep-Fl, only the chemical reaction between PLA and diisocyanate take place to form the urethane linkage on the reactive blend. On the other hand, in the presence of PAzep-Fl, not only the formation of urethane linkage but also the urea linkage occurs by the RB, because the feeding ratio of PLA and diisocyanate is the same in spite of the addition of PAzep-Fl. As shown in Table 1 and Fig. S1 (Supporting Information), the fluorescence $\lambda_{max}$ of the composite was almost the same wavelength as that of PLA-1. This suggests that the chemical bond is formed without inhibiting the fluorescence. Effect of the addition of PAzep-Fl in polymer blend composites. PAzep-Fl was effective as a fluorescent additive for PLA, but resins are sometimes used as blend composites of two or more kinds of resins. For example, the PLA’s impact strength was improved by RB with LTI, and soft type polyesters, such as PCL and PBS. To investigate the effect of PAzep-Fl on the blend composite, PAzep-Fl was blended to the PLA/PCL system because we improved the impact strength of PLA until that of the general-purpose ABS. First, the dependence of the resin on the fluorescence properties was investigated. The fluorescence spectra of PAzep-Fl on only PLA (PLA-1, Table 2) or PCL (PCL-1, Table 2) were compared. The fluorescence $\lambda_{max}$ of PAzep-Fl-containing PCL was almost the same region of that of PAzep-Fl cast film (see Fig. S2, Supporting Information), suggesting that $\pi$-stacking by aggregation of PAzep-Fl occurred in PCL because of its poor dispersibility in PCL. On the other hand, PAzep-Fl showed a good dispersibility to PLA. These results suggest that the compatibility of PAzep-Fl to the resin depended on the resin used, as shown in Fig. 5(a). This type of aggregation behavior of $\pi$-conjugated functional additive was observed when PCL was used as a matrix resin. When LTI was added to PLA-1 or PCL-1, the fluorescence $\lambda_{max}$ of the composites (PLA-L1, PCL-1) became shorter, as shown in Table 2 and Fig. S3 (Supporting Information). The distance between PAzep-Fl molecules seems to become longer because of chemical bond formation of the NH unit of PAzep-Fl and the resins via LTI. This can be explained as follows. A network

| Composite   | PAzep-Fl/ phr | MFI | Urea formation | Urethane formation | Fluorescence $\lambda_{max}$/nm | $M_n/10^4$ | $M_w/10^4$ |
|-------------|----------------|-----|----------------|-------------------|---------------------------------|------------|------------|
| PLA-1       | 0.01           | None| ×              | ×                 | 413                             | 5.1        | 11.1       |
| PLA-M1      | 0.01           | MDI | ○              | ○                 | 410                             | 8.6        | 15.7       |
| PLA-M2      | 0              | MDI | ×              | ○                 |                                 | 7.5        | 14.3       |
| PLA-H2M1    | 0.01           | $H_2$MDI | ○           | ○                 | 412                             | 8.4        | 14.4       |
| PLA-H2M2    | 0              | $H_2$MDI | ×              | ○                 |                                 | 8.3        | 14.0       |
| PLA-D1      | 0.01           | LDI | ○              | ×                 | 409                             | 8.1        | 14.9       |
| PLA-D2      | 0              | LDI | ×              | ○                 |                                 | 7.8        | 14.1       |
| PLA-H1      | 0.01           | HMDI | ○             | ○                 | 410                             | 7.8        | 14.9       |
| PLA-H2      | 0              | HMDI | ×              | ○                 |                                 | 7.3        | 14.2       |

a. ○, Chemical bond formation will occur; ×, chemical bond formation will not occur. b. Determined by GPC (eluent = CHCl3, polystyrene standard).

![Fig. 4 Reaction scheme of RB containing PLA, PAzep-Fl and diisocyanate.](image-url)
type structure was formed by the reaction of polyester and LTI, as shown in Fig. 5(b). This network structure causes the distance of PAzep-Fl molecules to become longer than in the absence of LTI. Therefore, a larger effect involving the addition of LTI was observed when PCL was used as a matrix resin than when PLA was used.

Next, the effect of the addition of PAzep-Fl to PLA/PCL/LTI blend composites on the fluorescent properties was investigated. The blend ratios and their fluorescent properties are given in Table 2. Fluorescent spectra are shown in Figs. S4 and S5 (Supporting Information). The fluorescence $\lambda_{\text{max}}$ of the resin vs. PLA ratio was plotted, as shown in Fig. 6. The fluorescence $\lambda_{\text{max}}$ of the LTI-added composite (PLA-T1, PCL-T1, Blend-T1, Blend-T2, and Blend-T3) and the composite without LTI (PLA-1, PCL-1, Blend-1, Blend-2, and Blend-3) were indicated as $\bullet$ and $\bigcirc$ in the figure, respectively. The solid line and dotted line indicate the fluorescence $\lambda_{\text{max}}$ of PAzep-Fl film and PAzep-Fl solution, respectively. When the PLA/PCL blend ratio was the same, the fluorescence $\lambda_{\text{max}}$ of LTI-containing resins was shorter than that of the resins in the absence of LTI.

We supposed the behavior of PAzep-Fl in the PLA/PCL/LTI blend composite to be as follows: when LTI was not used, PAzep-Fl aggregated near the interface between PLA and PCL, as shown in Fig. 7(a). On the other hand, when LTI was used as a compatibilizer, PAzep-Fl became dispersed in both PLA and PCL, as shown in Fig. 7(b). This result suggests that PAzep-Fl was effective as a probe for estimating the compatibility.

The fluorescent properties of PAzep-Fl were also measured in solution. The results are shown as $\times$ in Figs. 6, S6, and Table S1 (Supporting Information). As described above, the fluorescence $\lambda_{\text{max}}$ of the CHCl$_3$ solution of PAzep-Fl had almost the same wavelength as that of PLA-1, suggesting that PAzep-Fl shows good compatibility to PLA. However, the fluorescence $\lambda_{\text{max}}$ of a methanol solution of PAzep-Fl had almost the same wavelength

### Table 2: Prepared PLA/PCL blend composites and their properties

| Composite | PLA, wt% | PCL, wt% | PAzep-Fl/phr | LTI/phr | $M_n/10^4$ | $M_w/10^4$ | Fluorescence $\lambda_{\text{max}}$/nm |
|-----------|----------|----------|--------------|---------|------------|------------|-------------------------------|
| PLA-1     | 100      | 0        | 0.01         | 0       | 5.1        | 11.1       | 412                           |
| PCL-1     | 0        | 100      | 0.01         | 0       | 7.0        | 12.8       | 436                           |
| PLA-T1    | 100      | 0        | 0.01         | 0.5     | 7.0        | 12.7       | 405                           |
| PCL-T1    | 0        | 100      | 0.01         | 0.5     | 8.6        | 14.5       | 415                           |
| Blend-1   | 90       | 10       | 0.01         | 0       | 9.1        | 16.5       | 426                           |
| Blend-2   | 85       | 15       | 0.01         | 0       | 9.5        | 17.1       | 432                           |
| Blend-3   | 70       | 30       | 0.01         | 0       | 6.7        | 12.9       | 432                           |
| Blend-T1  | 90       | 10       | 0.01         | 0.5     | 13.4       | 24.8       | 413                           |
| Blend-T2  | 85       | 15       | 0.01         | 0.5     | 11.7       | 23.4       | 413                           |
| Blend-T3  | 70       | 30       | 0.01         | 0.5     | 8.0        | 17.0       | 415                           |
| Blend-1'  | 90       | 10       | 0           | 0       | 8.6        | 16.4       |                               |
| Blend-T1' | 90       | 10       | 0           | 0       | 10.8       | 22.2       |                               |
| Blend-2'  | 85       | 15       | 0           | 0       | 9.2        | 16.8       |                               |
| Blend-T2' | 85       | 15       | 0           | 0.5     | 11.6       | 22.9       |                               |
| Blend-1'  | 90       | 10       | 0           | 0       | 8.6        | 16.4       |                               |
| Blend-T1' | 90       | 10       | 0           | 0.5     | 10.8       | 22.2       |                               |
| Blend-2'  | 85       | 15       | 0           | 0       | 9.2        | 16.8       |                               |
| Blend-T2' | 85       | 15       | 0           | 0.5     | 11.6       | 22.9       |                               |

a. Measured from GPC (polystyrene standards, eluent = CHCl$_3$). b. Excited at absorption $\lambda_{\text{max}}$ of PAzep-Fl in CHCl$_3$.  

![Fig. 5 Dispersion scheme of PAzep-Fl in PLA or PCL.](image-url)
as PAZep-Fl cast film and PCL-1. This suggests that PAZep-Fl was aggregated in PCL as in methanol. In addition, we also measured the fluorescent spectra in a mixed solvent of chloroform and methanol with various weight ratios. As shown in the figure, the fluorescence $\lambda_{\text{max}}$ in a mixed solvent had almost the same wavelength as the fluorescence $\lambda_{\text{max}}$ in the PLA/PCL blend without using LTI. From this result, measuring the solvatochromism of a fluorescent additive seems to be expected to easily check whether the additive is suitable as a reagent for estimating the compatibility of a blend of resins.

**Effect of PAZep-Fl for impact strength of blend composites**

It was found that PAZep-Fl was effective as a sensing agent for estimating the compatibility; therefore, the effect of the impact strength by the addition of PAZep-Fl to PLA/PCL/LTI blend was also investigated. The impact strength of the blend composites is given in Table 3. As shown in the table, the order of the impact strength of the composites is Blend-T# > Blend-T#′ > Blend-#, Blend-#′ (# = 1 or 2). As described above, the addition of LTI to the PCL/PLA blend caused an increase in the molecular weight and an improvement of the impact strength by RB;2 also, it is suggested that the addition of PAZep-Fl to PLA/PCL/LTI blend improved the impact strength because of the chemical bond formation between PAZep-Fl and polyester via LTI. This chemical bond formation is suggested by based on the order of the molecular weight of the composites (Blend-T# > Blend-T#′ > Blend-#, Blend-′ (# = 1 or 2)), as shown in Table 2. From these results, we conclude that PAZep-Fl can not only afford fluorescent properties, but also improves the impact strength of polyester/ LTI blends.

**Conclusions**

PAZep-Fl was an effective agent for estimating the polymer blends. Usually, it is known that additives decrease the impact strength of blend composites; on the other hand, the addition of PAZep-Fl to reactive blend composites of polyester improved the impact strength.

Usually, it is necessary for estimating the compatibility to use difficult techniques, such as using AFM and measuring the physical properties. However, it is easy to estimate the compatibility by adding PAZep-Fl to the resins, because this method is a way to measure fluorescent spectra without breaking the samples. We already reported on a method to estimate the compatibility by adding PAZep-Fl to the resins, because this method is a way to measure fluorescent spectra without breaking the samples.25,35 but the reported method needed two kinds of fluorescent additives. By contrast, the method described in this paper needs only one fluorescent additive; therefore, it is expected that this estimation method of compatibility will be simplified.

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Supporting Information

A detailed explanation of phr is given. Fluorescent spectra of PAzep-FI in solution, cast film, and in resins are shown. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/

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