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GENERATION OF INTERNAL STRESS IN THE PROCESS OF
SOLIDIFICATION OF SYNTHETIC RESIN, IIIResearch of Molecular Structure Change related to Internal Stress
by Infrared Absorption Spectrum

BY SOGORO YAMAGUCHI

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The changes of molecular structures owing to the solidification by casting epoxy resin, and also owing to the solidification by injection molding of polystyrene copolymer were studied with infrared spectrum. Epoxy resin, with *cis*-cyclohexane-dicarboxylic acid anhydride hardener, firstly seems to be esterified through the opening of epoxy ring and combining with the acid anhydride, and finally to form a net work structure by di-ester and ether formation. This net work formation seems to be related with the generation of the internal stress when restrained. On the other hand, the polarized infrared spectrum of injection molded polystyrene copolymer shows that molecules orientate themselves by rapid cooling of molten flow under high shearing force, as in stretched film, and by heating an injection molded specimen the orientation diminishes and deformation occurs, and this orientation corresponds to the internal stress in the linear polymer.

Introduction

Previously, some experiments were reported about the generating process of the internal stress originating during the curing process of the net work polymer due to contraction under geometrical restraint, and also about the internal stress in the linear polymer originated by rapid cooling of molten flow subjected to shearing force^{1,2)}. In these reports, it is inferred that the one is the stress originated by the restraint of the reacting contraction accompanying the netting of polymers and also the stress originated by thermal contraction arising from expansion coefficient and temperature difference, and the other is the internal stress caused by the orientation of linear polymers and carbon chain stretching due to orientation, and by heating, through collapse of orientation and change of degree of stretching, deformation will appear. The above mentioned results are of great significance in the fact that the cause of the internal stress of solidified polymer and generating process have been clarified, but the significance would be still greater if their changing process as to polymer structure could be also clarified.

For this purpose, some experiments of the infrared absorption spectrum were performed to study the netting reaction of epoxy resin and the polymer structure change due to flow solidification

1) S. Yamaguchi, *This Journal*, **31**, 5 (1961)

2) S. Yamaguchi, *ibid.*, **31**, 18 (1961)

in the case of linear polymers.

Experimentals

Testing materials

1) *Epoxy resin* The same as in the previous report¹⁾, Epikote #834 was used as epoxy resin, and *cis*-cyclohexane-dicarboxylic acid anhydride was used as the curing agent, and molar mixing proportion of epoxy group to acid anhydride was 1:0.9.

2) *α -methylstyrene—styrene copolymer* The same as described in the previous report²⁾, the copolymer Dow Chem. Styron #700 viscosity average molecular weights of which was 140,000, was used.

Measuring apparatus of infrared absorption spectrum As the measuring apparatus of infrared absorption spectrum Perkin Elmer #21 was used, and the measuring range was from 2.5 to 15 μ with NaCl prism.

Measuring method of netting reaction of epoxy resin Regarding epoxy resin, the measurement was made first with Epikote #834 and curing agent *cis*-cyclohexane-dicarboxylic acid anhydride. That is, spectrum was measured by placing the former sample between NaCl plates at room temperature and by placing the latter sample between NaCl plates after heating and made into liquid state. Secondly, Epikote #834 and the curing agent were mixed at room temperature, and at once, placing the mixed sample between NaCl plates, measurement was carried out. Then spectrum measurements with the KBr disk method were carried out at room temperature on the testing materials heated for 11.5, 25, 50 and 70 hrs.

Measuring method of solidification of molten flow of α -methylstyrene—styrene copolymer With α -methylstyrene—styrene copolymer, polarized infrared absorption spectrum measurements were carried out at room temperature on specimens of about 0.06 mm thickness, which were cut out very slowly so that there would be no temperature rise, from the interior of injection molded articles described in the item of the previous report³⁾ on the measuring method for the relation between heating deformation and temperature.

For the purpose of comparing with this, similarly polarized infrared absorption spectrum measurements at room temperature were carried out on a thin film of the testing material, which was made by solving with benzene and applied on NaCl plates, with benzene being evaporated, and also on the thin film of the testing materials, stretched 50% and 118% respectively at 145°C beforehand.

Results

Netting reaction of epoxy resin The experimental result of Epikote #834 is shown in Fig. 1, that of *cis*-cyclohexane-dicarboxylic acid anhydride in Fig. 2, and those immediately after mixing and during the curing heated at 130°C are shown in Fig. 3.

Flow solidification state of α -methylstyrene—styrene copolymer On α -me-

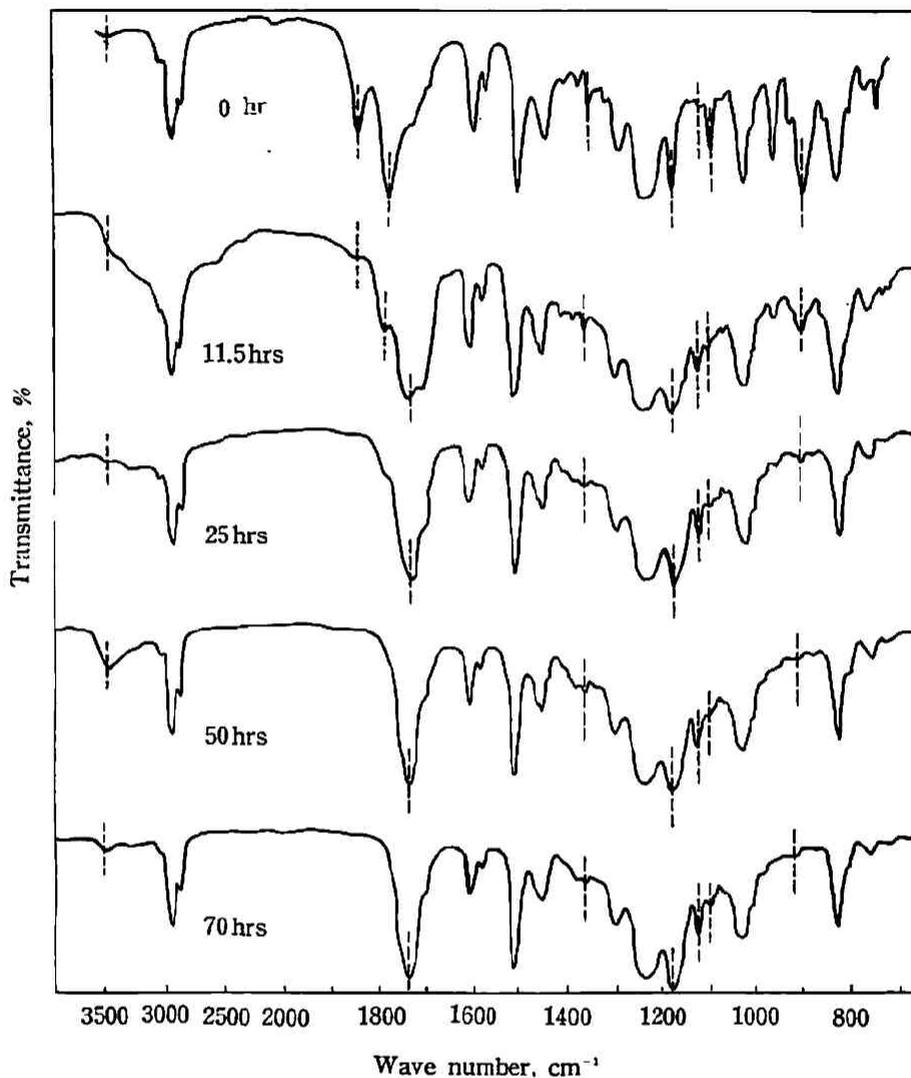
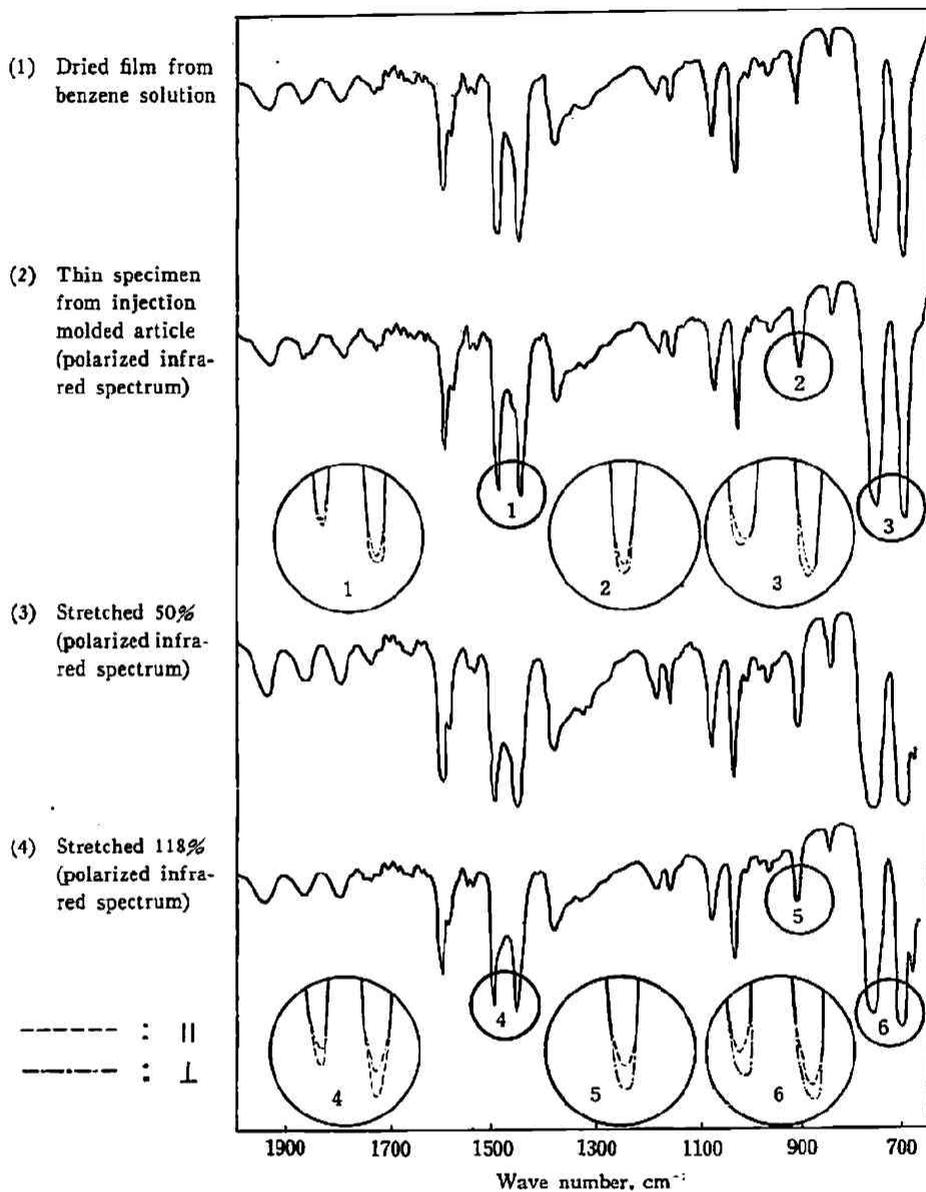
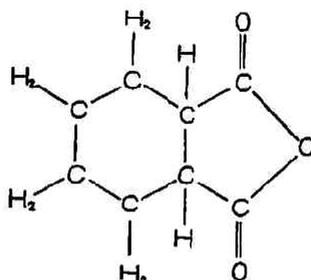


Fig. 3 Infrared absorption spectrum of epoxy casting resin soon after compounding and after curing at 130°C
Number beside spectrum curve indicates curing hours.

zene are 1570, 1470, and 1170 cm^{-1} , CH vibration out-of-plane of parasubstituted benzene is 820 cm^{-1} , epoxy group absorption is 910 cm^{-1} , the vibrations related to C-O-C stretching are 1225 and 1030 cm^{-1} , etc.

Next, the spectrum of *cis*-cyclohexane-dicarboxylic acid anhydride is shown in Fig. 2. This molecular structure is shown next;

Fig. 4 Infrared absorption spectrum of α -methylstyrene-styrene copolymer



As shown in Fig. 2 about the acid anhydride the absorption band of CH stretching vibration of alicyclic structure ranges from 2800 to 2930cm^{-1} , typical vibrations of $\text{C}=\text{O}$ stretching about acid anhydride are 1830 and 1770cm^{-1} , the $\text{C}-\text{O}-\text{C}$ stretching vibration is 1200cm^{-1} and the CH_2 deformation vibration is 1440cm^{-1} .

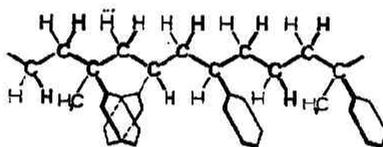
The spectrum of the mixture shown in Fig. 3 becomes a superposed spectrum of Epikote #834 and of *cis*-cyclohexane-dicarboxylic acid anhydride spectrums, and the fact that shifts of absorption band can be noticed in the spectrum is more or less attributed to the change of the state through mixing them, but any change in the chemical combination cannot be noticed considering the correspondence of absorption bands.

However, as the mixture is heated at 130°C , a great change will be noticed in the aspect of the spectrum. That is, if remarkable points are indicated, first it will be seen in Fig. 3, by comparing the state immediately after mixing and that after heating for 11.5 hrs. that $\text{C}=\text{O}$ stretching vibration of $1770\sim 1850\text{cm}^{-1}$ of the curing agent, *cis*-cyclohexane-dicarboxylic acid, decreases markedly and that absorption due to $\text{C}=\text{O}$ stretching of ester near 1730cm^{-1} begins to appear, and these results are considered to be the bonding of anhydride with bisphenol derivatives due to the ring-opening of the curing agent of anhydride. The next marked point is the characteristic absorption of epoxy group at the absorption band near $900\sim 915\text{cm}^{-1}$ which is the absorption existing also in acid anhydrides, and this absorption, following the ring-opening of acid anhydride, gradually disappears and so it can be understood that, as expected, the ring-opening of epoxy group has taken place and the esterification reaction between acid anhydrides will occur. Further, due to this ring-opening, it can be presumed from the appearance of that absorption band near 3400cm^{-1} of spectrum in Fig. 3 that free OH group is being produced on the way. Such a change of spectrum is further investigated for the specimens heated at 130°C for 25~75 hrs, and it can be judged, through the rise and fall of $\text{C}=\text{O}$ stretching vibration between $1700\sim 1850\text{cm}^{-1}$, that acid anhydride of the curing agent will nearly completely disappear in 25 hrs and has become esterified. Further, this fact is also evident by the disappearance of absorption spectrum of epoxy group and acid anhydrides near 910cm^{-1} which more or less still remain in 25 hrs but can not be noticed any more in 50 hrs. That only free OH exists more or less near 70 hrs is to be supported from the absorption spectrum near 3500cm^{-1} .

All these changes show that Epikote #834 of epoxy resin is giving rise to the bridge-making reaction by *cis*-cyclohexane-dicarboxylic acid anhydride and the netting of molecules is progressing.

It can be understood from the above mentioned results that the contraction accompanying the curing reaction, as previously reported, is ascribed to the progress of this bridge-making reaction, and as the netting of molecules progresses, completely free arrangement in molecular structure cannot be attained owing to geometrical restraint, and as the results the internal stress appears.

Solidification accompanying molten flow of α -methylstyrene—styrene copolymer The schematic molecular structure of α -methylstyrene—styrene copolymer is shown next ;



This is an atactic linear polymer in which α -methylstyrene and styrene copolymerize. The ordinary infrared absorption spectrum of this copolymer is shown in Fig. 4-(1). As there are several reports³⁾, the spectrum of polystyrene will not be explained here, but some special features appearing through the copolymerizing of α -methylstyrene are mainly that of the existence of the absorption spectra due to methyl group belong to α -methylstyrene. That is, the shoulder of 1465cm^{-1} corresponds to the degenerated deformation vibration of CH_3 , and the absorption band of 1357cm^{-1} to the symmetrical deformation vibration and original polystyrene absorption. No great change can be noticed any more. About the testing material from the interior of the injection molded article the results of polarized infrared absorption spectrum are shown in Fig. 4-(2). No remarkable dependency of the direction of polarization can be noticed, but at least among the absorption spectra caused by phenyl group, the absorption bands of $1600, 1580, 1490, 1450, 1375$ and 1030cm^{-1} , etc., which are supposed to belong to in plane deformation vibration of benzene nucleus, become deeper through parallel polarization in molten flow direction, and the absorption bands, $910, 760$ and 705cm^{-1} , which are supposed to belong to out of plane deformation vibration of benzene nucleus, become slightly deeper due to polarized light in perpendicular direction to molten flow. On this point, among the spectra of the testing materials stretched above 118%, that similar behavior of the absorption band change can be noticed as shown in Fig. 4-(4), etc. and as it is recognized clearly that the orientation happens in this case, the molecular orientation by molten flow can be demonstrated as previously estimated. Naturally, in polystyrene group, the difference due to stretching by the polarized infrared spectrum is not so great, but the above stated difference in absorption spectrum is clear, and so the view that the residual stress caused by sudden cooling of molten flow corresponds to molecular orientation can be considered as having been verified qualitatively through infrared absorption spectrum.

That is, in molten flow, molecules have the tendency to orientate themselves as that carbon chain becomes parallel to flow direction and solidified as they are, and by heating, this orientation will be lost, and it can be affirmed that in molded articles contraction will appear in molten flow

3) C. Y. Liang and S. Krimm, *J. Polymer Sci.*, 27, 241 (1958)

Generation of Internal Stress in the Process of Solidification of Synthetic Resin, III 33

direction and elongation will appear in perpendicular direction of molten flow. As explained in the previous report, the activation energy of 13~16kcal/mol for the heat deformation is about an expected amount of energy for the disappearance of orientation.

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*The Research Department
Fuji Electric Manufacturing Co., Ltd.
Kawasaki, Japan*