

A SELF-HEALING MATERIAL FORMED FROM A CRYSTALLINE POLYMER END-FUNCTIONALIZED WITH HYDROGEN BONDING UNITS

Nobuhiro Oya and Naoko Yoshie

International Research Center for Sustainable Materials
Institute of Industrial Science, The University of Tokyo
Komaba, Meguro-ku, Tokyo 153-8505, Japan
Email: nohya@iis.u-tokyo.ac.jp

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ABSTRACT

Healable materials have attracted great interest in recent years. Being capable of healing cracks either automatically or by activation with heat or light, they can maintain their original mechanical properties for a long period. Healing abilities have been achieved by mixing microencapsules containing healing agents into polymer matrices, incorporation of active reversible or irreversible covalent bond into polymer chain and supramolecular self-assembly. However, except the utility of microencapsules, it is difficult to obtain crystalline polymers with self-healing abilities at room temperature. Because of the low molecular mobility of them, self-healing mechanism cannot work. Healing was realized in some crystalline polymers by staying them in the melt or supercooled state [1].

When a crystalline polymer is cut, the degree of crystallinity at the cut surface is decreased by frictional heat, which results in the higher molecular mobility at the cut surface. If crystallization at the cut surface can be suppressed for a long period, self-healing mechanism may work in the supercooled state. In this study, a crystalline polymer with a repeatable healing ability at room temperature was obtained by controlling the crystalline rate.

Two poly(ethylene adipate) (PEA) end-functionalized with hydrogen bonding units were prepared. PEA is a crystalline polyester with $T_m \approx 45$ °C. The hydrogen bonding units were linked to both ends of the PEA chain through hexyl (PEA-Hex), and tolylene units (PEA-TI), respectively. The crystallization of the samples was monitored by DSC (Table 1). Because of the hydrogen bonding units, crystallization rates of PEA-Hex and PEA-TI were slower than the parent polymer, PEA. Especially, the crystallization rate of PEA-TI was very low due to the bulky tolylene units.

Table 1. Progress of Crystallization in PEA-Hex and PEA-TI

Polymer	Crystallization Period ^a	T_m / °C	ΔH_m / Jg ⁻¹	Degree of Crystallinity / % ^b
PEA	40 mins	48	60	47
PEA-Hex	1 day	42	22	18
	2 days	42	46	36
	1 month	- ^c	- ^c	- ^c
PEA-TI	2 months	45	7.1	6
	5 months	44	18	14
	9 months	51	33	26

^a Crystallization period at room temperature after melt quenching.

^b Estimated based on $DH_m = 128$ Jg⁻¹ for PEA with 100% crystallinity.

^c No melting peak was observed by DSC.

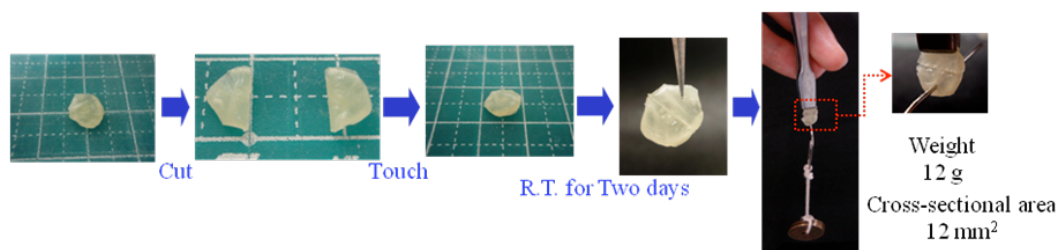


Figure 1. Self-healing properties of PEA-TI

Crystallized samples were used for healing experiments. Samples were cut by a knife into separated pieces, which were brought into contact and kept at room temperature without any external stress. After two days, the cut pieces of PEA-Hex were still separated, while PEA-TI was healed enough to suspend some weights (Figure 1). Additionally, this healing phenomenon seems to be site-specific. The original uncut surfaces, which are not adhesive, do not connect. When the healing experiment was repeated at the same position, the sample healed again. Therefore, PEA-TI is a repeatable self-healing polymer.

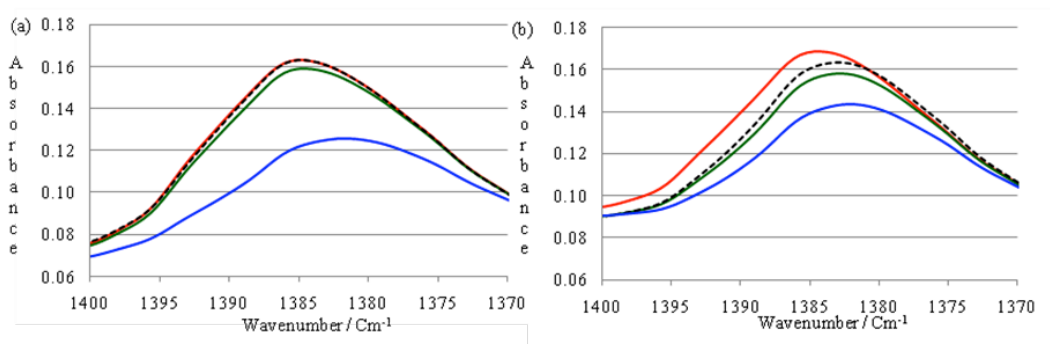


Figure 2. ATR-IR spectra at around 1380 cm^{-1} of (a) PEA-Hex and (b) PEA-TI: original surface (red line), surfaces right (green line) and two days (black dashed line) after cutting, and melting surface (blue line).

The surface crystallinity of the samples was analyzed by ATR-IR spectroscopy (Figure 2). The band at 1385 cm^{-1} is sensitive to crystallinity of PEA. By melting the crystal, this band becomes smaller and shifts to smaller wavenumber. The crystallinities at the cut surfaces of PEA-Hex and PEA-TI were slightly lower than the original uncut surfaces. When the cut samples were kept at room temperature for two days, the cut surface of PEA-Hex recovered the crystallinity similar to the original uncut surfaces while that of PEA-TI still kept lower crystallinity. Persistence of low crystallinity for a long period in PEA-TI allowed reassociation of the free hydrogen-bonding units generated by cut. This results in the enhancement of self-healing ability of this crystalline polymer.

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REFERENCES

- [1] N. Yoshie, M. Watanabe, H. Araki, K. Ishida, Thermo-Responsive Mending of Polymers Crosslinked by Thermally Reversible Covalent Bond: Polymers from Bisfuranic Terminated Poly(ethylene adipate) and Trismaleimide, *Polym. Degrad. Stab.*, **95**, 2010, pp. 826-829