On resinic cure shrinkage, shrink stress measurement and the analysis

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Introduction

Expansion of the resin consumption is continuing bed leno with ant De-solvents makings, quality level of improvements, productivity of speed up as environmental measure etc. is use are developed in variety of industrial products with recent years, progres of UV curable resin as purpose. Also, following by thermosetting resins, hybrid various range of a variety of functional activities products development of adhesives that combined UV sclerosis and thermosetting not only ultraviolet curing resin. Even if the said film formations, structural member fixed etc, Electricals, devices, automobiles, construction related etc use by officials is officials fields, it is not exaggeration.

However, recent resin being very high spec is required is facts, too. Maintaining international competitiveness, reduce yields to continue to supply high-quality products, and use consistent Productivity, and need to reduce products costs.

The part, trace was applied resins or thin films applied Changes in resins of retraction, shrinkage stress or time-lapse need to grasp exactly.

However, retraction was not measured from contraction after volumes change so far before viscoelasticity measuring instrument, resin shrinkage that method that measure in water displacement method that is listed in JIS only in measurement of retraction, but there is method that resin action is gauged continuously.

Also, the contraction stress to cure the plate-like plastic is applied indirectly. In contraction stress, warp sheet is hauled in do so accompanied by resin shrinkage. Method that calculate modulus from the patients with the warpage is described for various papers, too. The method is to the utmost indirect, and a complicated calculation formulas modulus of need to metal, information that obtain from film Atsushi etc. of being coated plastic on the basis. This equipment directly was accurately continuously and can measure the curing shrinkage contraction stress, but the had been produced by expectations from various quarters to such production equipment put together opinions from each user is a curing shrinkage rate of resin of CUSTRON(Cure Shrincage and Stress Analysis System), meanwhile, are used to measure stress, but this time, let us consider the hardening contraction stress of resin from the basic principle of resin shrinkage, analysis of data measured by the CUSTRON.

1. Curing the epoxy resin contraction model

Epoxy resins hardening schematic diagram is recorded in the Fig.1 below first. Liquid state A of normal temperature is heated, and reaction with curing temperature B and point that the reaction terminates are C. After sample release is cooled from the this point, and reaching D: this glass transition temperatures Tg of curing system, reach room temperature E, and this cycle is concluded. Contraction by cures reaction occurs in this schematic diagram drawings between B-C, and contraction by coolants after cure is shown in C-D-E. With the proviso, as D corresponds to this tg of system, contraction in glassy areas(<Tg) is equivalent between D-E, and contractioning in rubbery region(>Tg) occurs between C-D turn on. It does that for purposes of illustration, contraction among A-E is called by overall shrinkage, contraction among B-E with contraction maximum in addition. Retractioning of conventional thermosetting epoxys measuring A-E this turns on. In Kansai University, the Yamaoka clan 1) et al substitution density measurement example, for ethylenediamine, Total shrinkage is A-ing 5.1% Max shrinkage B-E is 10.5%. In ethylenediamine tetra, Total shrinkage is A-ing 4.8% Max shrinkage B-E is 10.1%. Epoxy resins hardening schematic diagram is recorded in the Fig2 below first. Liquid state A of normal temperature is heated, and reaction with curing temperature B and point that the reaction terminates are C. After sample release is cooled from the this point, and reaching D: this glass transition temperatures Tg of curing system, reach room temperature E, and this cycle is concluded. Contraction by cures reaction occurs in this schematic diagram drawings between B-C, and contraction by coolants after cure is shown in C-D-E. With the proviso, as D corresponds to this tg of system, contraction in glassy areas(<Tg) is equivalent between D-E, and contractioning in rubbery region(>Tg) occurs between C-D turn on. It does that for purposes of illustration, contraction among A-E is called by overall shrinkage, contraction among B-E with contraction maximum in addition. Retractioning of conventional thermosetting epoxys measuring A-E this turns on. In Kansai University, substitution density measurement example of the Yamaoka clan, for Etylenediamine, Total shrinkage is A-ing 5.1% Max shrinkage B-E is 10.5%. In Tetrametylenediamine, Total shrinkage is A-ing 4.8% Max shrinkage B-E is 10.1%.
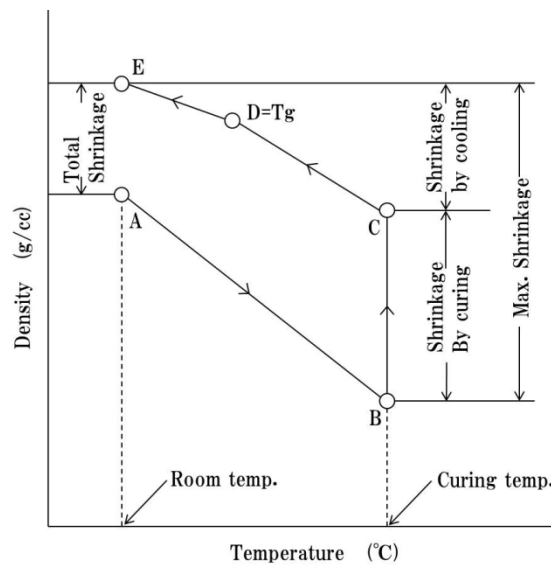
Density Change in curing cycle of epoxide resins.

Fig.1 cure shrinkages model

Coming into to be repeated again, but while when hardens process of density variation of thermosets is seen, expanding with liquid state by temperature rise by application of heat at first, and two quantum crosslink of resins begins by curing reaction, and is accompanied by volumes contraction, achieving gel point, ends of two quantum bridges. Epoxys migrate in this case from liquids to behavior as individual. Proceeding to 3 dimension crosslinkings then, and reach hardening point as this ends. Cooling process is returned in room temperature were through it in addition. In this process, difference with solidifying volume of gel point and volume after coolants result in cured internals strains.

A conventional strain, and have glass tube method as a matter of assay. "Glass tube method", something about method that determines volumes change from the patients with Oils liquid level change to cure resin samples in oils is told. In addition, in this method, measurement in microdetermination and thin film condition does not build up exactly.

2.   On ultraviolet curing resin cure shrinkage

Cure shrinkage occurs in gap that being accompanied by multimolecular such as UV cured resin in polymerization reaction that trim in a numerator from van der Waals distance to conversion to covalent bond distance. Van der Waals distance of monomer molecular together(approximately 3-6 Å)'s shrinking to covalent bond length(carbon — carbon approximately 1.4 Å) by curing reaction is causes. However, this becomes talks in model system to the utmost. As be consisted of by volatiles of monomer, multiple formulations including inorganic Materials(this does not constrict basically) that

is adding as filler, retraction varies by prescription in resin component actually. Volumes contraction of ragged edge of painting to paint coating by curing reaction limit to coating inside as residual stress, and shoot to one of causes that is reduced adhesions. It is a less degrees and low temperature reaction with ambient temperature of the high curing reactions than room temperature or room temperature, and is very at tens seconds and a short since seconds also, reaction time, compared with curing system conventional heating, as evenes, and there is no time to stress that is generated in curing reactions process is relaxed, in the first place, UV curing system residual stress is higher, and is reaction. 2)

３． Resin hardening retraction measurement example

（1） Measurement method

Measurements with basics CUSTRON are as follows.

① Teflon ring of thickness 1 mm is placed in dumb figure on glass slides on glass

② In it resins are injected.

③ Measuring analytes are located on measurement stage

④ Curing conditions settings perform

⑤ Starting measurement

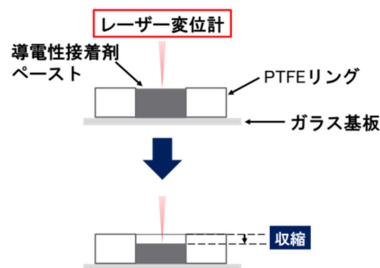⑥ After end of the measurement, in excel, data, graph Display is performed

Fig.3 measurement

(2) Thermosetting resins, the sclerosis contraction cases 1

Following Fig.4-1 make after 30 hold temperature rise in 15 mins for 15 mins, and is cure the thermosetting epoxy resin retraction measurement example that measured at program that cool to room temperatures from room temperatures to 130 C. Expansion of liquids begins, and situation that when reach reaction temperatures, contraction begins rapidly observes accompanied by temperature risings. Also, after 130 C holdings, the contraction Tg times when enter coolants maximum after discipline water end. This is examples that fit into cure

contraction model of above Fig. 1, too.
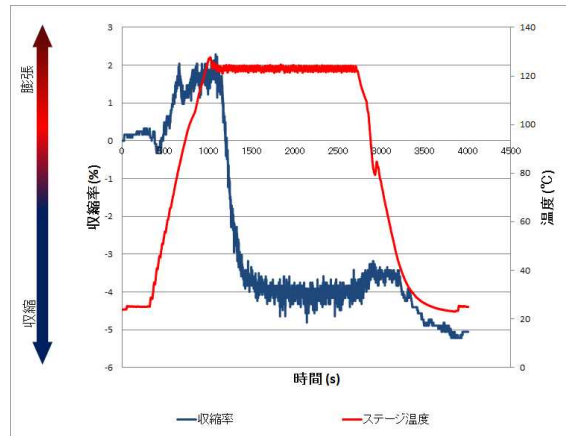
The Fig.4-1 epoxies cure retraction measurement example1

(3) Thermosetting resins, the sclerosis contraction cases 2

When heated to 200 C from the patients with room temperatures at once, and be rapid cooling, 50 keep, and is measurement of thermosetting epoxys of size excess that returned to room temperatures. A liquid resin turns expansion into solids with temperature risings with at first, quick cooling, and is examples that trimed in retraction of finals 2% degree.
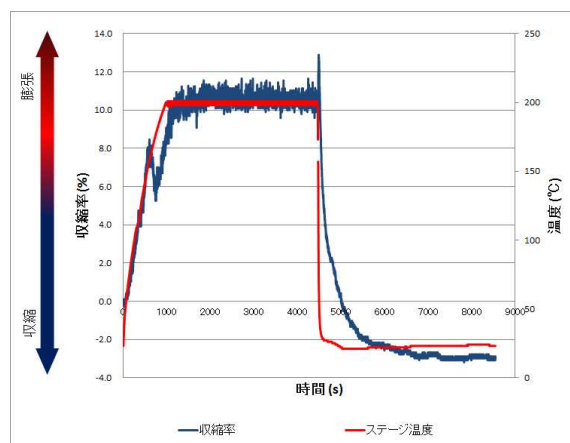

The Fig.4-2 epoxies cure retraction measurement example2

The measurement example(4) thermoset cures shrink stress 3

Fig.5 below, the temperature rise, and keeps for 30 mins from room temperatures to 200 C, and it is examples that determined stress developmental processes in

case of hacking as room temperatures quick cooling. When sclerosis start in liquid state, begins to generate stress gradually, and the preceding paragraphs Fig.4 shrinkage contraction stress is maximum 200 C with maximum with quick cooling with .
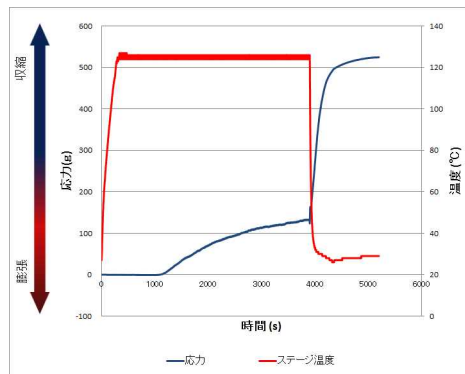
The Fig.5 epoxy curing resins cure shrink stress measurement example3

The measurement example(5) thermoset cures shrink stress 4

Following Fig.6 temperature from room temperatures to 100 C, and is figure that resulted stress expressions states that did 200C60 hold after 30 hold. When raises the temperature to 200 C in if 100 C this after holdings, it is exhibited that stress is acting in negatives(be distended). After the, expressions of stress is occurring in steep slopes with quick cooling. "Adhesiving with deposition material is thought in fact", interfacial separation by development of rapid strength is the state of being to imagine can be done, too. Also, sudden stress expressions are skewed adhesive with adherend, and can factors that hitoshi causes, too, too.
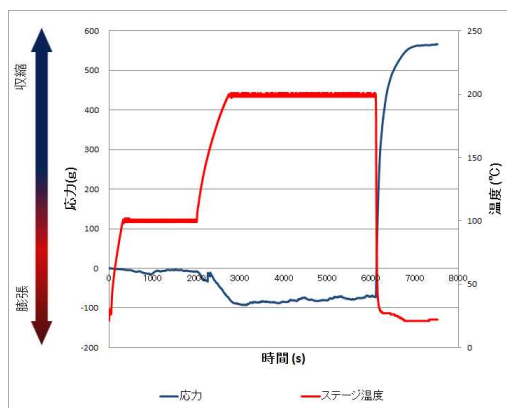
The Fig.6 epoxy curing resins cure shrink stress measurement example4

The(6) UV curing resins cure shrink stress measurement example 5

Following Fig.7 is comparative data with products that are billed as UV curing acrylic resin and hypokinesis acrylics in UV cured resin. Difference of retraction after UV radiation comes in, seeing clearly.
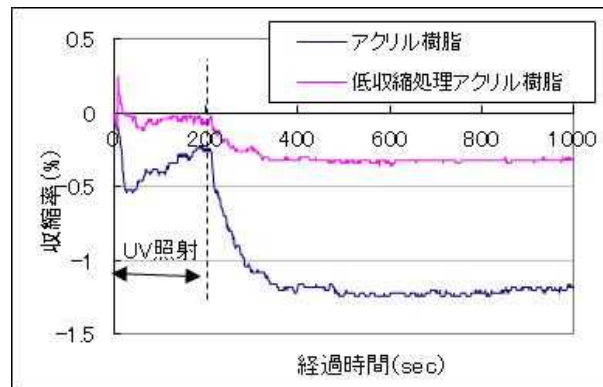

Fig.7 Comparisons of UV curing acrylic resin and hypokinesis acrylics

The(7) UV curing resins cure shrink stress measurement example 6

Following Fig.8 is performance Review data of adhesives that are deemed to improve on retraction of UV curing acrylics. After UV radiation, is dedicated for heating for 3 hours, and retraction after coolants' being improved product improvement expressly. This, for example, change dosage of fillers shrinkage during the thermal curing epoxy to suppressed, and frequently used method that contraction and intrinsic material stress is suppressed, but it is such contraction by addition of a binder examples that stress process can be observed, too, easily.
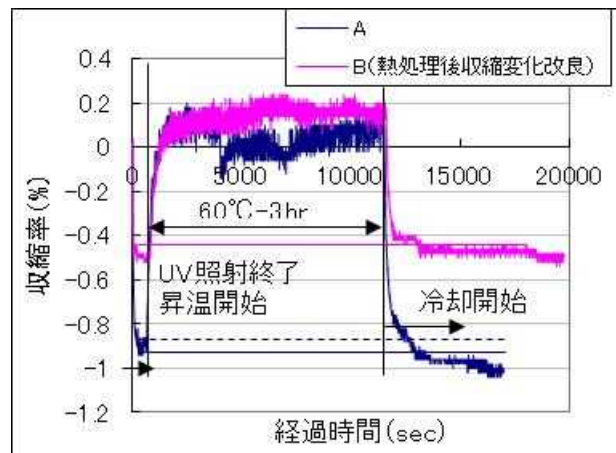
Performance verification of the Fig.8 modified resin

4. Summary

Measurement of the hardening shrinkage contraction stress of the resin, a complex system such as hybrid adhesives, 2 step composite type adhesive due to the development of a high-performance resins increased, shrinkage percentage accordingly, grasp of the stress more has become required. Also, production in overseas Market increases, too, and establishment of the manufacturing process is necessary to production activities in locations that environment are different significantly. Gripping adhesive mold shrinkage factors, stress due is nothing else than the quality itself of products in manufacturing process. If this time, introduced retraction, principl expressions of stress trims in architects future plastic, help of user, it is fortunately.

1) Yamaoka Kazumi "materials" Volume 29No.323 Kansai University August, 1980

2) Kawasaki Noriaki UV curing the process optimization 2 Sakai Chemical Industru Co., Ltd. ㈱February, 2010