

***IN SITU*-POLYMERIZING THERMOPLASTIC EPOXY RESIN WHICH ENABLES MOLDING PROCESSES CORRESPONDING TO VARIOUS FORMS OF THERMOPLASTIC COMPOSITES**

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Abstract

Our laboratory has been investigating *in situ*-polymerizing thermoplastic epoxy resin, a liquid epoxy resin mixture in the initial state that can be allowed to polymerize linearly by heating to produce a thermoplastic polymer. This resin is very useful for the production of thermoplastic composites reinforced with continuous fibers at a high volume content because the liquid resin mixture can easily impregnate into dense reinforcing fiber fabrics. After impregnation, the resin mixture can rapidly polymerize and be converted into a non-cross-linked polymer.

The thermoplastic resin can be stably in several stages from initial monomer mixture to fully extended polymer. In each stage, the rheological property of the resin drastically changes and different molding processes including infusion, RTM, stamping, roll forming, etc. can be accordingly applied.

1. Introduction

Recently, thermoplastic resins have been attracting attention from a variety of industries such as aerospace, automobile, transportation, building and infrastructure, etc. as a matrix resin of composites reinforced with long or continuous fiber. That's because thermoplastic resins usually have more excellent toughness than thermosets and secondary formability. Especially, in specific fields which require high-cycled mass production like automobile industry, the secondary formability or reshapability of fiber reinforced thermoplastics is expected to be effectively taken advantage of by adopting stamping molding process and/or, if necessary, heat-fused jointing. Thermoplastic resins also have even the possibility of reuse and recycle, which might lead to protect the environment.

Contrary to this, when used as the matrix of composites particularly with long or continuous reinforcing fiber, ordinary thermoplastic resins have a big problem of difficulty in impregnation of the resin into a tremendous number of very narrow gaps of reinforcing fibers because they have very high melt viscosity due to their high molecular weight. Therefore, a great effort for the completion of impregnation has been spent mainly by pressing under high pressure at a high temperature for a long time with a pricy large-scaled apparatus. Moreover, in many cases, a critical problem about poor

adhesion between the resin and reinforcing fiber still remains even after the completion of impregnation because of low wettability of melting thermoplastic resin.

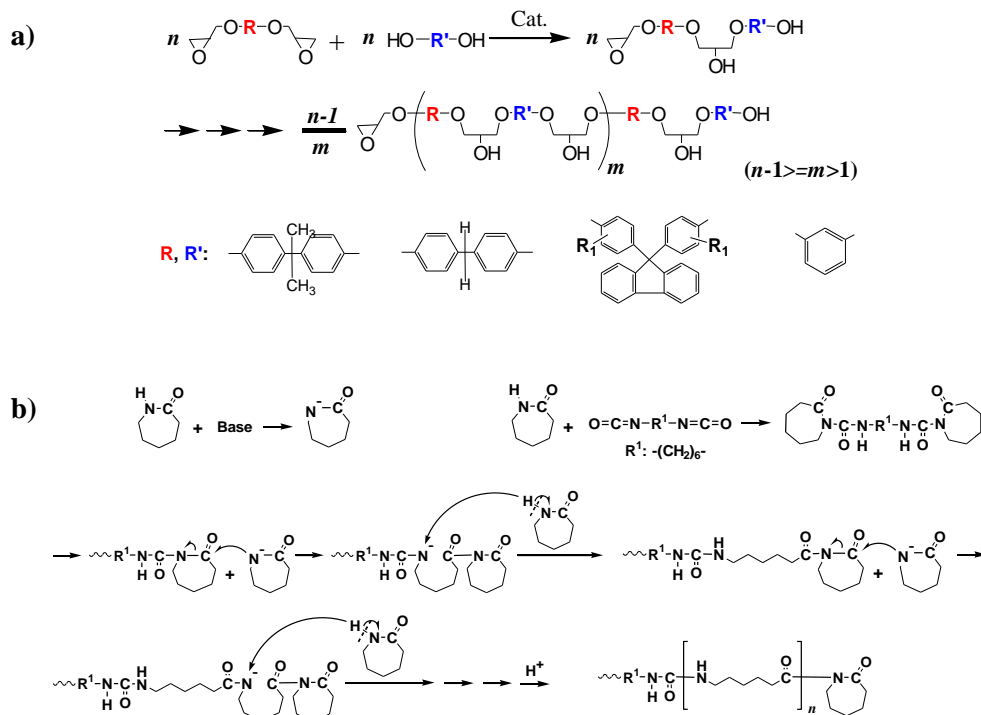


Fig. 1 Polymerization mechanism of **a)** Thermoplastic epoxy resin, **b)** Anionic ϵ -caprolactam.

On the other hand, a differently categorized solution for this problem including the use of several kinds of, so-called, *in situ*-polymerizing thermoplastic resins have been developed. Such materials include, for instance, anionically polymerizing ϵ -caprolactam, radically polymerizing mono-functional acrylic resin, ring-opening cyclic butylene terephthalate resin and thermoplastic epoxy resin. These resins are a polymerizable resin mixture with low molecular weight in the initial state and exhibit so excellent flowability that they can easily impregnate in the reinforcing fiber like most of thermosetting resins. After the completion of impregnation, heating the resin impregnated in the fiber to the cure temperature allows the resin to polymerize immediately to produce a robust composite part. At that time, low molecular weight monomeric resin might be able to easily achieve good adhesion between the fiber surface and the resin due to its low viscosity and good wettability.

In our laboratory, ‘thermoplastic epoxy resin’, one of *in situ*-polymerizing thermoplastic resins, has been studied for the matrix resin of thermoplastic composites reinforced with long or continuous fiber. This resin is totally different from any other *in situ*-polymerizing thermoplastic resin in the point that the polymerization mechanism of thermoplastic epoxy resin is step-growth polymerization while the polymerization of the others proceeds by chain polymerization (see Fig. 1-b)). That namely means the polymerization of thermoplastic epoxy resin can be stopped at any stage. In this study, molding processes for composites using thermoplastic epoxy resin applicable to each polymerization stage were investigated.

2. Thermoplastic epoxy resin

Fig.1-a) shows the polymerization mechanism of thermoplastic epoxy resin. In this system, di-functional epoxy resin and di-functional phenolic compound are mixed so that the ratio of both functional groups is 1 to 1, and when temperature is elevated, only the addition reaction of the phenolic hydroxyl group to the epoxy group occurs in succession under successful control by a specially designed catalyst to form a non-crosslinking polymer. As a result, the polymer thus obtained shows thermoplastic behavior. The polymer is amorphous and has not a melting point but a softening point above its glass transition temperature, T_g . In the case that Bisphenol-A structure (the left one in the bottom of Fig. 1-a)) is taken as both R and R', the finally produced polymer has a T_g at 100°C. When the temperature is elevated over the softening point, it can be in molten state. This phase transition can reversibly occur.

The strong points of this resin include excellent toughness, *in situ*-polymerizability, thermoformability and recyclability. During the fracture toughness test for the polymer, the *in situ*-polymerizing thermoplastic epoxy resin achieved a K_{Ic} value of approximately 2.0 MPa·m^{1/2} while a typical cross-linked epoxy resin showed less than 1.0 MPa·m^{1/2}. The Izod impact test revealed that this resin is tougher than even polycarbonate, which is known to be one of the toughest thermoplastic resins.[1]-[3]

The impact energy absorption and interlayer shear strength of thermoplastic composites using this resin as the matrix have also been evaluated. The results suggested that such thermoplastic composites are suitable for automotive applications such as impact energy absorbers.[4]

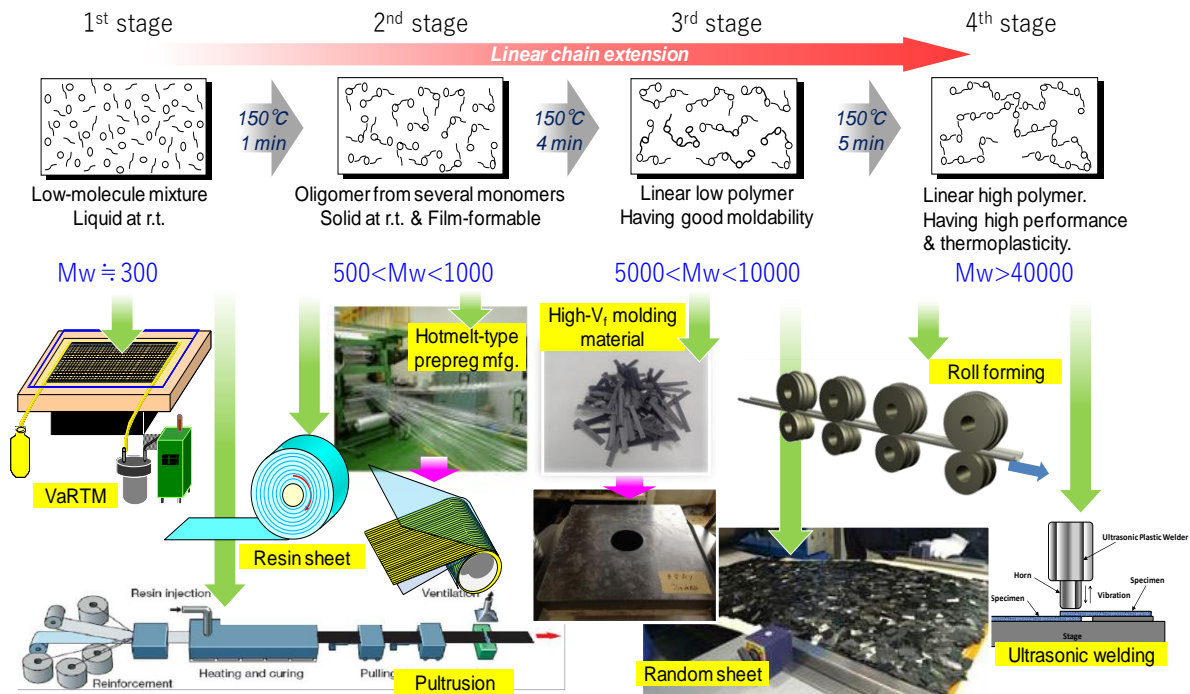


Fig. 2 Change in molecular weight with the progress of polymerization of thermoplastic epoxy resin and various molding processes applicable to each polymerization stage.

By the way, the linear-link polymerization of thermoplastic epoxy resin proceeds by step-growth mechanism, so it can be stopped temporarily at any stage of polymerization as described above. We defined 4 stages for the sake of convenience as shown in Fig. 2. The first stage means just a monomeric mixture of di-functional epoxy resin, di-functional phenolic compound and polymerization

catalyst. All ingredients of this mixture are compounds with low molecular weight ($M_w < 300$), so the mixture is flowable at moderate temperatures. The second stage means the mixture of oligomers whose molecular weights vary in the range from 500 to 1000 and can be obtained by heating the first stage mixture at 150°C for 1 min, for example, and then by cooling down to prohibit further polymerization. The second stage mixture is solid at room temperature and film-formable. At elevated temperatures, it can still become flowable. Additional heating of the second stage mixture at 150°C for 4 min gives the third stage mixture whose molecular weight in average reaches 5000 to 10000. The molecules in this stage haven't reached high-polymer level which exhibits practical mechanical strength yet while they have good moldability. After further additional heating of the third stage mixture at 150°C for 5 min, the fourth stage mixture is finally obtained. At this stage, the molecular weight of the resin has already exceeded 40000, so the polymer can be called high-polymer, which exhibits not only excellent mechanical properties such as bending strength, impact strength and fracture toughness but also thermoplasticity.

3. Molding processes

Fig. 3 shows the temperature dependence of viscosity of 'XNR6850A', the resin part of thermoplastic epoxy resin available from Nagase ChemteX Corporation. While addition of 'XNH6850B', the catalyst part of thermoplastic epoxy resin, is necessary to start polymerization, the designated amount of 'XNH6850B' is very small, so the viscosity of only 'XNR6850A' can be regarded as the same as the initial viscosity of the mixture of resin and catalyst. According to Fig. 3, the resin viscosity is reduced to approximately 80 mPa·s by warming at 100°C, and this viscosity was favorable for VaRTM to produce even a thick CFRTP board like 10 mm thickness using thermoplastic epoxy resin (see Fig. 4). In this process, the infusion of thermoplastic epoxy resin on the hot plate kept at 100°C was quickly completed within 10 min.

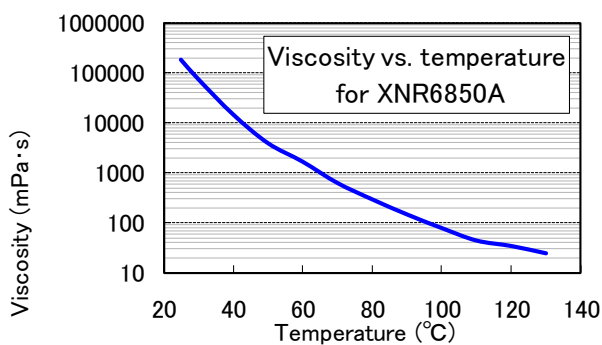


Fig. 3 Relationship between viscosity and temperature for 'XNR6850A', the resin part of thermoplastic epoxy resin.

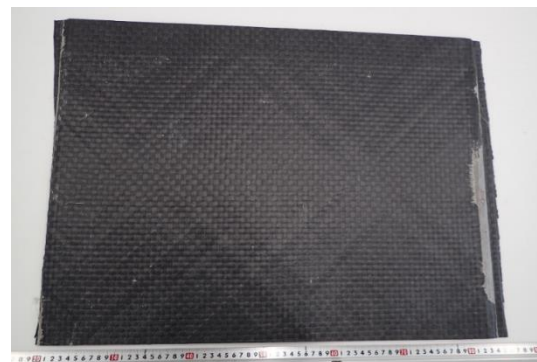


Fig. 4 Photo of a CFRTP board using thermoplastic epoxy resin successfully manufactured by VaRTM. (size: 500×650×10 mm)

This monomeric resin mixture is also utilized in other manufacturing processes which need less viscous resin impregnation such as pultrusion process. Fig. 5 illustrates the conceptual diagram of non-solvent pultrusion process to produce CFRTP pipes using thermoplastic epoxy resin via braiding process. Laboratory-scaled apparatus of this process has been investigated in Gifu University. They have already succeeded to produce a CFRTP pipe, where the ratio of non-impregnation part in each carbon fiber bundle was less than only 1 %.

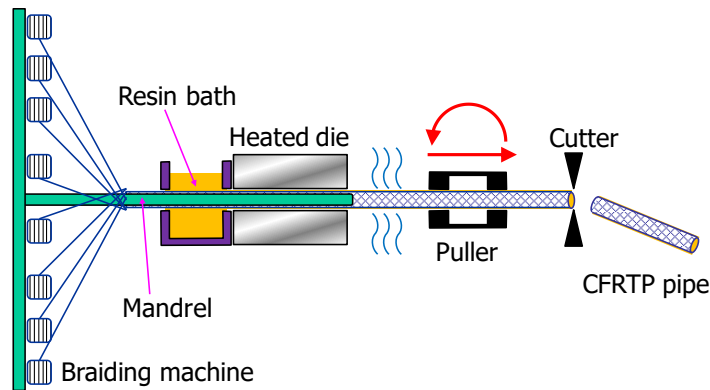


Fig. 5 Pultrusion process to produce CFRTP pipes using thermoplastic epoxy resin.

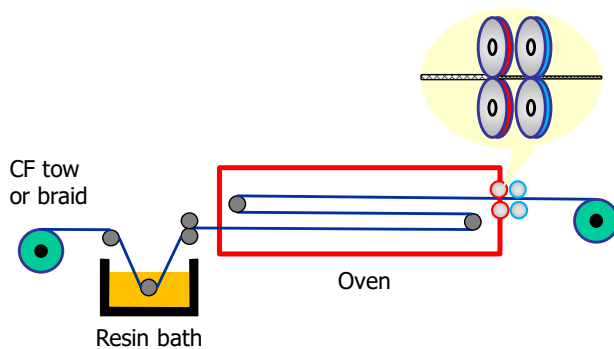


Fig. 6 Pultrusion process to produce CFRTP rods by using dipping method into a resin bath filled with thermoplastic epoxy resin diluted with organic solvent.



Fig. 7 Photo of 'CABKOMA™ STRAND ROD', a CFRTP rod using thermoplastic epoxy resin manufactured by Komatsu Seiren Co. Ltd.

On the other hand, this resin can be utilized in the solvent dilution system as well. Fig. 6 illustrates the conceptual diagram of another pultrusion process by using dipping method into a resin bath filled with thermoplastic epoxy resin diluted with organic solvent. In the case that the dry fiber fed to the resin bath is thick and/or twisted bundle, undiluted resin is commonly difficult to impregnate in the narrow gaps of fibers closely tightened. In that case, dilution with a solvent effectively helps the resin soak into the fiber bundle. After squeezing out the excess resin with double rolls, the bundle is put in an oven to evaporate the solvent and to polymerize the thermoplastic epoxy resin impregnated in the fiber bundle. At the exit of the oven, the bundle is squeezed tightly to remove voids and form it in the predetermined cross-section shape. A representative example using this process is the manufacture of 'CABKOMA™ STRAND ROD', a CFRTP rod using thermoplastic epoxy resin manufactured by Komatsu Seiren Co. Ltd. as shown in Fig. 7. This product has potential performance enough to replace steel wire and is being expected to contribute for lightweighting and avoiding rusting in the field of building and infrastructure. In these fields, lightweighting construction materials could shorten construction period and reduce cost effectively.

Another favorable example of this manufacturing process is 'Tow Chip', a thermoplastic molding material which consists of unidirectional carbon fiber chopped tow and almost fully polymerized thermoplastic epoxy resin, where the resin has completely impregnated into the tow. This product, which is also manufactured by Komatsu Seiren Co. Ltd., enables to produce a large and thick part like a block with long reinforcing fiber by compression molding or injection molding because any uncontrollable reaction doesn't occur due to accumulation of reaction heat during the molding process, as shown in the middle of Fig. 2.

Filament bundle-spread carbon fiber tow is more easily impregnated with thermoplastic epoxy resin. At that time, not only monomeric resin mixture of thermoplastic epoxy resin at the first stage of polymerization but also the resin film at the second stage can be utilized in the impregnation process. The latter case is particularly called 'hotmelt method'. The prepreg tape thus obtained is chopped and randomly spread on the releasing film, and then hot-pressed for unification to produce a thin-layered random stampable sheet. A good example of this kind of sheet material is 'FlexcarbonTM', manufactured by SUNCORONA ODA Co. Ltd. This product is favorably used for stamping molding as shown in Fig. 8. In particular, each layer is so thin that the uniform excellent mechanical properties are stably obtained in any direction even in the case of thin-walled molding. Such stampable sheets are considered to contribute to the realization of high-cycled molding process which is usually needed in automobile industry because stamping molding takes advantage of thermoplastic materials' instant formability very well.



Fig. 8 Photo of a spare tire cover molded by using 'FlexcarbonTM', a thin-layered random stampable sheet manufactured by SUNCORONA ODA Co. Ltd.

By the way, long plate CFRTP materials whose matrices are fully polymerized (i.e. at the fourth stage) thermoplastic epoxy resin can be reshaped by roll forming shown on the right side of Fig. 2. Continuous mass-production of CFRTP parts in a manufacturing line would lead to the lowest-cost manufacturing of structural material. The CFRTP parts with a fully polymerized thermoplastic matrix can be also joined by various fusion-bonding methods such as ultrasonically welding and bonding shown in the lower right of Fig. 2. In the case of fusion-bonding of CFRTP plates using thermoplastic epoxy resin, around 30 MPa in lap shear strength was obtained by only 0.3 second of ultrasonic wave oscillation. Since no adhesives are necessary and excellent bond strength is obtained in a very short time, fully polymerized thermoplastic epoxy resin reinforced with fibers would enable to realize joining process with low cost and high productivity.

3. Conclusions

As a result of investigation on composites using thermoplastic epoxy resin as the matrix and molding processes for them, following conclusions were obtained.

- Thermoplastic epoxy resin is a very unique *in situ*-polymerizing thermoplastic resin because its chain extension proceeds by step-growth polymerization while most of other *in situ*-polymerizing thermoplastic resins' cases are chain polymerization.
- Therefore the polymerization of thermoplastic epoxy resin can be stopped temporarily at any stage in polymerization degree and also can be restarted by heating again.
- A variety of molding processes for composite using thermoplastic epoxy resin can be adopted corresponding to a different rheological property at each stage of polymerization.
- Most especially, pultrusion, stamping and roll forming have a lot of potential to well contribute to realization of low cost and high-cycled mass production of CFRTP parts.

Acknowledgments

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References

- [1] Hirayama N., Tomomitsu N., Nishida H. and Kan K. "Development of FRP using thermally fusible epoxy resin", *Reinforced Plastics*, 50 (12), pp 519-529, 2004.
- [2] Nishida H., "The Development of Thermoplastic Epoxy Resin and Continuous Fiber Reinforced Thermoplastics using it". *J. Adhesion Soc. Jpn*, 51 (12), pp 516-523, 2015.
- [3] Nishida H., "Aiming to Create Novel Composites". *J. Adhesion Soc. Jpn*, 47(9), pp 361-368, 2011.
- [4] Ozawa M., Satake H., *J. Soc. Automotive Eng. Jpn*, 64 (7), pp 55, 2010.