Real Time Photo-Curing Reaction Measurement and Thermal Properties of UV Curing Resin for Nanoimprint

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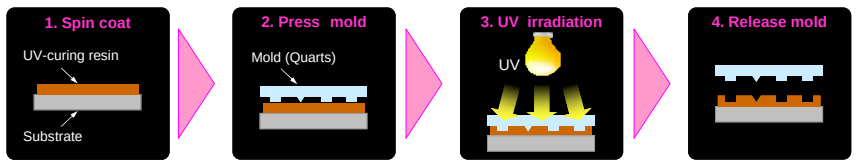
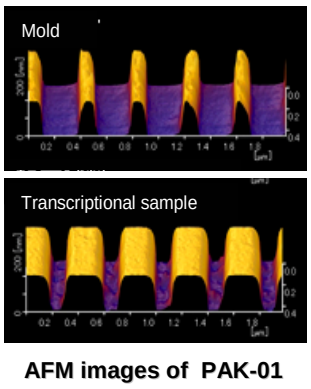
Introduction

Nanoimprint is a processing technology which fabricates the nanoscopic concavo-convex structure on the resin surface by the fine patterned mold. The UV nanoimprint technology is the transfer printing technology. The spin coated UV curing resin is pressurized by the fine patterned mold, the ultraviolet light is irradiated, and the fine pattern of the mold is printed onto the UV curing resin surface.

In this study, with regard to the liquid ultraviolet curable resins of the three different amount of functional group equivalent, curing reaction rate, curing reaction heat, glass transition temperature, decomposition temperature, thermal expansion properties, and viscoelastic properties are analyzed by UV irradiation DSC, constant rate heating DSC, TGA, and DMA.



UV Nanoimprint Process



AFM images of PAK-01

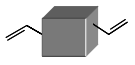
Materials

Ultraviolet curable resins for nanoimprint are used which have different amount of functional group; PAK-01(TOYO GOSEI CO., LTD.), C-TGC-02, C-TGC-03. These samples are epoxide ester which has vinyl group at the terminal of the molecule.

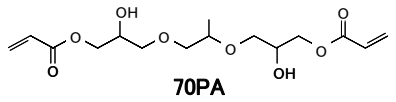
Functional group equivalent : PAK-01 < C-TGC-02 < C-TGC-03

- Uncured resin samples are measured as it is.
- Cured resin samples are prepared by the irradiation of Hg-Xe light for 10 minutes with wavelength 365nm and strength 1mW/cm^2 in advance.

PAK-01

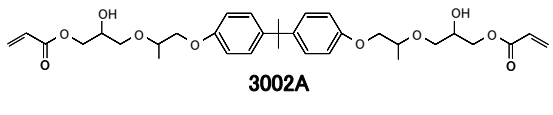


C-TGC-02 70PA : IRGACURE 907 = 95 : 5 (wt%)



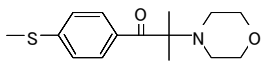
70PA

C-TGC-03 3002A : IRGACURE 907 = 95 : 5 (wt%)



3002A

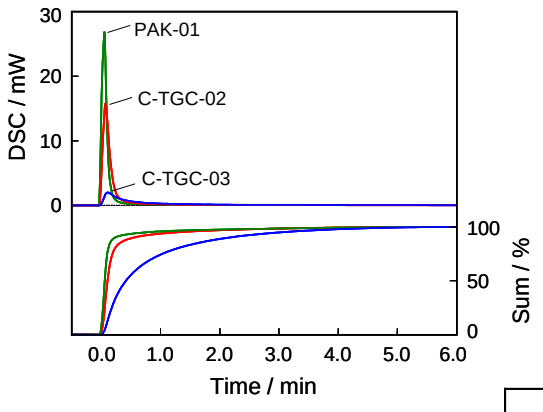
Initiator of radical photopolymerization



IRGACURE 907

Results and discussions

Photo Chemical Reaction Measurements



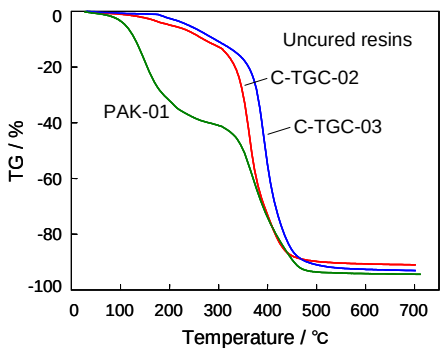
Wavelength : 365nm
Irradiation intensity : 1mW/cm^2
Irradiation time : 10min
Sample weight : 0.5mg
Temperature : 25℃ isothermal
Atmosphere : N_2 30ml/min

Photochemical Reaction DSC System
DSC7020＋PDC-7

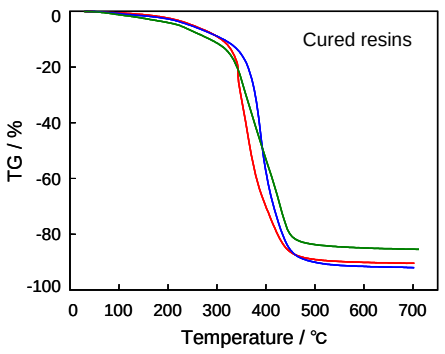
Sample	Reaction time (Peak top, min)	Reaction enthalpy (ΔH, J/g)
PAC-01	0.053	27.0
C-TGC-02	0.070	15.8
C-TGC-03	0.108	1.99

Radical is generated from the polymeric initiator by UV irradiation onto the uncured resin. Nucleophilic attack to the acryl group is done. Double bond at the terminal of the molecule is polymerized and cross-linking reaction progresses and the resin is cured. One of the major factors which have an influence on the curing reaction is effect of steric hindrance. Figure show that the resin which has smaller amount of functional group equivalent does not have an influence on the effect of steric hindrance and higher molecular motion freedom. It suggests the effective polymerization.

Decomposition Measurements



Heating rate : 10℃/min
Sample Weight : 10mg
Sample pan : Pt open pan
Atmosphere : N_2 200ml/min

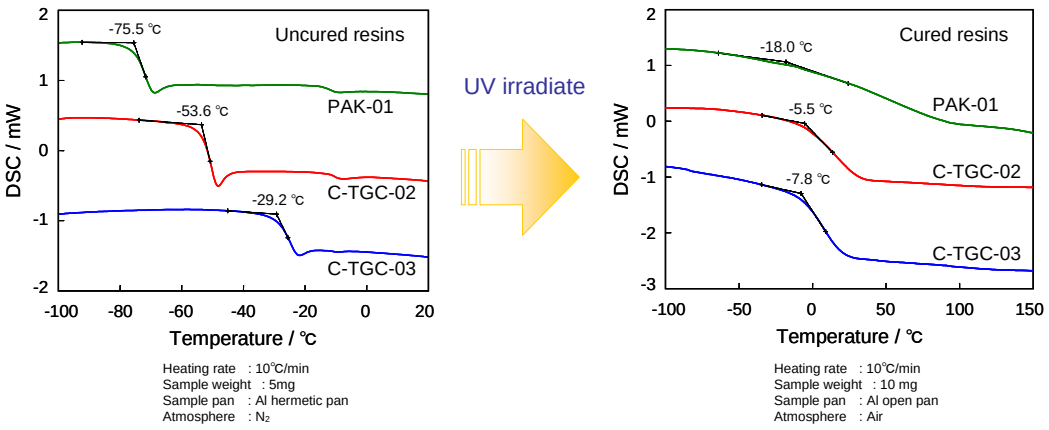


Heating rate : 10℃/min
Sample Weight : 10mg
Sample pan : Pt open pan
Atmosphere : N_2 200ml/min

The higher amount of functional group equivalent, the higher decomposition temperature of both uncured resin and cured resin becomes. In particular, as C-TGC-3 contains phenyl in main chain, the highest decomposition temperature is likely to be obtained.

TG/DTA7200
Thermogravimetry / Differential Thermal Analyzer

Glass Transition Temperature Measurements

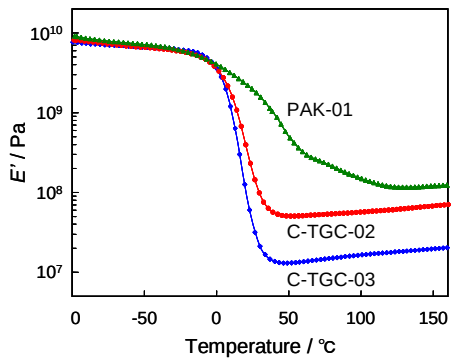


Heating rate : 10℃/min
Sample weight : 5mg
Sample pan : Al hermetic pan
Atmosphere : N_2

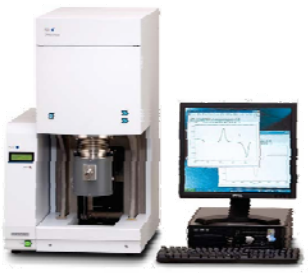
Heating rate : 10℃/min
Sample weight : 10 mg
Sample pan : Al open pan
Atmosphere : Air

In case of same molecular structure polymer, the smaller the molecular weight, the lower the glass transition temperature becomes. Uncured resin, i.e. monomer, glass transition temperature is dependent on the amount of functional group equivalent. However as cured resin is already polymerized, the bigger the molecular weight by polymerization, the bigger the glass transition temperature difference might be.

Viscoelasticity Measurements



Deformation mode : Tension mode
Sample size : H 10×W 10×t 0.4mm
Heating rate : 2℃/min
Frequency : 1Hz
Atmosphere : N_2 200ml/min



DMS6100 Dynamic Mechanical Spectrometer

In case of cross-linked polymer, *E'* of the rubbery plateau region is detected higher the higher the crosslink density. Figure shows the smaller amount of functional group equivalent, the higher the crosslink density. It suggests that the resins which have smaller amount of functional group equivalent have small influence on the effect of steric hindrance and the effective polymerization.

Conclusions

Thermal analysis is very effective to the product evaluation of each nanoimprint process and enables the evaluation of volatility characteristics at coating, amount of heat and separation properties at transfer printing, hardness and thermal stability.

The smaller amount of functional group,

- The faster curing reaction rate, the stronger peak intensity and bigger peak area by photochemical DSC.
- The lower glass transition temperature (Tg) in uncured resin. However cured resins almost same Tg by DSC
- The lower decomposition temperature both uncured and cured by TG/DTA
- The higher cross-link density sample cured by DMA.