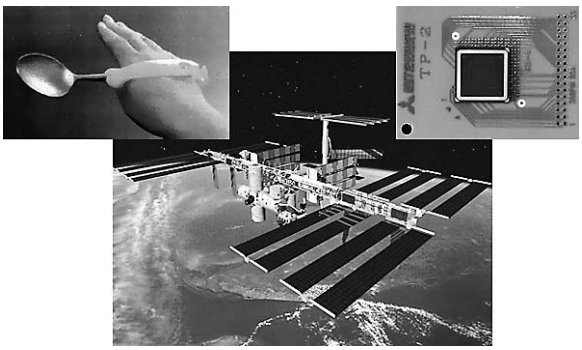

Development of Smart Polymer Materials and its Various Applications

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1. Introduction

Polymer materials are applied in various forms in our products such as air conditioning and refrigeration equipments, aircrafts, etc., and Mitsubishi Heavy Industries, Ltd. (MHI) is engaged in product improvement also in terms of materials. We developed the shape memory polymers and the chain curing polymers, which are the unique and smart materials. And they are expected to be used more widely in various application fields than the field they were initially developed for.

2. Shape Memory Polymer (SMP)

2.1 Principle of shape memory

The polymer materials have various elasticity from hard one like a glass to soft one like a rubber. The shape memory polymers, however, have the characteristics of both of them, and its elasticity modulus shows reversible change with the glass transition temperature (hereafter called Tg) as the border[(1)]. The dependence of the elasticity modulus to the temperature is shown in **Fig. 1**.

The shape memory polymers, when heated above Tg, get as soft as rubber and is easy to change the shape, and when cooled below Tg, it retains the shape intact (shape fixing characteristic). When heated up again above Tg, the material autonomously returns to the original shape (shape recovery characteristic). The material property which is repeatedly returning back to the original shape is called "shape memory."

2.2 Tg control and change in solid state properties

The Tg of polymer materials generally depends on the strength of intermolecular force (hydrogen bond and polarization), stiffness and symmetry of the backbone chain, and geometrical factor (side chain and functional groups), etc.

MHI's SMPs are polyurethanes made from polyols and isocyanates, with its Tg freely adjustable between –40 and 120°C by controlling the type of material component (molecular structure), molecular weight and composition.

The changes in solid state properties at the vicinity of Tg include water vapor permeation, cubical expansion, refractivity, and permittivity in addition to elasticity modulus. The material is therefore considered applicable to various fields by using these changes in solid state properties.

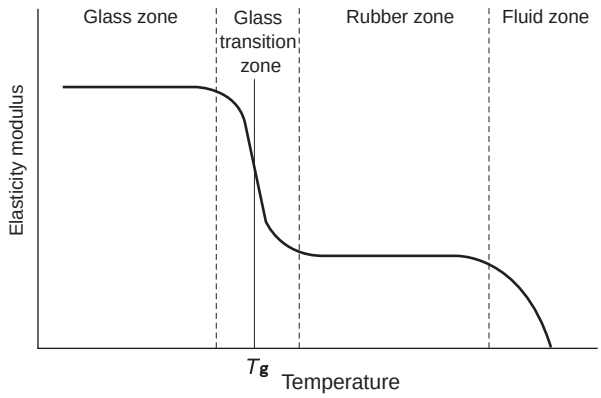

Fig. 1 Temperature dependency of elasticity modulus of SMP

2-3 Expansion of application

By making an effective use of the polymer's function as a temperature sensor, a mechanism was developed to carry out automatic choking in cold season, and was applied to the small-size engines. Further, the polymer was adopted for the handgrips of spoon, toothbrush, razor and kitchen knife by making use of its function of having the shape freely changeable, and then keeping the shape intact.

By making use of its property of getting soft at body temperature and outstanding tactile feature, the polymer has come to be applied in medical field as the self-retaining needle for drip (instillation), catheter, etc. By making use of the temperature change of water vapor permeation, epochal clothing have been successfully developed which keep you warm in cold season and cool in hot season.

Study is now under way to apply the FRP (fiber reinforced plastics) where the SMP is used as matrix resin to the inflatable structure in space. This program aims at compact folding of the FRP molded to final shape to transport to the space before expanding it to the original shape in space (**Fig. 2**). Further, porous foam with similar function is also under development (**Fig. 3**).

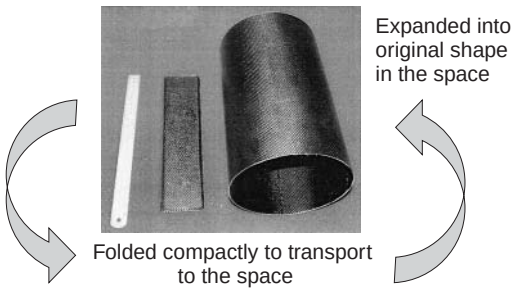

Fig. 2 Inflatable material for space structure

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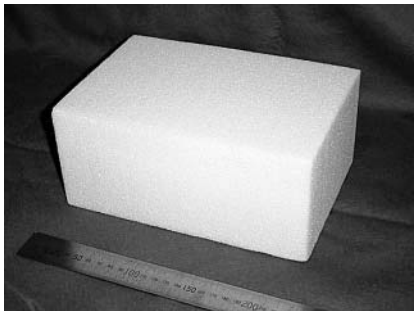

Fig. 3 Inflatable material for porous foam

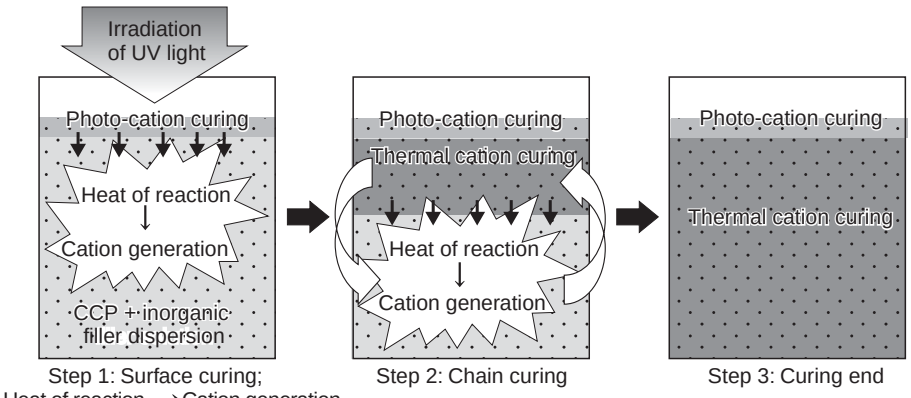

Fig. 4 Chain curing system of CCP (Pattern diagram)

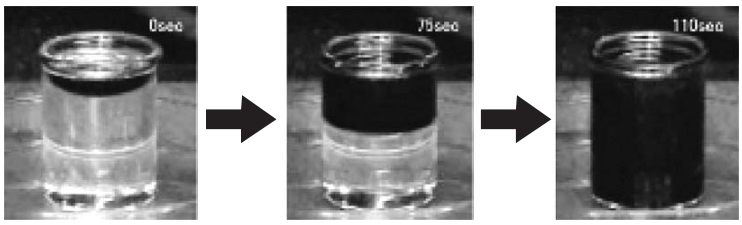

Fig. 5 Curing behavior of chain curing polymer

Table 1 Features of CCP

- Takes shorter time for curing even when the polymer is thick or contains filler.
- Even the light shielding part gets cured simply by irradiating UV light.
- Either UV light or heat energy can be used for curing.
- Does not contain organic solvent.

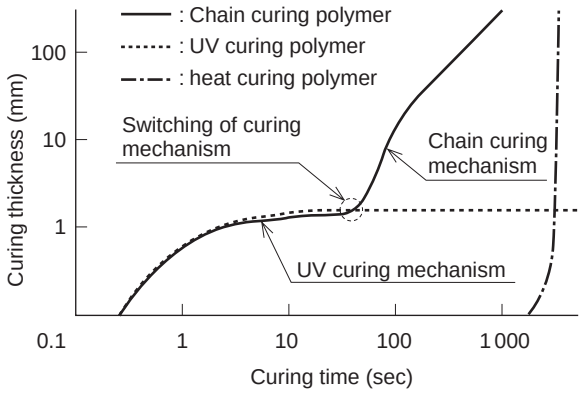

Fig. 6 Relationship between curing time and curing thickness per curing mechanism

3. Chain Curing Polymer (CCP)

3.1 Principle of chain curing polymer

The chain curing polymer (hereafter "CCP") enables curing through UV light or heat by means of continuous chain curing reaction, irrespective of the thickness, shape, amount of filler and UV light shielding characteristic[2].

Fig. 4 shows the pattern diagram of the chain curing system of CCP. In the case of MHI's CCPs, the heat of reaction generated at the time of initial curing by UV light or heat is used to trigger the generation of cation required for chain curing (Fig. 4; Step 1). This leads to a repeated and chain curing cycle of cation curing → generation of heat of reaction (self-generation of heat) → cation generation (Fig. 4; Step 2), ensuring a perfect curing even for thick substance where UV light fails to reach or for the substance containing a large amount of filler such as carbon fiber, metal powder, etc. (Fig. 4; Step 3)

In the case of general UV curing polymer, on the other hand, the chain curing does not occur, so that curing takes place only on the extreme surface where UV light can reach.

Fig. 5 shows the chain curing behavior of CCP when UV light is irradiated on the CCP for 60 seconds. It can be confirmed that the surface curing due to UV light triggers chain curing polymerization which progress toward the direction of depth.

In **Fig. 6** the correlation between curing time and curing thickness per curing mechanism of polymers are compared between the representative UV curing polymers and heat curing polymers. The UV curing polymers have shortcomings that it must be thin (no more than several mm) and transparent to get cured. And the heat curing polymers have a shortcoming that it needs long time (several hours) for curing. In the case of CCP, however, it ensures curing of thickness 40 mm (for example) in a short time of 3 minutes.

3.2 Features

Compared with UV curing or heat curing polymer, the features and solid state properties of CCP are given respectively in **Table 1** and **Table 2**.

3.3 Application expansion

The CCP can be applied to various fields (structural member, paint, adhesive, etc.) such as in the field where the conventional UV curing polymers cannot be used, and as a substitute to heat curing polymers, ensuring improvement in productivity by shortening the curing time (thus leading to reduction in processing cost) and drastic simplification of curing process (such as no need of heating).

Table 2 Solid state properties of cured material (Ex. alicyclic epoxy)

Characteristic items		Basic composition	Remark
Viscosity (pre-curing)	(cps (RT))	200 to 300	Changes from 100 to several hundred thousand possible
Density	(g/cm^3)	1.16	
Color	(-)	Colorless and transparent	
Curing time	(Min)	2 or under	For thickness 4 cm
Mold shrinkage factor (size)	(%)	1.47	Shrinkage factor can be reduced by inclusion of filler
Tensile break point stress	(kgf/mm^2)	4.0	
Tensile modulus of elasticity	(kgf/mm^2)	370	
Bending strength	(kgf/mm^2)	9.8	
Bending (flexural) modulus	(kgf/mm^2)	293	
Stiffness (pencil hardness)	(-)	4 to 5H	Stiffness can be improved by inclusion of filler
Adhesiveness (against glass)	(kgf/cm^2)	70 or above	100 or above also possible
Glass transition temperature (Tg)	(^oC)	170	190 (^oC also possible)
Coefficient of linear expansion (<Tg)	($/^oC$)	6×10^{-5}	The coefficient can be reduced by inclusion of filler
Volume resistivity	(Ω・cm)	1×10^{16}	
Storage-stability (single-liquid) (year) (at −20°C)		1 or over	1 year or over at RT in case of 2 liquids

Table 3 Fields where CCP is applicable

- Field of electronic materials (sealers, adhesives, under-fillers, etc.)
- Field of paints, various pastes and coatings
- Field of adhesives
- Field of compound materials (CFRP and GFRP) and structural materials
- Other applicable fields in epoxy resin

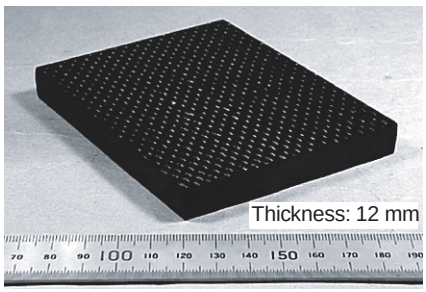

Fig. 7 CFRP molded sample using chain curing polymer

The examples where CCP can be applied are given in **Table 3**. And the appearance of CFRP molded by using CCP is shown in **Fig. 7**.

4. Conclusion

We have so far introduced the cases of expanded application as well as the unique features of MHI's functional polymers. We are determined to expand its application in various fields by making effective use of its features in the future through cooperation with our customers.

References

(1) Hayashi et al., Development of Polymeric Shape Memory Material, Mitsubishi Technical Bulletin No. 184 (1988)

(2) Akita et al., Function and Materials, Vol. 22 No. 5 (2002) pp.5-11


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