

IN-SITU POLYMERIZABLE THERMOPLASTIC EPOXY RESIN AND HIGH PERFORMANCE FRTP USING IT AND FIBER FABRICS

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Abstract

In this paper, a newly categorized epoxy resin in-situ polymerizing linearly without cross-linking was successfully developed. The resulting polymer softened at higher temperature than its glass transition temperature (T_g). This phase transition was confirmed to occur reversibly and that means the polymer was thermoplastic. Applying this new epoxy resin as the matrix to the fiber reinforced thermoplastic (FRTP), the process of manufacturing could be simplified much more than using conventional thermoplastics. The obtained FRTP had good mechanical properties at ambient temperature. Immersion experiment into organic solvents revealed that there were no cross-links in the matrix resin. FRTP whose matrix is the newly developed epoxy resin was manufactured by the direct impregnation method. Further, the T_g of the matrix polymer was raised to improve heat-resistance.

1 Introduction

Epoxy resin is well-known as one of the most high performance thermosets with good handling property. However, fiber reinforced plastic (FRP) using epoxy resin as the matrix cannot be dismantled because epoxy resin is generally neither fusible nor soluble after curing due to the presence of cross-links in the chemical structure of cured resin. This fact significantly restricts the possibility of recycling or reuse, which is important in an environmental aspect. On the other hand, FRTPs are fusible, but the manufacturing of them usually needs much higher energy because high temperature and high pressure are necessary in the impregnation

process of thermoplastic polymer having a large molecular weight into continuous fiber fabrics such as cloths [1]. So new material, which has both good workability and thermoplastic property, has been desired for the matrix of FRTP.

In this study, we reported a new epoxy resin that was still thermoplastic even after curing. It can in-situ polymerize linearly without cross-linking during curing at the working place by the reaction mechanism shown in Fig. 1. The properties and advantages of FRTP in the case that the newly developed epoxy resin is applied to a matrix of FRTP are then discussed.

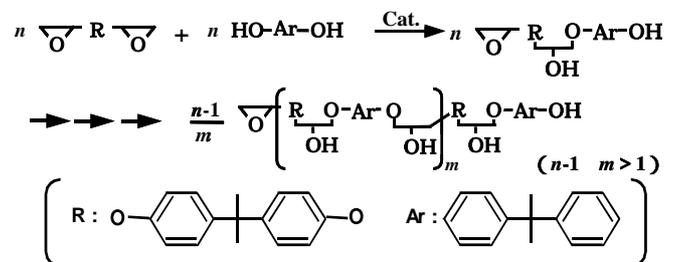


Fig. 1. The reaction mechanism of linear polymerization

2 Experimental

2.1 Materials

AER260 and Epikote 1002 (Bisphenol A type difunctional epoxy resin, epoxy equivalent values are 190 and 650 g/eq, respectively) were purchased from Asahi Kasei Corporation and Japan Epoxy Resin Co., Ltd., Bisphenol A and Bisphenol F (difunctional phenolic compound, OH equivalent values are 114 and 100g/eq, respectively) from Mitsui Chemicals Inc., and Bisresol fluorene (190g/eq) from Osaka Gas co., Ltd.,. All reagents were commercially available and used without

Table 1. The formulation of the Newly developed epoxy resin

Newly developed epoxy resin	Epoxy resin	Phenolic compound	Epoxy resin / Phenolic compound [phr]
TM80	AER260	Bisphenol F	100 / 53
TM100	AER260 / Epikote 1002	Bisphenol A / Bisphenol F	100(20/80) / 22(16/6)
TM100D	AER260	Bisphenol A	100 / 60
TM150	AER260	Biscresol fluorene	100 / 100

further purification. Glass fiber fabric (Glass Cloth WF230, manufactured by Nitto Boseki Co., Ltd.) was used as reinforcement.

Glass fiber fabrics laminated 9-ply was impregnated directly with TM100D (Fig. 2). After then, it was heated at 160 and pressed at 1.0 MPa for 20 minutes. The Vf was 40 vol%.

2.2 Formulation of newly developed epoxy resin

The formulation of the matrices for FRTP are shown in Table 1. In all formulations, difunctional epoxy resin and difunctional phenolic compound were mixed at a stoichiometric ratio, and the amount of catalyst was fixed to 2 phr.

Biscresol fluorene has so high crystallinity that the melting point is too high to enable us to handle at moderate temperature. So, the mixture of TM150 was pre-reacted prior to use to lower the crystallinity. The pre-reaction product thus obtained was pulverized. The powder of TM150 was sandwiched between glass fiber fabrics and subsequently pressed at 150 to impregnate into the fabrics (Fig. 2). Next, the laminated prepregs was pressed at 200 for 60 minutes under a pressure of 5.0 MPa by using the plane metal mold. The Vf was 42 vol%.

2.3 Preparation of composite

The glass fiber fabrics were immersed into methyl cellosolve solution of the newly developed epoxy resin (TM100) and then dried. Some impregnated sheets (prepreg) thus obtained were laminated 12-ply, and pressed at 150 for 60 minutes under a pressure of 1.0 MPa by using the plane metal mold. The fiber content (Vf), which was determined from the weight content and the specific gravity of TM100 and the glass fiber fabrics, was 43 vol%.

2.4 Secondary molding

TM100 based FRTP plate was heated at 160 and put on a wave-shaped aluminum mold. Then, FRTP plate was pressed between two aluminum molds. Finally, we obtained a wave-shaped FRTP.

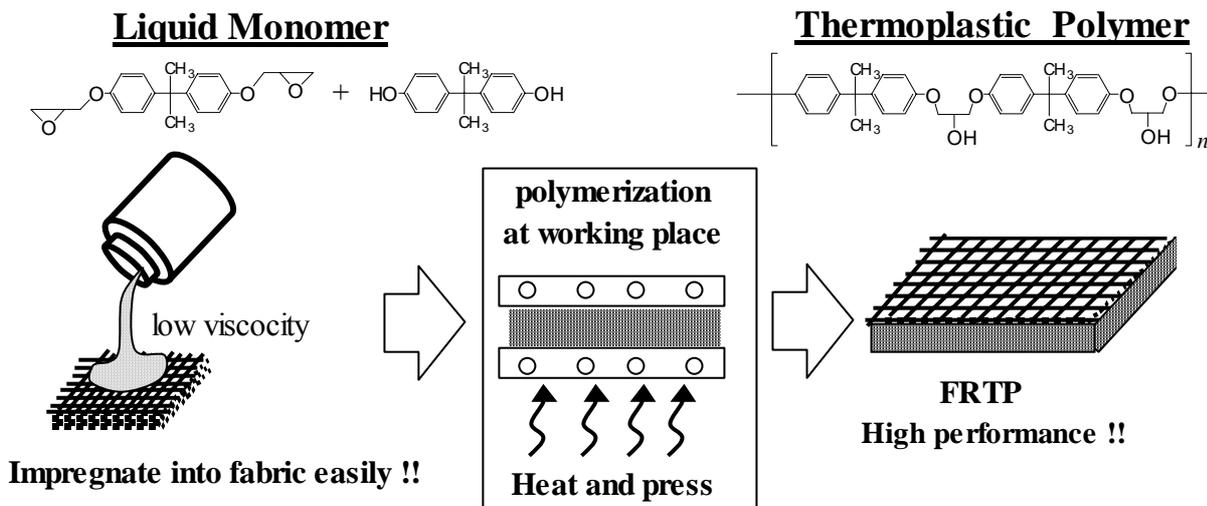


Fig. 2. Preparation of the composite whose matrix is TM100D

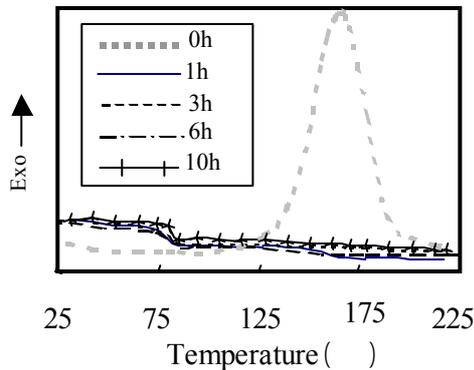


Fig. 3. DSC thermograms of the linearly polymerizing epoxy resin (TM80) cured at 150 for various times.

2.5 Immersion test

Solubility in organic solvents was checked for the TM100 based FRTP. Changes in appearance of the small pieces of the FRTP were observed before and after immersion into acetone, DMAc and toluene at room temperature for three days.

2.6 Characterization of composites

The mechanical properties of composites were evaluated by 3-point bending test carried out at room temperature by using Universal Test Machine AGS-G made by Shimazu Co., Ltd. The dimensions of the test piece were (b) 15mm width, (l) 80mm length and (t) 2mm thickness. Dynamic viscoelastic measurements for various FRP and FRTP were performed by using DMS-6100 made by SEIKO Instruments Co., Ltd at a frequency of 1Hz (bending mode) and a heating rate of 2 /min.

3 Results and Discussion

3.1 Fundamental study on thermoplastic epoxy resin

Fig. 3. and Fig. 4. show DSC thermograms and GPC chromatograms of TM80 before and after curing at 150 °C, respectively. Even after only 1h curing the exothermic heat of reaction became no longer detectable, and glass transition temperature was scarcely raised from 80 °C by further heating (Fig. 3). That means almost all functional groups in the composition were rapidly consumed in the heating at 150 °C for 1h. However, number average

Table 2. Results of the GPC

Polymerizing time at 150 [h]	Mw	Mn	Mw/ Mn
1	23000	11000	2.1
3	49000	16000	3.1
5	72000	18000	4.0
7	87000	19000	4.6
10	97000	20000	4.9

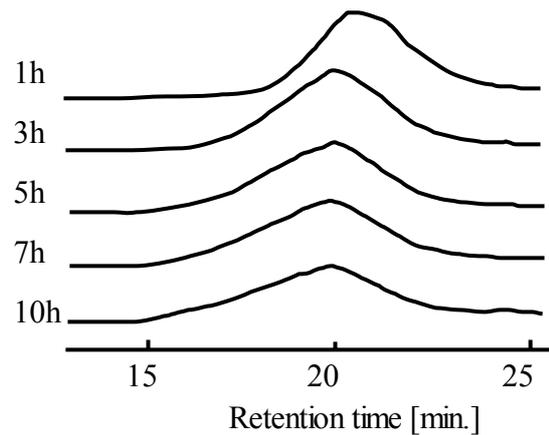


Fig. 4. GPC chromatograms of the linearly polymerizing TM80 cured at 150 °C for various times.

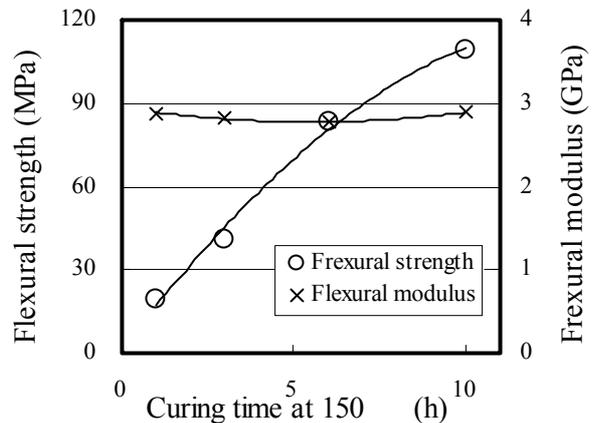


Fig. 5. The result of flexural test for the TM80.

molecular weight (Mn) of the polymer increased from about 10000 to 20000 during polymer curing for up to 10h (Table 2). The both results suggest the chain growing in this system occurs in the way of not chain reaction like vinyl polymerization but step-wise polymerization.

Fig. 5 and Fig. 6 show the results of flexural test for the same composition after curing at 150 °C

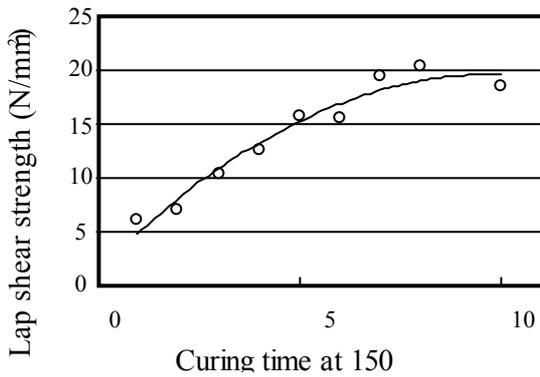


Fig. 6. Adhesiveness of TM80 cured at 150 for various time.

for the various times and the dependence of lap shear strength on curing time in the case of using TM80 as an adhesives (substrate was iron), respectively. The flexural strength increased drastically as the curing was prolonged, and the same tendency was observed in adhesion test while the flexural modulus did not change. It can be concluded from these results that the strength of polymer depends on its molecular weight while elastic modulus and Tg related on the rigidity of chain do not but are determined by the chemical structure of components. Moreover, this fairly high adhesion TM80 in spite of no cross-links is considered due to the adequate positioning of aromatic rings and highly polarized hydroxyl groups (refer to scheme 1).

3.2 Characterization of composites

The results of 3-point bending test for the obtained composites by using TM100, TM100D, and TM150 are shown in Table 3, in comparison with the general-purpose FRP with almost the same content of glass fiber fabric reinforcement, in which unsaturated polyester resin was used as the matrix. These results proved that the FRTP using the thermoplastic epoxy resin as the matrix has sufficient mechanical properties in spite of no cross-links in the matrix since all the FRTP tested here exhibited higher level than the general purpose FRP in bending strength and modulus. Fig. 7 shows the results of dynamic viscoelastic measurement for the FRTPs whose matrices are TM100, Nylon and the FRP whose matrix is vinyl ester resin (LP-1BQ). In the case of LP-1BQ, $\tan \delta$ exhibited a peak at 135 and came back to low value after that during

Table 3. The results of 3-point bending test for the ne developed FRTP and general-purpose FRP.

Test piece	Matrix resin	Bending strength [MPa]	Bending modulus [GPa]
Newly developed FRTP	TM100	403	21.5
	TM100D	486	19.0
	TM150	424	20.1
General purpose FRP	Unsaturated polyester	391	24.7

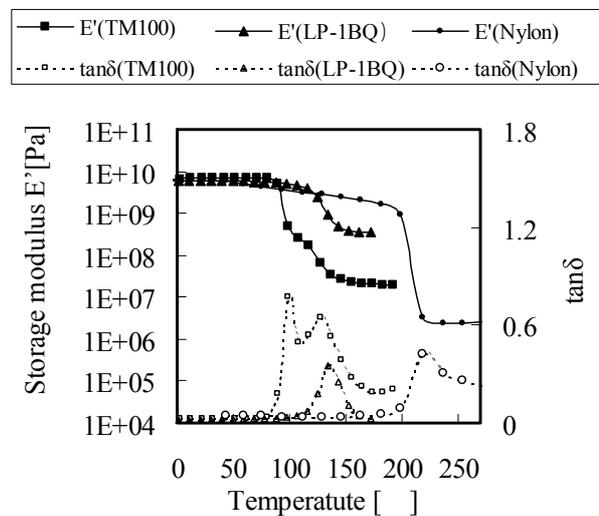


Fig. 7. Dynamic viscoelastic behavior of the various FRP and FRTPs.

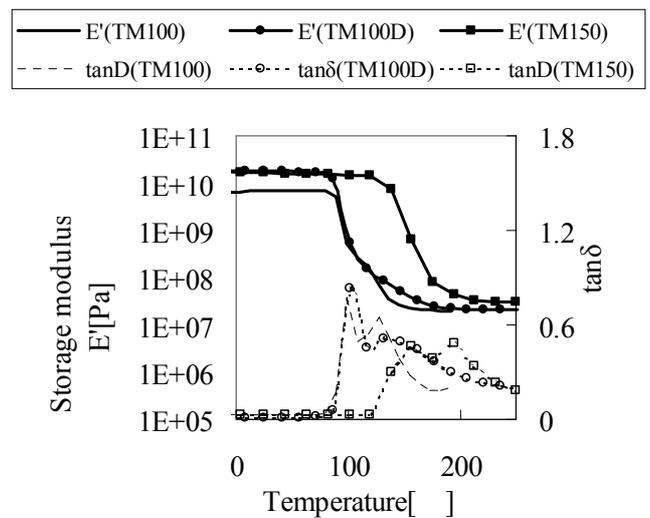


Fig. 8. Dynamic viscoelastic behavior of the various FRTPs.

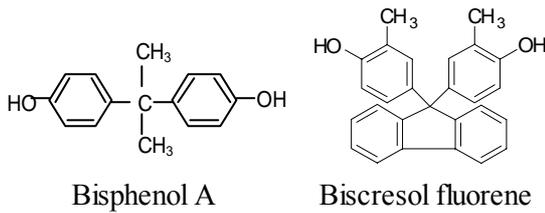


Fig. 9. Chemical structures of Bisphenol A and Bisresol fluorene

elevating temperature. On the other hand, in the case of Nylon, the peak of $\tan \delta$ was observed at 220 °C, but $\tan \delta$ maintained high value with slightly lowering which suggested the matrix was melting. The composite based on TM100 had a peak of $\tan \delta$ at 100 °C and behaved like Nylon. This results clarified TM100 still maintained thermoplastic property even after built in a composite as the matrix resin. In addition, because Nylon was a thermoplastic polymer with so high molecular weight that impregnation of the polymer into a glass cloth was impossible, instead a glass chopped strand was used as the reinforcement in this study. Fig. 8 showed the results of dynamic viscoelastic measurement of TM100, TM100D and TM150. Both composites using TM100D and TM150 exhibited the same behavior in the viscoelasticity as the composite using TM100. These results indicated that the composites using TM100D and TM150 also had thermoplastic property. In the case of TM150, the temperature of $\tan \delta$ peak corresponding to T_g was 150 °C. For this reason of the high T_g , the

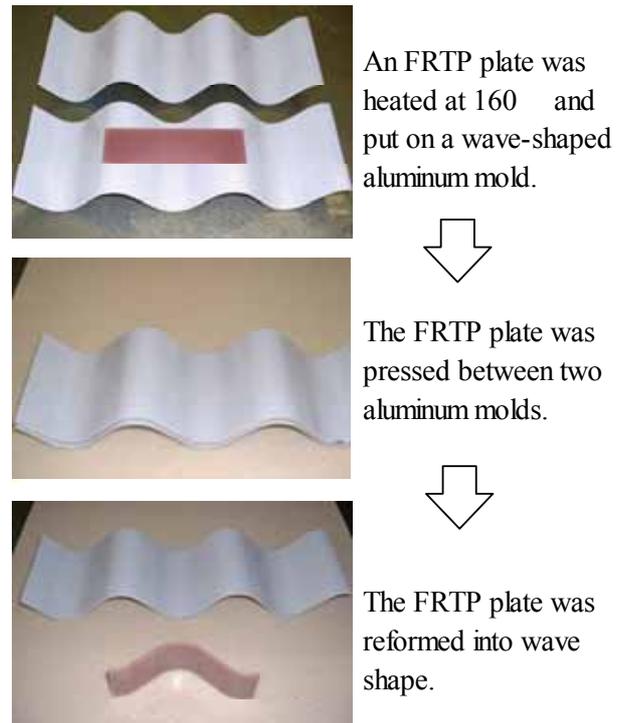


Fig. 10. Secondary molding process of the FRTP with TM100.

Bisresol fluorene compound which has bulky structure was built in the backbone of the polymer. Fig. 9 showed the chemical structures of Bisphenol A and Bisresol fluorene. Bulky structure of Bisresol fluorene restricted the motion of the main chain, so higher energy was needed at the time the main chain of this polymer started micro-Brownian

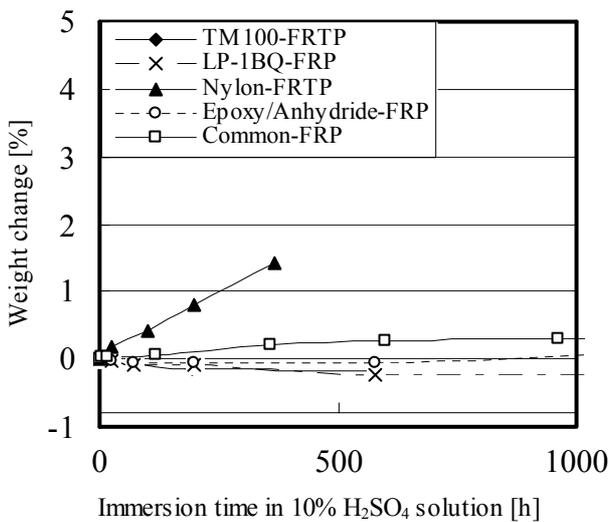


Fig. 11. Acid resistance of the various FRTPs and FRTTPs.

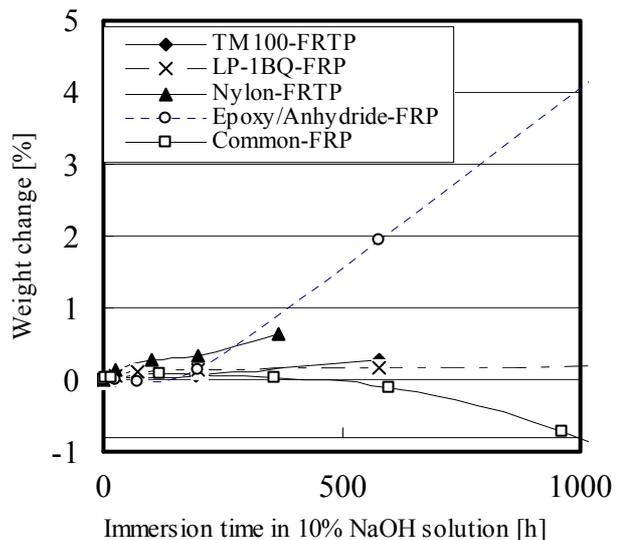


Fig. 12. Alkali resistance of the various FRTPs and FRTTPs.

motion.

The FRTP based on TM100 can be utilized for secondary molding as illustrated in Fig. 10. First, an FRTP plate was manufactured by an ordinary process of FRP and then it was pressed again between two wave-shaped molds at the elevated temperature above 150 to reshape into a wave-shaped FRTP by taking advantage of its thermoplasticity.

Corrosion resistance of the FRTP based on TM100 seemed to be almost the highest level as shown in Fig. 11 and Fig. 12. Test pieces were immersed into 10% H₂SO₄ solution or 10% NaOH solution at room temperature for acid- or alkali-resistance test, respectively. In Fig. 12, only Nylon-FRTP significantly changed in weight because amide linkage existing in Nylon main chain was subject to the hydrolysis on the acidic condition. On the other hand, on the alkaline condition, FRPs including ester linkage in the backbone of matrix resin (Epoxy/Anhydride-FRP and Common-FRP in Fig. 12) changed significantly because ester linkage was very sensitive to alkali. LP-1BQ, which was widely recognized as a high corrosion-resistant grade, exhibited only slight change in weight on the both conditions. TM100 showed very similar behavior to LP-1BQ in spite of no cross-links. It is considered that such high corrosion-resistance of TM100 resulted from the facts that TM100 was extended by only ether linkage during polymerization and there was neither amide nor ester linkage in its backbone.

Solubility in organic solvents was checked for the TM100 based FRTP. Changes in appearance of the small pieces of the FRTP were observed before and after immersion into acetone, DMAc (N,N-dimethyl acetoamide) and toluene at room temperature for three days as shown in Fig. 13. While few change was noticed after immersion into toluene of a non-polar solvent, a drastic change occurred after immersion into acetone or DMAc of a polar solvent. In the latter cases, the matrix resin dissolved in each solvent completely and the glass cloths built in FRTP separated from each other. The solubility was considered to be due to no cross-links in the matrix and existence of many secondary alcoholic OH groups. Making the best use of the solubility of thermoplastic epoxy resin in selected organic solvents might enable us to separate and collect raw materials after the use of FRTP.

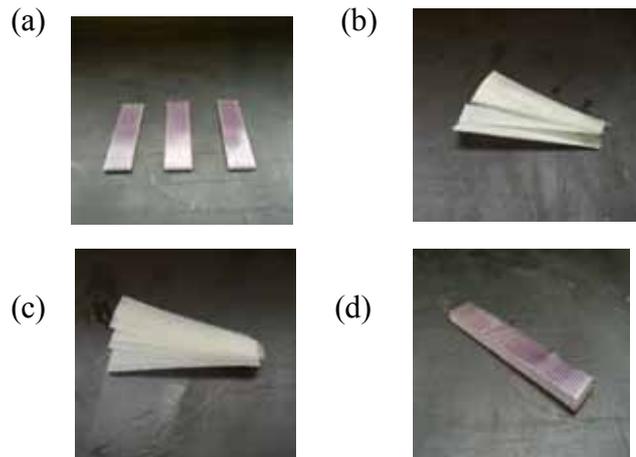


Fig. 13. Immersion test of TM100 based FRTP into the various solvents at 25 °C for 3 days.

(a) before immersion, (b) into DMAc, (c) into acetone, (d) into toluene

4 Conclusion

The basic technology of a newly categorized epoxy resin, which is thermoplastic even after curing, was established. By utilizing this new epoxy resin as the matrix of composite, a lot of advantages are expected. Only as low energy as in the manufacture of general purpose FRP is needed because the resin is consist of low molecular weight compounds and has good workability before curing at the first stage. It was also possible to manufacture the FRTP even by the method of direct impregnation. Sufficient mechanical properties for practical uses are obtained in spite of no cross-links in the matrix. Top level of corrosion resistance is obtained because of the absence of amide or ester linkage in the backbone of the matrix resin. After the use of the FRTP, separation and collection of raw materials were possible because the matrix resin is soluble in polar solvents.

5 References

- [1] E.L.d'Hooge, C.M.Edwards: Advanced Materials, 2000, vol.12, no.23, Dec.1