

Trehalose-Based Thermosetting Resins. I. Synthesis and Thermal Properties of Trehalose Vinylbenzyl Ether

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Received 3 December 2002; accepted 13 April 2003

ABSTRACT: Trehalose vinylbenzyl ether was synthesized from trehalose and *p*-chloromethylstyrene (CMS) in DMSO in the presence of powdered NaOH. The structure of the product was characterized by IR and ¹H NMR spectroscopy. Degree of substitution (DS) on a trehalose unit calculated from the ¹H NMR spectrum varied from 2.4 to 3.2 by changing the feed ratio of *p*-chloromethylstyrene to trehalose. Thermal properties of the resin were analyzed by differential scanning calorimetry (DSC). DSC analysis revealed that the resin DS 2.4 has one exothermal peak at 132°C, whereas the resins DS 2.8 and 3.0 have two exothermal peaks. Furthermore, the resin DS 3.2 was found to have only one

exothermal peak at 191°C. Dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) revealed that the cured resin has one transition, implying a glass transition. Biodegradability was assayed by the BOD method, and several percent of the cured resin was found to be degraded with activated sludge for 50 days. Further degradation, however, was not observed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 46–51, 2004

Key words: thermosets; renewable resources; thermal properties

INTRODUCTION

Trehalose is a disaccharide consisting of two glucose units coupled at the 1,1'-position, that is, 1-O- α -D-glucopyranosyl- α -D-glucopyranoside. It is a nonreducing saccharide and relatively stable to alkaline and acid conditions. Recently, trehalose has been produced industrially from starch with enzymes, and has become available with lower cost than before. Thus, trehalose can be regarded as a renewable resource. For the purpose of conserving our petrochemical resources, thermosetting resins should preferably be made from such renewable resources, because cured thermosetting resins are generally difficult to recycle. More ideally, they would be biodegradable. Trehalose has eight hydroxyl groups per molecule, and so it is suitable for use as a starting material for thermosetting resins or crosslinking agents. Furthermore, two of the eight hydroxyl groups of trehalose are primary hydroxyl groups, whereas others are secondary hydroxyl groups. The difference in reactivity of these hydroxyl groups is considered to be an advantage for the control of reaction sites in the reaction of trehalose with a limited amount of modifier.

Sachinvala et al.^{1–3} prepared sucrose-based crosslinkers for PMMA. They reported that octa-O-allyl- or octa-O-crotylsucrose imparts thermal stability to PMMA. This is one example of the application of the modified disaccharide for a crosslinker. However, they did not use the sucrose ethers alone as a monomer. Dordick and their coworkers^{4,5} prepared sucrose acrylate for hydrogel by the enzymatic reaction. Acylation of sucrose was limited to the 6- and 1'-hydroxyl groups. They used sucrose monoacrylate and diacrylate as monomer and crosslinker, respectively. The hydrogel was degraded in a weak alkaline buffer or by enzymatic hydrolysis. They did not study the physical properties of the crosslinked resins (without water) in detail. For a similar purpose, Shantha and Harding⁶ synthesized sucrose-containing polymeric hydrogels by free-radical polymerization.

In the present study, trehalose vinylbenzyl ether (TVB) was prepared (Scheme 1) and investigated for its thermal properties. A vinylbenzyl group is susceptible to radical reaction at heating to yield a polymer without an initiator. The degree of substitution (DS), which is calculated as the number of substituted groups in one trehalose derivative, was regulated at around two to three.

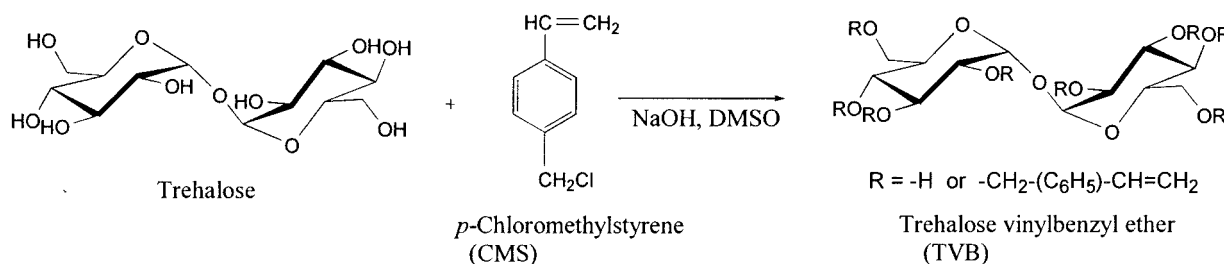
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Contract grant sponsor: the Ministry of Education, Science, Sports, and Culture, Japan.

EXPERIMENTAL

Materials

Trehalose was generously provided by Hayashibara Co., Ltd. (Japan). *p*-Chloromethylstyrene (CMS) was



Scheme 1 Reaction of trehalose with *p*-chloromethylstyrene (CMS).

generously provided by Seimi Chemical Co. Ltd. (Japan). Sodium hydroxide was purchased from Kanto Chemical (Japan). These reagents were used as received. Dimethyl sulfoxide (DMSO) was purchased from Kishida Chemical (Japan) and dried on Molecular Sieve 4A.

Synthesis of trehalose vinylbenzyl ether (TVB)

Trehalose (10 mmol) was dissolved in DMSO (100 mL). Sodium hydroxide was milled into fine powder by a home mill mixer, and weighed immediately. The powdered sodium hydroxide (80 mmol) was added to the solution, and the mixture was stirred by a magnetic stirrer for 30 min at room temperature under a nitrogen atmosphere. CMS was added to the mixture dropwise, and the solution was vigorously stirred for 24 h at room temperature. The feed ratio of CMS to trehalose varied from 1.5 to 4.0 (mol/mol). The solution became viscous as the reaction proceeded. After the reaction, the mixture was poured into excess water, yielding in a yellow sticky precipitate. After washing with diethyl ether–hexane (4 : 1), white yellow powder was obtained.

Characterization of TVB

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AMX-400 spectrometer using CDCl_3 as solvent for TVB and $\text{DMSO}-d_6$ for trehalose. Prior to the measurement, the solution was filtered through a 0.2- μm filter. DS was defined as the number of vinylbenzyl ether groups substituted for hydroxyl groups on one trehalose unit, and calculated from peak integral values of NMR spectra. Infrared (IR) spectra were recorded on a Shimadzu FTIR 8100 spectrometer. TVB was mixed with KBr powder and pressed into a pellet prior to the FTIR measurement.

Decomposition behavior was analyzed by a Perkin-Elmer TGA 7 thermogravimetric analyzer at a heating rate of 20°C per min. Thermal transitions were analyzed by a Perkin-Elmer Pyris 1 differential scanning calorimeter. The sample for DSC was weighed (~10 mg) on a small aluminum pan, followed by sealing the

pan. The heat capacity was scanned from -15 to 220°C at a heating rate of 20°C per min.

Curing of TVB and measurement of thermal properties

TVB powder was inserted between two aluminum sheets with 0.8-mm spacers. TVB was cured and molded into a sheet by pressing at a pressure of 30 kgf/cm^2 (29 bar) at 200°C for 30 min with a hot press machine (SA-303 Tabletop Test Press Type S, Tester Sngyo Co., Ltd.). The resin was postcured at 200°C for 30 min in a dry oven.

Thermomechanical properties were analyzed by a Mac Science TMA 4000S thermomechanical analyzer equipped with a quartz probe bar. The sample plate was cut into pieces of 4 × 4 mm with 0.8 mm thickness, and thermal expansion was measured at a heating rate of 5°C per min under a load of 98 mN. The response to a dynamic stress was analyzed by a Perkin-Elmer DMA 7e dynamic mechanical analyzer. The sample piece of 10 × 3 mm with 0.8 mm thickness was prepared and heated from 0 to 200°C at a heating rate of 5°C per min under a static stress of 1 MPa and a dynamic stress of 0.5 MPa with a frequency of 1 Hz. The span between the supports of the three-point bending platform was 5 mm.

Biodegradability

Biodegradability was determined by measuring biochemical oxygen demand (BOD) under an aerobic condition. To phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl_2 , 0.09 mM MgSO_4 , 0.09 mM NH_4Cl , and 0.9 μM FeCl_3 , were added 4.35 mL of activated sludge containing a 30-mg insoluble part, which was obtained from sewerage facilities of Chiba Institute of Technology, and 20 mg of the thermoset powder. The dispersion was steadily stirred with a magnetic stirring bar. BOD was measured at 25°C by using a Taitec BOD tester 200F. CO_2 was absorbed into 50% sodium hydroxide aqueous concentrate in a cup equipped within a glass bottle. The volume of con-

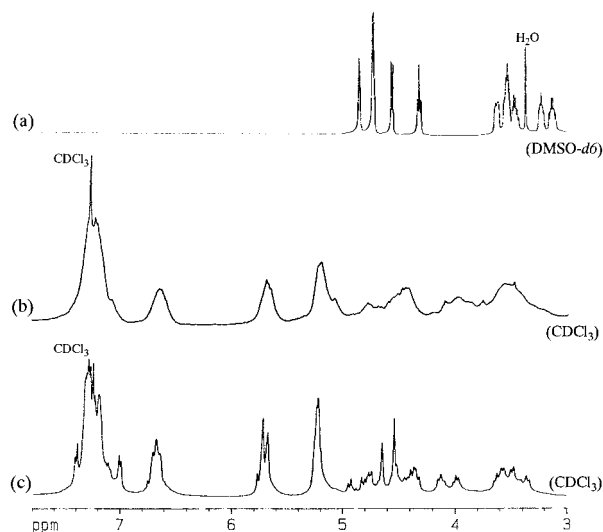


Figure 1 ^1H NMR spectra of trehalose and reaction products with different CMS feed ratios: (a) trehalose in $\text{DMSO-}d_6$, (b) 1 : 1.5 (trehalose : CMS) in CDCl_3 , (c) 1 : 4.0 (trehalose : CMS) in CDCl_3 .

sumed oxygen was directly measured with a scaled cylinder.

RESULTS AND DISCUSSION

Synthesis of TVB

The reaction was carried out at room temperature to yield trehalose vinylbenzyl ether. When the reaction temperature was raised to 50°C , much insoluble material appeared, and it was insoluble in most organic solvents. This may be due to crosslinking between vinylbenzyl groups. Some liquid side product appeared, and it was washed out together with unreacted CMS during washing with diethyl ether–hexane (4 : 1).

Figure 1 shows the ^1H NMR spectra of trehalose and products. The peaks around δ 7.0–7.4 ppm are assigned to aryl protons and those at δ 6.7, 5.7, and 5.2 ppm are assigned to vinyl protons. The peak at δ 4.5 ppm is assigned to methylene protons adjacent to the aryl group. The area of these peaks slightly increased with an increase of the CMS feed ratio, compared to the area of the peaks around δ 3.4–3.6 ppm, which are assigned to methine and methylene protons of trehalose. Shifts of the methine and methylene peaks of trehalose toward the lower magnetic field were observed, which is due to the substitution for the hydroxyl groups. When the CMS feed ratio was 1.5, peaks were broadened because the solubility of the product in CDCl_3 was low.

Figure 2 shows the relationship between CMS feed ratio and DS of the products calculated from NMR spectra. When the feed ratio was 1.5, the DS of the

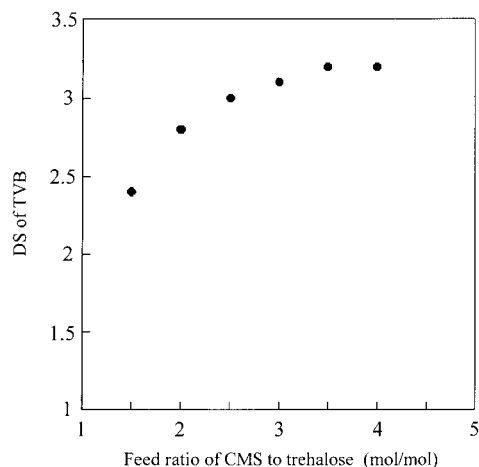


Figure 2 Plot of degree of substitution (DS) of TVB vs mol feed ratio of CMS to trehalose.

product was 2.4. This result means that TVB with the lower DS (0 or 1) was removed in the washing process with water. On the other hand, when the feed ratio was 4.0, the DS of the product was 3.2. Two reasons for this result can be considered: TVB with the higher DS (over 5) might be soluble in diethyl ether–hexane (4 : 1), and washed out. Alternatively, the substitution might not proceed over DS 4 at room temperature because of crowding of vinylbenzyl groups.

Figure 3 shows IR spectra of products with various DS values. The absorption at ca. 3300 cm^{-1} is assigned to the O–H stretching vibration of hydroxyl groups of trehalose. This absorption was reduced with an

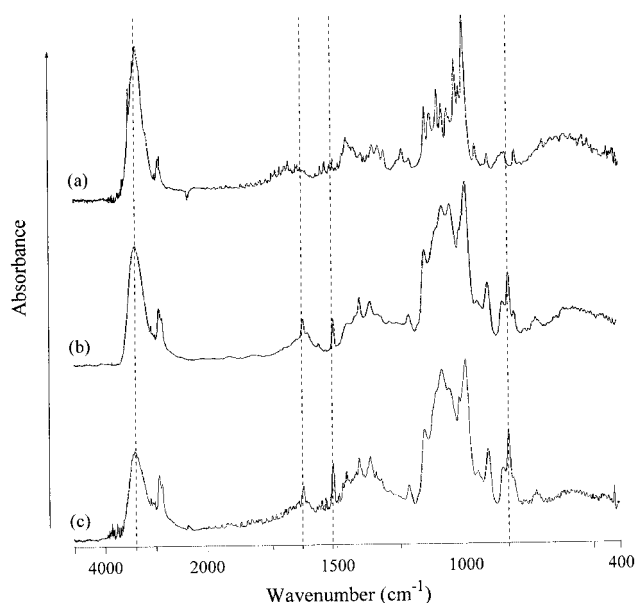


Figure 3 IR spectra of trehalose and TVB with different DS values: (a) trehalose, (b) TVB with DS 2.4, (c) TVB with DS 3.2.

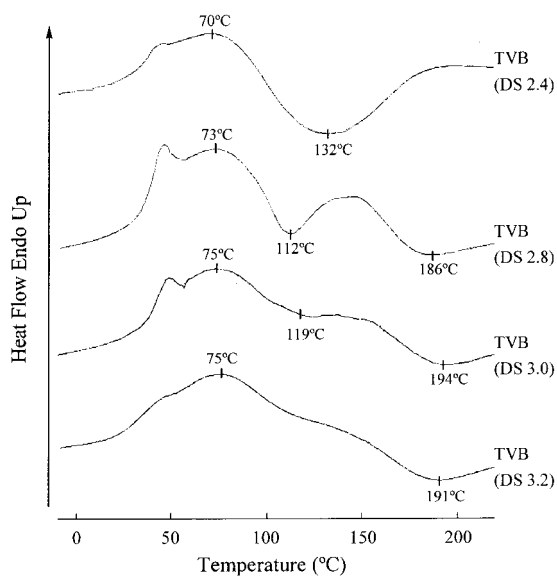


Figure 4 DSC thermograms of TVB with various DS values. The first heating process is represented. The heating rate was 20°C per min.

increase of DS. On the other hand, the absorptions at 1630 cm^{-1} and 1510 cm^{-1} increased considerably with an increase of DS. These absorptions are assigned to the C=C stretching vibrations of vinyl and aryl groups, respectively. The absorption at 1080 cm^{-1} , which may be assigned to C—O—C groups between trehalose and benzyl groups, also increased with an increase of DS. The absorption at 820 cm^{-1} corresponds to the C—H out-of-plane bending vibration of the aryl groups. Thus, production of TVB was confirmed by NMR spectra and IR spectra.

Thermal properties of TVB

The thermal properties were studied prior to curing TVB. First, melting behavior of TVB was observed with a melting point measuring apparatus attached with a microscope. The transparency of the pieces gradually increased at 55–60°C, and the sample gradually became sticky at 60–70°C, and melted at 80°C. The melted sample was a viscous fluid at 80°C, and the viscosity increased with the rise of temperature. It hardened over 120–130°C. Similar melting behavior was observed for TVB with different DS values.

DSC thermograms for TVB with various DS values are shown in Figure 4. These thermograms have a broad endothermic peak at 70–75°C, which is considered to be related to the melting of TVB. Observed exothermic peaks varied with DS values. For TVB with DS 2.4, only one broad exothermic peak was found at 132°C, while for DS 3.2, it was found at 191°C. On the other hand, two exothermic peaks were found at 112–119°C and at 186–194°C for DS 2.8 and

3.0. The exothermic peaks are considered to be related to the reaction heat of vinyl groups. These results suggest that there are two stages for curing of TVB, depending on the DS. When DS is increased, the remaining polymerizable groups may increase after the first curing stage, and the exothermic peak for the second stage becomes relatively significant, in which unreacted groups may be crosslinked by activating thermal motion of the polymer network. We cannot give a reason for the appearance of an endothermic peak at ~50°C, which might be related to melting of TVB with a certain DS.

T_d was defined as the temperature at 5% weight loss in the heating process measured by TGA and is shown in Table I. T_d was raised by substitution for hydroxyl groups of trehalose, although the relationship between DS and T_d was not clear. Such a T_d increase by substitution for carbohydrate hydroxyl groups was found in other research,^{7,8} and these results suggest that thermal decomposition of carbohydrates is initiated with elimination of water from hydroxyl groups.⁹

Thermal properties of TVB after curing

When the heat capacity of TVB after curing at 200°C was measured by DSC from -15 to 220°C, no thermal transition was found (data not shown). In thermomechanical analysis (TMA), cured TVB showed one transition. The thermal expansion curve has one gentle bending point, which may correspond to a glass transition. Figure 5 shows the TMA curves for DS 2.4 and 3.2. The onset temperature of the bending point was calculated for each DS and tabulated in Table II. Supposing that the temperature represents the glass transition temperature (T_g), T_g of cured TVB was lowered with an increase of DS. Although the reason has not been elucidated, one possible reason is that the cured TVB with higher DS has more flexibility on heating because of losing hydroxyl groups, which may contribute to hydrogen bonds. This result implies that an increase of crosslinking points accompanied by an increase of DS does not influence T_g exclusively, and that the acceleration of thermal motion of polymer chains is more influential than the increase of

TABLE I
Thermal Decomposition temperature (T_d) of Trehalose and TVB with Various DS

DS	T_d (°C) ^a
0 (trehalose)	284
2.4	334
2.8	315
3.0	336
3.2	335

^a Decomposition temperature was determined by TGA as the temperature of 5% weight loss.

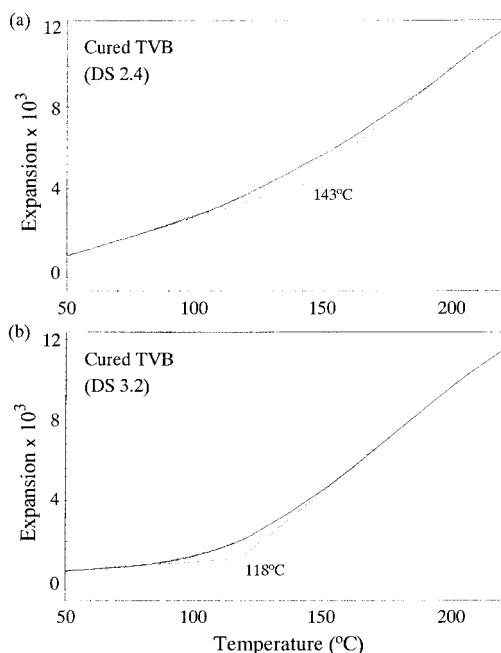


Figure 5 Typical thermomechanical curve of cured TVB: (a) DS 2.4, (b) DS 3.2.

crosslinking points for low DS (2–3). The thermal expansion coefficient was $\sim 4 \times 10^{-5} \text{ K}^{-1}$ from 50 to 100°C.

Figure 6 shows the storage modulus and $\tan \delta$ of cured TVB measured by dynamic mechanical analysis (DMA). Storage modulus of cured TVB began to decrease at 80–100°C for each sample. The point that the storage modulus began to decrease in DMA was near the point that the expansion ratio began to increase in TMA. A significant $\tan \delta$ peak was not observed for DS 2.4, and a broad $\tan \delta$ peak was observed at 140–180°C for DS 2.8, 3.0, and 3.2. When DS was 2.8 and more, the peak temperature was slightly lowered with an increase of DS, although major changes depending on DS were not found in the $\tan \delta$ curves. Assuming that the $\tan \delta$ peak is related to T_g , the tendency of the result was similar to that of TMA, and the $\tan \delta$ peak of TVB DS 2.4 may be at higher than 200°C. Generally, T_g determined by DMA is higher than T_g determined by TMA, and our result is consistent with this ten-

TABLE II
Glass Transition Temperature of Cured TVB with Various DS Measured by TMA

DS	T_g (°C) ^a
2.4	143
2.8	134
3.0	123
3.2	118

^a Onset temperature of the bending point of the TMA curve.

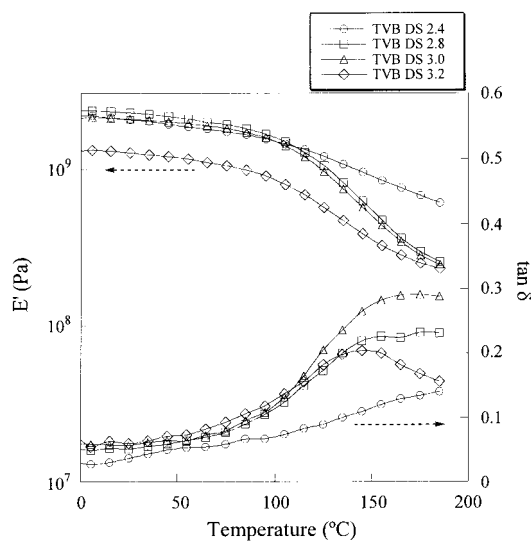


Figure 6 Dynamic mechanical analysis of cured TVB with various DS values. Storage modulus and $\tan \delta$ are depicted. The heating rate was 5°C per min. The static and dynamic stress were 1.0 MPa and 0.5 MPa, respectively.

dency. Storage modulus of cured TVB was lowered with an increase of DS, and this may be due to the loss of hydroxyl groups as considered in the previous paragraph.

Biodegradability of cured TVB

Biodegradability of cured TVB was tested by BOD measurement with activated sludge under an aerobic condition. Percentage of degraded TVB was calculated from BOD values and plotted as a function of degradation time. The result of the degradation test are shown in Figure 7. About 5% of added cured resin was degraded over 50 days, and after this period almost no further degradation was observed to 90 days of aging (data not shown). It is conceivable that the crosslinked network, whose backbone is polystyrene, was not degraded. It is imagined that the mechanism of the bio-

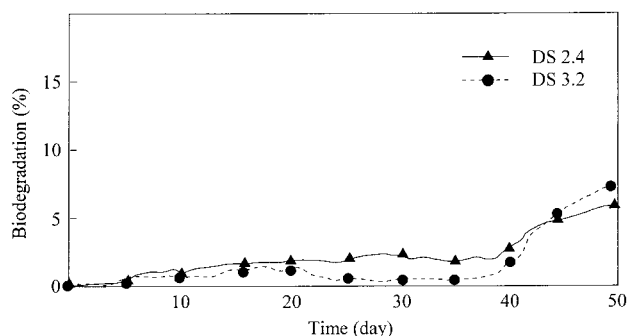


Figure 7 Biodegradability test of cured TVB with DS 2.4 and 3.2. Biodegradability was measured by BOD test at 25°C using activated sludge.

degradation is via the ends of crosslinked chains that consist of TVB units with lower DS being degraded. Remarkable differences between TVB DS 2.4 and 3.2 were not observed.

CONCLUSIONS

Trehalose vinylbenzyl ether (TVB) with DS 2.4-3.2 was synthesized by the reaction of trehalose and *p*-chloromethylstyrene (CMS) in the presence of sodium hydroxide in DMSO. The synthesis of TVB was confirmed by FTIR and ¹H NMR. DSC thermograms of TVB showed one broad endothermic peak at 70–75°C, which corresponds to melting. They also revealed that both TVB with DS 2.8 and 3.0 have two exothermic peaks around 115 and 190°C, while TVB, with DS 2.4 and 3.2, has one exothermic peak each at 132 and 191°C, respectively. TMA revealed that the thermal expansion curve of TVB, cured at 200°C, has one bending point at 100–150°C, suggesting a glass transition.

The T_g of cured TVB, determined by DMA, was higher than that determined by TMA, and the T_g was lowered with an increase of DS. About 5% of cured TVB was degraded after BOD test for 50 days with activated sludge.

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