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April 21, 1994

Mr. Carroll Collier
Office of Agriculture
Bureau for Science & Technology
Agency for International Development
Room 420 SA-18
Washington, D.C.

Dear Mr. Collier,

I understand that you have not received the final technical research report from Dr. Stoil Dirlikov on the project entitled "Reactive Diluents for High Solids Coatings Based on Vernonia Oil".

This project resulted in 4 papers recently published in the proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering, 69, pp. 390, 32, 392, and 394, as well as a more complete paper in the Proceedings of the Society for the Plastics Industry, Boston, March 7-9, 1994.. The enclosed package of five papers constitutes our final report on the project. All of these papers acknowledge the Agency for International Development financial support. Just this week we received a request from a scientist in Mexico asking to be put in touch with a source of Vernonia g. seeds.

Please let me know if this format is acceptable. Dr. Dirlikov is no longer with the University and I write this letter as project administrator in his absence. As a new researcher at the University, I would be interested in hearing more about your Agency's research interests. I am interested in developing resins for coatings and paints based on sugars and derivatives.

Yours truly,

John Massingill

John L. Massingill, Ph.D.
Director

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Coatings Research Institute
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TWO-PHASE EPOXY THERMOSETS.
I. DIGLYCIDYL ETHER OF BISPHENOL A, VERNONIA OIL, AND 4,4'-DIAMINODIPHENYL SULFONE

Isabelle Frischinger and Stoil Dirlikov
Eastern Michigan University, Coatings Research Institute, Ypsilanti, MI 48197

Recently, it was reported that homogeneous mixtures of diglycidyl ether of Bisphenol A (DGEBA) epoxy resins and commercial diamines containing epoxidized vegetable oils form under certain conditions two-phase epoxy thermosets which consist of a rigid DGEBA epoxy matrix and randomly distributed small "vegetable" rubbery particles (1,2). In the present paper, the morphology, particle size, and phase inversion of two-phase epoxy thermosets based on DGEBA, vernonia oil, and 4,4'-diaminodiphenyl sulfone (DDS) have been described.

EXPERIMENTAL

Vernonia oil was kindly supplied by Dr. Jim Elmore (Rhône Poulenc). DGEBA is solid epoxy EPON® resin 825 from Shell Company. 4,4'-Diaminodiphenylmethane (DDM) and DDS were obtained from Aldrich Chemicals.

Vernonia liquid rubber (VR) was obtained by prepolymerization of a mixture of 100g of vernonia oil and 25.63g (twice the stoichiometric amount) of DDM under nitrogen at 180°C for about 37-40 h. The time of prepolymerization varied slightly from batch to batch depending on the quality of the oil. The exact conversion of the rubber is not known but further heating for several hours leads to gelation. Vernonia rubber consists of soluble oligomers with a broad molecular weight distribution in addition to a small amount of the unreacted initial oil (3).

The two-phase DGEBA/DDS/VR(x) thermosets were prepared from homogeneous stoichiometric mixtures of DGEBA and DDS, containing varying amounts of VR. The content of the liquid rubber (x) was varied between 0 and 100 weight percent. X equal to 0 corresponds to neat DGEBA/DDS thermoset, whereas, x equal to 100 is a pure vernonia rubber. The rubber was dissolved first in DGEBA at 70°C. Then, DDS was added and the mixture stirred (at 70°C) until the diamine was dissolved (about 15 min.). The homogeneous (one-phase) transparent mixture was then degassed before reaching its cloud point (phase separation). The formulations were cured at 150°C for 2 hours.

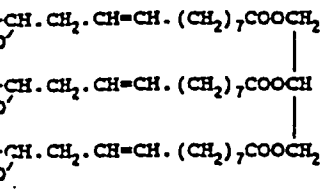
The morphology of the fracture surface of the neat and rubber modified epoxy resins was examined by scanning electron microscopy (SEM) using an Amray Electron Microscope, Model 1000B. SEM specimens were coated with a thin film of gold by sputtering. Some specimens were stained with an aqueous solution of osmium tetroxide (OsO_4) and then, coated with a layer of carbon by evaporation. Backscattered electron imaging technique was also used especially to visualize the phase inversion phenomena.

A DuPont Thermal Analyzer 2100 instrument with DMA model 983, based on a flexural bending deformation measurement, and rectangular bar specimens with approximate dimensions of 45mm x 7.8mm x 3.5mm were used to study the dynamic mechanical properties over the temperature range from -130°C to +200°C at a heating rate of 2°C/min. Specimen preparation was described previously (3).

RESULTS AND DISCUSSION

Vernonia oil was selected in this study because it stains with osmium tetroxide. The selective reaction of the electrondense OsO_4 with vernonia carbon-carbon double bonds provided a contrast in SEM between the rubbery phase (a lighter appearance) and DGEBA epoxy phase (a darker shade). This enabled us to identify easily the vernonia phase in the final two-phase thermosets.

Vernonia oil, a naturally epoxidized vegetable oil, consists mainly of a mixture of similar triglycerides (1):



Vernonia oil has relative low average epoxy functionality of 2.4. Its rubbers with diamines, therefore, have relative low cross- linked density and polarity.

Vernonia galamensis, the plant that produces vernonia oil, is a potential industrial crop presently at developmental stage.

The initial attempts on rubber toughening epoxy resins were carried out directly with vernonia oil. For this purpose, homogeneous mixtures of DGEBA, a diamine, and vernonia oil were cured initially at 70°C. The diamines have a much higher reactivity with DGEBA than with vernonia oil. They, therefore, react first with DGEBA and form the rigid epoxy phase at 70°C. Vernonia oil separates at this stage as a second phase of small randomly distributed vernonia oil droplets with a diameter in the range of 1 micron (3).

Unfortunately, at a higher temperature in the range from 120 to 220°C, vernonia oil droplets do not cure with the unreacted diamine fast enough to form rubbery particles and two-phase thermosets. Instead, vernonia oil appears to dissolve and plasticize the rigid DGEBA matrix and one phase homogeneous final thermosets were obtained.

Two-phase thermosets were obtained under the same curing conditions by using vernonia liquid rubber instead of the initial pure vernonia oil. Vernonia rubber has lower reactivity than DGEBA. Vernonia droplets, therefore, again phase separated at 70°C from the initial homogeneous mixture of DGEBA, diamine and liquid rubber. In contrast to vernonia oil, the liquid rubber has higher molecular weight and lower miscibility with the epoxy DGEBA phase. The liquid rubber also has an advanced degree of prepolymerization close to the gel point. It rapidly cures at higher temperature (150°C) with the remaining unreacted amino groups and cross-links. As a result, the final thermosets, after being cured at 150°C, consist of two phases: continuous phase (matrix) with randomly distributed small spherical particles. DGEBA forms the rigid phase, whereas, vernonia oil forms the rubber. The diamine molecules on the interface react probably with both the epoxy groups of the DGEBA and the unreacted epoxy groups of vernonia rubber and form chemical bonds between the continuous phase and the particles.

Table I summarizes the results on the morphology, particle size distribution, and phase inversion in DGEBA/DDS/VR thermosets. Their morphology is illustrated on Figure 1 and 2.

At low rubber content (below 15 wt percent), the DGEBA/DDS/VR formulations form two-phase thermosets with continuous rigid DGEBA phase (matrix) and randomly distributed small spherical vernonia rubbery particles of several microns.

At 15 wt percent of rubber, the DGEBA/DDS/VR thermosets undergo phase inversion which is characterized with the formation of small (several microns) and large (several hundred microns) rubbery particles dispersed in the DGEBA matrix. The small particles are formed by neat cross-linked vernonia rubber. The large rubbery

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particles contain many small spherical occlusions (several microns) of rigid DGEBA resin.

DMA confirmed this result. It shows two glass transition temperatures: Tg = -36°C and Tg = +10°C for the small and the large rubbery particles, respectively. In good agreement with our previous results (3) DMA shows that a certain amount of rubber has plasticized the rigid DGEBA matrix and decreased its glass transition temperature from 185°C (unmodified) to 171°C at 20 percent rubber content.

At the end of the phase inversion (30 wt percent rubber), small (several microns) and large DGEBA particles (several hundred microns) are dispersed in the continuous vernonia rubbery phase.

Further increase of the rubber content leads to a complete phase inversion with the formation of two-phase thermosets with a continuous rubbery phase and randomly distributed small DGEBA rigid particles.

CONCLUSION

Homogeneous formulations of DGEBA epoxy resin and DDS diamine containing liquid rubber, based on vernonia oil and DDM diamine, form two-phase epoxy thermosets. Phase inversion is observed at intermediate rubber content (15-30 wt percent).

ACKNOWLEDGEMENT

The authors would like to thank the SCAQMD and U.S.A.I.D. for their financial support.

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(1) Dirlikov, S. K.; Frischinger, I.; Islam, M.S.; Lepkowski, T.J. In Biotechnology and Polymers; Gebelein, C. G., Ed.; Plenum Press: New York, NY, 1991, pp 79-94. (2) Frischinger, I.; Dirlikov, S. Polym. Mater. Sci. Eng. 1991, 65, 178-9. (3) Frischinger, I.; Dirlikov, S.; In Toughened Plastics: Science and Engineering; Riew, K.C.; Kinloch, A.J., Eds.; Advances in Chemistry Series, No. 233; American Chemical Society: Washington, DC, 1993; pp. 451-89.

Table I. Morphology and Particle Size Distribution for DGEBA/DDS/VR Formulations.

Thermoset Formulation	Morphology	Dispersed Phase	Particle Size Microns
DGEBA/DDS	homogeneous		
DGEBA/DDS/VR(5)	two phase	vernonia	3-10
DGEBA/DDS/VR(10)	two phase	vernonia	3-25
DGEBA/DDS/VR(15)	two phase	vernonia	3-25, 25-100
		PI[a] start	
DGEBA/DDS/VR(20)	two phase	vernonia	3-25, 25-350
		PI[a]	
DGEBA/DDS/VR(30)	two phase	DGEBA	2-5, 20-400
		PI[a] end	
DGEBA/DDS/VR(50)	two phase	DGEBA	0.5-4
DGEBA/DDS/VR(60)	two phase	DGEBA	[b]
DGEBA/DDS/VR(70)	two phase	DGEBA	[b]
VR[c]	homogeneous		

[a] PI = Phase Inversion
[b] Data not available
[c] Neat cross-linked vernonia rubber

Figure 1. SEM Micrograph of the Fracture Surface of DGEBA/DDS/VR(15) Specimen.

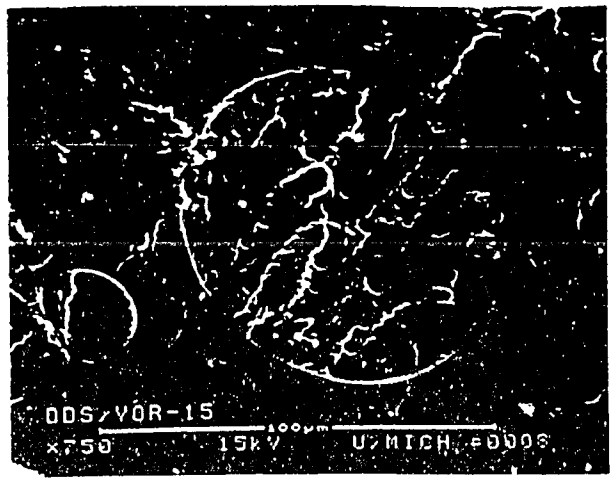


Figure 2. SEM Micrograph of the Fracture Surface of DGEBA/DDS/VR(50) Specimen.

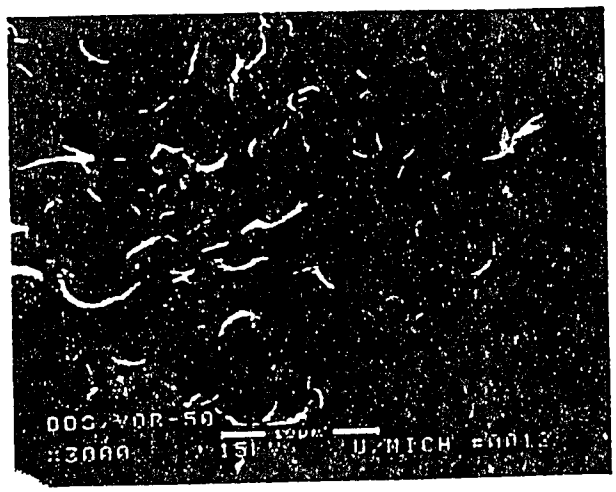
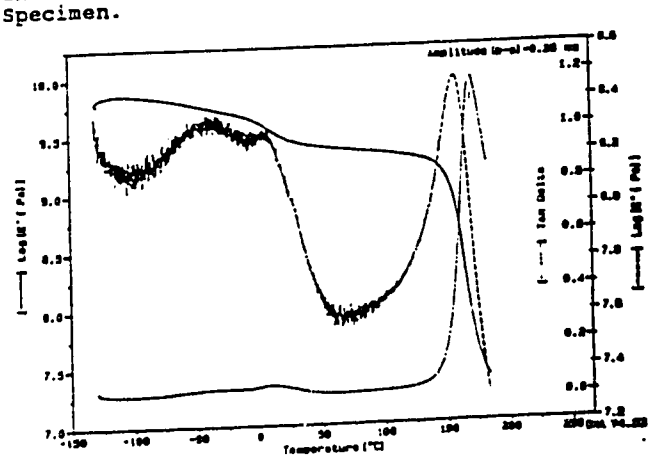


Figure 3. DMA Temperature Dependence of the Dynamic Loss (Flexure) Modulus, E" (Solid Line) and Tan Delta (Dashed Line) of DGEBA/DDS/VR(20) Specimen.



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TWO-PHASE EPOXY THERMOSETS.
II. DIGLYCIDYL ETHER OF BISPHENOL A, VERNONIA OIL, AND 4,4'-DIAMINODIPHENYLMETHANE

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Research Institute, Ypsilanti, MI 48197

It was reported in Part I (1) that homogeneous mixtures of diglycidyl ether of Bisphenol A (DGEBA) epoxy resin and a commercial diamine (DDS) containing vernonia liquid rubber (VR) form two-phase epoxy thermosets. In the present paper, the morphology, particle size, and phase inversion of two-phase epoxy thermosets DGEBA/DDM/VR(x) based on DGEBA, 4,4'-diaminodiphenylmethane (DDM), and vernonia rubber are described. The content of the liquid rubber (x) was varied between 0 and 100 weight percent. X equal to 0 corresponds to neat DGEBA/DDM thermoset, whereas, x equal to 100 is a pure vernonia rubber.

EXPERIMENTAL

The initial materials, and the preparation and characterization of vernonia liquid rubber and the two-phase epoxy thermosets were carried out as described in Part I (1). The DGEBA/DDM/VR formulations, however, were cured first at 75°C for 4 hours and then at 150°C for 2 hours.

RESULTS AND DISCUSSION

The fracture surfaces of DGEBA/DDM/VR thermosets with increasing content of vernonia rubber were studied by SEM and DMA. The results on the morphology, phase inversion, and particle size distribution of these two-phase thermosets are summarized in Table I.

The initial neat DGEBA/DDM formulation forms homogeneous one-phase epoxy thermosets.

The introduction of 5 percent vernonia liquid rubber results in two-phase epoxy thermosets. DGEBA/DDM/VR(5) consists of a rigid DGEBA/DDM matrix and randomly distributed small vernonia spherical rubbery particles (0.5 to 2.0 microns) with unimodal distribution.

Similar two-phase thermosets are observed for the formulations with 10 and 15 percent vernonia rubber. The particle size, however, gradually increases with the rubber content ranging from 1 to 4 microns in DGEBA/DDM/VR(10) and from 1 to 5 microns in DGEBA/DDM/VR(15). The rubber particles at the DGEBA/DDM/VR(15) fracture surface and their internal structure are especially clearly observed by backscattered electron imaging technique on specimens stained with OsO_4 (Figure 1). Osmium high electron density produces higher intensity of backscattered electrons from vernonia particles and increases the contrast (1).

Most of the rubbery particles at the fracture surface of these three formulations have undergone internal (partial or complete) cavitation with the formation of voids observed as dark circles within the particles or at the particle/matrix interface (Figure 1). Once formed, the voids grow upon stress and dissipate energy. The remaining cavitated rubber is observed distinctly as a lining on their walls. The cavitation phenomenon increases with the increasing rubber content. It can greatly enhance the shear yielding process (2,3) and is the main epoxy toughening mechanism.

The matrix surrounding the particles is characterized with ripled fracture surface with striations. It appears to exhibit plastic shear deformation.

Ejection or debonding of rubbery particles is not observed under the shear deformation during fracture. This indicates a good adhesion between the DGEBA matrix and rubbery particles. As mentioned earlier (1) the diamine molecules on the interface react probably with the epoxy groups of both DGEBA and rubber and form chemical bonds between the two phases. Although some debonding is observed as craters at higher rubber content, it is not a major toughening mechanism.

A different morphology is observed at 20 percent of vernonia rubber. The DGEBA/DDM/VR(20) thermosets contain two types of particles: larger and smaller (Figures 2-5, Table I) and are characterized by a bimodal particle size distribution. It indicates a beginning of phase inversion phenomenon.

The smaller rubbery particles (0.5 to 2 microns) correspond to the rubbery particles observed in the thermosets with lower rubber content (below 20 percent). Cavitation and shear banding as well as the voids formed by debonding of the smaller particles from the DGEBA matrix are clearly observed.

The larger particles have a very broad particle size distribution (20 to 100 microns). Some of them are characterized by the so-called "salami" type of morphology (3). Figures 3-5 show the same section of the fracture surface with gradually increasing magnification. Figure 3 is a conventional SEM micrograph of the initial unstained specimen. Figure 4 shows the same section of the fracture surface after staining with OsO_4 using backscattered electron imaging technique. A single salami type of particle is shown in Figure 5 at higher magnification. Obviously, the larger particles are formed predominantly by vernonia rubbery phase (in lighter shade). The smaller spherical DGEBA/DDM particles (1 to 8 microns) in darker shade, dispersed within the larger vernonia domains, are a result of local phase inversion phenomenon.

DMA of DGEBA/DDM/VR(20) confirmed its bimodal particle size distribution (Figure 6). It shows two distinct glass transition temperatures for the rubbery phase which are assigned tentatively to that of the two types of rubbery particles. The lower glass transition temperature of -35°C is assigned to the small particles of neat vernonia rubber. It corresponds to the T_g of the small neat vernonia particles observed in the formulations with lower rubber content and unimodal particle size distribution (4). The larger particles are believed to have glass transition at higher temperature (+10°C) due to DGEBA occlusion (probably coreacting and mixing). The glass transition temperature of the DGEBA matrix of DGEBA/DDM/VR(20) is observed at 172°C. It is slightly depressed by 18°C below that of a neat DGEBA/DDM thermoset (190°C) prepared under the same conditions (5). This indicates that DGEBA/DDM matrix of DGEBA/DDM/VR thermosets is plasticized by a small amount of vernonia rubber. These results are in agreement with a mass balance calculation based on the rubber content.

Larger particles (100-200 microns) are known to act as bridging particles and to induce the cavitation and shear banding of the small particles in their vicinity (6). They create a large deformation zone with the formation of very sharp and wide ridges between the neighboring large particles. Figure 2 shows a large vernonia particle fractured across the equator, a part of a second particle incorporated in the matrix, and a crater left by a particle debonded from the matrix.

In summary, the DGEBA/DDM/VR(20) thermosets display two different types of toughening mechanism depending on the particle size. Internal cavitation and shear banding are observed for the small particles. Bridging, fracture, and debonding are exhibited mainly by the larger particles. Although recently Yee (6) disputed,

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the bimodal particle size distribution could lead to synergistic toughening effect (7).

In addition, an extensive plastic deformation of the matrix is evident by the appearance of numerous striations. In general, the fracture surface of DGEBA/DDM/VR(20) is more rough than that of the thermosets with lower "vernonia" content. At higher rubber content the higher concentration of particles leads to a smaller distance between particles. This is probably the reason why the plastic deformation becomes a more prominent toughening mechanism in DGEBA/DDM/VR(20).

At higher rubber content, the DGEBA epoxy becomes progressively the dispersed phase. DGEBA/DDM/VR(30) thermosets are characterized still with a bimodal particle size distribution. Further studies (8) show that their morphology is exactly the reverse of that of DGEBA/DDM/VR(20); a continuous rubbery phase contains both small (2 to 4 microns) and large (20 to 250 microns) DGEBA particles. The large particles are expected to contain rubber (within the particle). These rigid particles, however, do not undergo fracture when surrounded by a continuous rubbery phase, and do not reveal their interior. DGEBA/DDM/VR(30) morphology appears to reflect the end of the phase inversion phenomenon.

Further increase of the rubber content leads to a complete phase inversion. DGEBA/DDM/VR(50) thermoset consists of continuous rubbery phase in which small spherical rigid DGEBA particles (0.5 to 2 microns) are randomly distributed (Figure 7).

As expected, the neat vernonia liquid rubber, cured under the same condition, forms a homogeneous cross-linked rubber (Table I).

CONCLUSION

Homogeneous formulations of DGEBA epoxy resin and DDM diamine containing liquid rubber, based on vernonia oil and DDM diamine, form two-phase epoxy thermosets. At lower rubber content, they consist of a rigid DGEBA matrix and randomly distributed small "vernonia" rubbery particles. At higher rubber content, the thermosets are characterized by continuous "vernonia" rubbery phase and small rigid DGEBA particles. Phase inversion is observed at intermediate rubber content (20-30 wt percent).

ACKNOWLEDGEMENT

The authors thank the SCAQMD and U.S.A.I.D. for their financial support.

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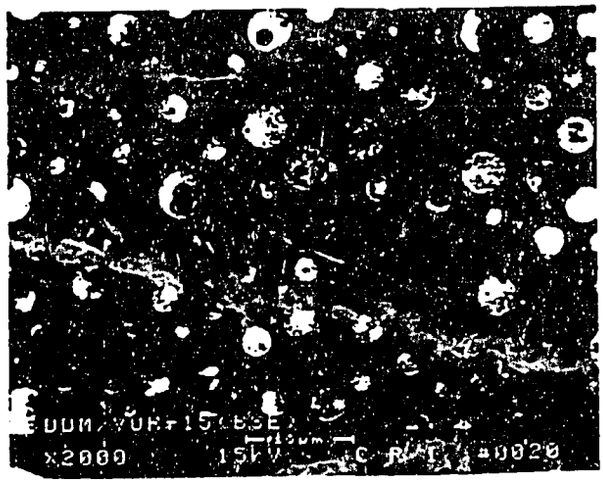
Table I. Morphology and Particle Size Distribution for DGEBA/DDM/VR Formulations.

Thermoset Formulation	Morphology	Dispersed Phase	Particle Size Microns
DGEBA/DDM	homogeneous		
DGEBA/DDM/VR(5)	two phase	vernonia	0.5-2
DGEBA/DDM/VR(10)	two phase	vernonia	1-4
DGEBA/DDM/VR(15)	two phase	vernonia	1-5
DGEBA/DDM/VR(20)	two phase	vernonia PI[a] start	0.5-2, 20-100
DGEBA/DDM/VR(30)	two phase	DGEBA PI[a] end	2-4, 20-250
DGEBA/DDM/VR(50)	two phase	DGEBA	0.5-2
DGEBA/DDM/VR(60)	two phase	DGEBA	[b]
DGEBA/DDM/VR(70)	two phase	DGEBA	[b]
VR[c]	homogeneous		

[a] PI = Phase Inversion
[b] Data not available
[c] Neat cross-linked vernonia rubber

Figure 1. SEM Micrograph Using Back-Scattered Electron Imaging Technique of the Fracture Surface of DGEBA/DDM/VR(15) Specimen Stained with Osmium Tetroxide.



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TWO-PHASE EPOXY THERMOSETS. III. DIGLYCIDYL ETHER OF BISPHENOL A, EPOXIDIZED SOYBEAN OIL, AND 4,4'-DIAMINODIPHENYL SULFONE

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Eastern Michigan University, Coatings Research Institute, Ypsilanti, MI 48197

Homogeneous mixtures of diglycidyl ether of Bisphenol A (DGEBA) and commercial diamines containing vernonia liquid rubber form two-phase epoxy thermosets (1,2). In the present study, the morphology, particle size, and phase inversion of two-phase epoxy thermosets, DGEBA/DDS/ESR(x), based on DGEBA, 4,4'-diaminodiphenyl sulfone (DDS), and epoxidized soybean liquid rubber (ESR) have been evaluated. The content of the liquid rubber (x) was varied between 0 and 100 weight percent. X equal to 0 corresponds to neat DGEBA/DDS thermoset, whereas, x equal to 100 is a pure soybean rubber.

EXPERIMENTAL

Epoxidized soybean oil (ESO), Flexol® Plasticizer EPO, with average epoxy functionality of approximately 4.5 is a product of Union Carbide Co. DGEBA is solid epoxy EPON® resin 825 from Shell Company. 4,4'-Diaminodiphenylmethane (DDM) and DDS were obtained from Aldrich Chemicals. ESR was obtained by prepolymerization of a mixture of 100g of ESO and 22.8g (stoichiometric amount) of DDM, at 135°C under nitrogen for about 37-40 h. Two-phase epoxy thermosets were prepared and characterized as previously described (1).

RESULTS AND DISCUSSION

ESO is industrially produced at $0.50 per pound. It consists of a mixture of different triglycerides with an average molecular structure:

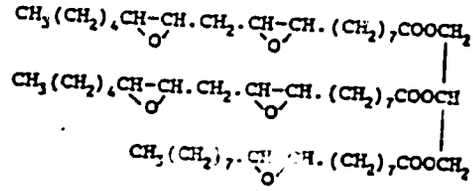

Table I summarizes the results on the morphology, particle size distribution, and phase inversion in DGEBA/DDS/ESR thermosets. Their morphology is illustrated in Figures 1-6.

At low rubber content (below 30 wt percent), the DGEBA/DDS/ESR formulations form two-phase thermosets with continuous rigid DGEBA phase matrix) and randomly distributed small spherical soybean" rubbery particles of several microns.

DMA of DGEBA/DDS/ESR(20) (Figure 7) shows two lass transition temperatures: at -43°C and 166°C, for the rubbery particles and the GEBA/DDS matrix, respectively. DMA shows that a ertain small amount of rubber has plasticized the igid DGEBA/DDS matrix and decreased its Tg from 15°C (unmodified) to 166°C at 20 percent rubber ontent.

At 30 wt percent of rubber, the DGEBA/DDS/ESR ermosets undergo phase inversion which, is aracterized with the formation of small (several crons) and large (saveral hundred microns) bbery particles dispersed in the DGEBA matrix. e small particles are formed by neat oss-linked soybean rubber. The large rubbery rticles contain many small occlusions (several crons) of rigid DGEBA resin.

At the end of the phase inversion (35 wt rcent rubber), small (several microns) and large BA particles (several hundred microns) are spersed in the continuous "soybean" rubbery se.

Further increase of the rubber content leads to a complete phase inversion with the formation of two-phase thermosets with a continuous rubbery phase and randomly distributed small DGEBA rigid particles.

CONCLUSION

Homogeneous formulations of DGEBA and DDS containing liquid rubber, based on ESO and DDM, form two-phase epoxy thermosets. Phase inversion is observed at 30-35 wt percent of rubber.

ACKNOWLEDGEMENT

The authors would like to thank SCAQMD and U.S.A.I.D. for their financial support.

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(1) Frischinger, I.; Dirlikov, S., Polym. Mater. Sci. Eng., 1993, 69 (in press). (2) Ibid.

Table I. Morphology and Particle Size Distribution for DGEBA/DDS/ESR Formulations.

Thermoset Formulation	Morphology	Dispersed Phase	Particle Size Microns
DGEBA/DDS	homogeneous		
DGEBA/DDS/ESR(10)	two phase	soybean	1 - 2
DGEBA/DDS/ESR(20)	two phase	soybean	1 - 5
DGEBA/DDS/ESR(25)	two phase	soybean	2 - 10
DGEBA/DDS/ESR(30)	two phase	soybean	2-10, 10-100
DGEBA/DDS/ESR(35)	two phase	PI[a] start DGEBA	3-5, 10-100
		PI[a] end DGEBA	1 - 3
DGEBA/DDS/ESR(50)	two phase	DGEBA	
DGEBA/DDS/ESR(60)	two phase	DGEBA	
DGEBA/DDS/ESR(70)	homogeneous		
ESR[c]	homogeneous		

[a] PI = Phase Inversion
[b] Data not available
[c] Neat cross-linked soybean rubber

Figure 1. SEM Micrograph of the Fracture Surfac of DGEBA/DDS/ESR(10) Specimen.

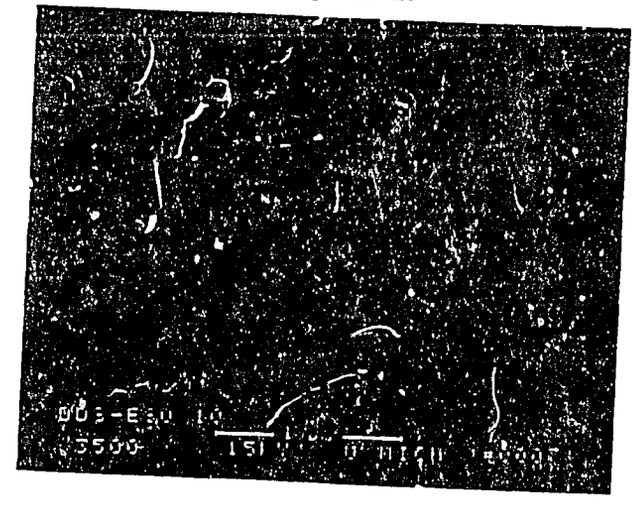

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Figure 2. SEM Micrograph of the Fracture Surface of DGEBA/DDS/ESR(20) Specimen.

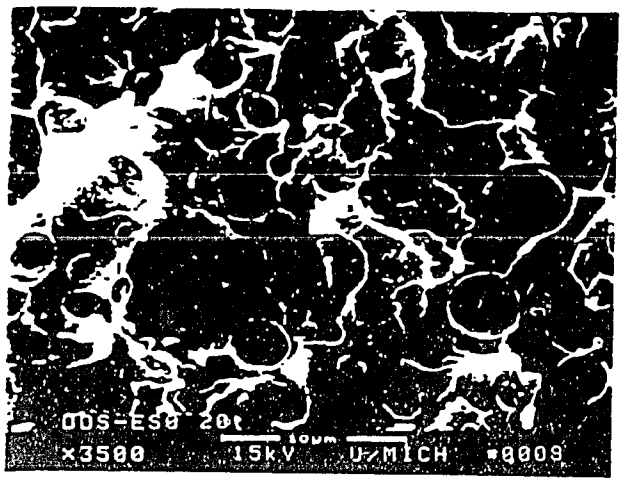


Figure 3. SEM Micrograph of the Fracture Surface of DGEBA/DDS/ESR(25) Specimen.

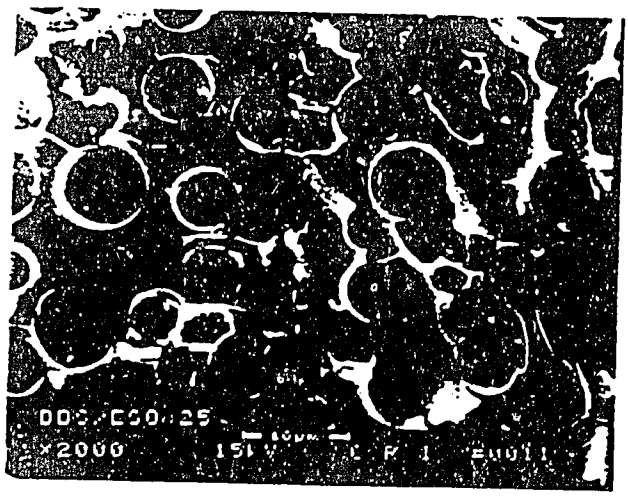


Figure 4. SEM Micrograph of the Fracture Surface of DGEBA/DDS/ESR(30) Specimen.

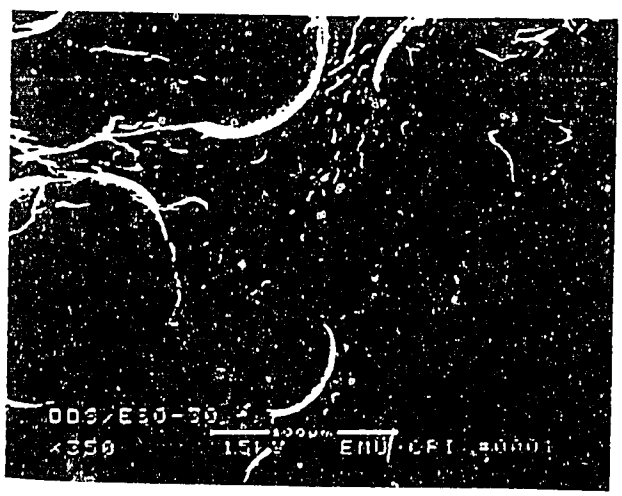


Figure 5. SEM Micrograph of the Fracture Surface of DGEBA/DDS/ESR(35) Specimen.

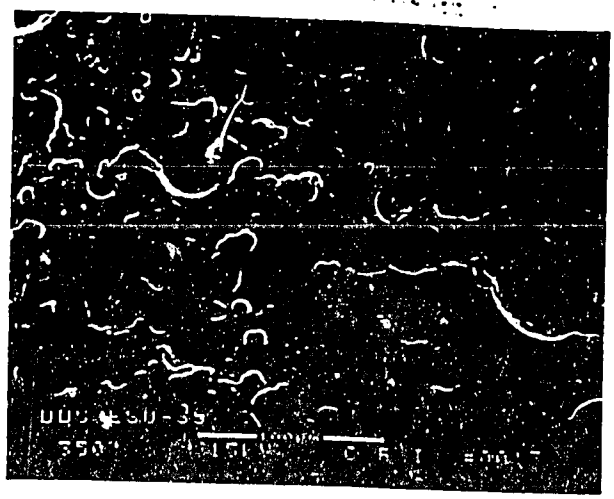


Figure 6. SEM Micrograph of the Fracture Surface of DGEBA/DDS/ESR(50) Specimen.

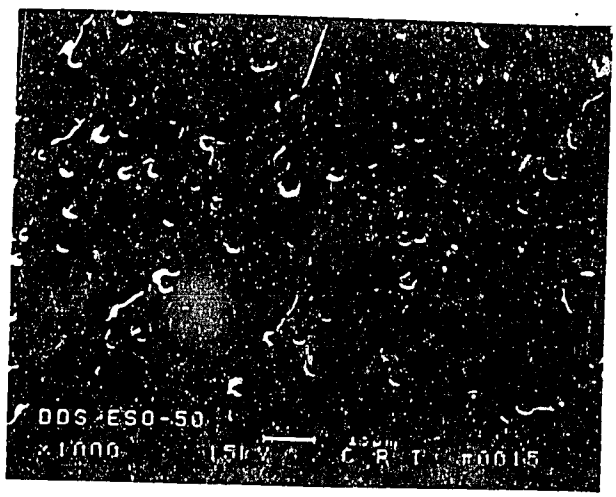
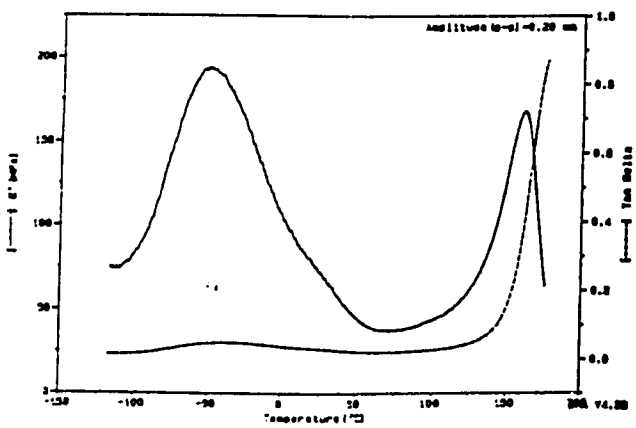


Figure 7. DMA Temperature Dependence of the Dynamic Loss (Flexure) Modulus, E" (Solid Line) and Tan Delta (Dashed Line) of DGEBA/DDS/ESR(20) Specimen.



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TWO-PHASE EPOXY THERMOSETS. IV. DIGLYCIDYL ETHER OF BISPHENOL A, EPOXIDIZED SOYBEAN OIL, AND 4,4'-DIAMINODIPHENYLMETHANE

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It was reported that homogeneous mixtures of diglycidyl ether of Bisphenol A (DGEBA) epoxy resin and a commercial diamine (DDS) concaining vernonia liquid rubber (VR) or epoxidized soybean liquid rubber (ESR) form two-phase epoxy thermosets (1). In the present study, the morphology, particle size, and phase inversion of epoxy thermosets, DGEBA/DDM/ESR(x), based on DGEBA, 4,4'-diaminodiphenylmethane (DDM), and ESR have been evaluated. The content of the liquid rubber (x) was varied between 0 and 100 weight percent. X equal to 0 corresponds to neat DGEBA/DDM thermoset, whereas, x equal to 100 is a pure soybean rubber.

EXPERIMENTAL

The initial materials, and the preparation and characterization of the ESR and the two-phase epoxy thermosets were carried out as described in Part III (1). The DGEBA/DDM/ESR formulations, however, were cured first at 75°C for 4 hours and then at 150°C for 2 hours.

RESULTS AND DISCUSSION

Table I summarizes the results on the morphology, particle size distribution, and phase inversion in DGEBA/DDM/ESR thermosets. Their morphology is illustrated in Figures 1-6.

At low rubber content (below 30 wt percent), the DGEBA/DDM/ESR formulations form two-phase thermosets with continuous rigid DGEBA phase (matrix) and randomly distributed small spherical "soybean" rubbery particles with a diameter below one micron.

The dynamic mechanical analysis (DMA) of DGEBA/DDM/ESR(20) (Figure 7) shows two glass transition temperatures: at -33°C and +165°C, for the small rubbery particles and the DGEBA/DDM matrix, respectively. DMA shows that a certain small amount of rubber has plasticized the rigid DGEBA/DDM matrix and decreased its glass transition temperature from 190°C (unmodified) to 165°C at 20 percent rubber content.

The phase inversion of the DGEBA/DDM/ESR formulations proceeds without formation of larger particles and transitional states with bimodal particle size distribution. These intermediate stages of phase inversion found in the other three formulations: DGEBA/DDS/ESR (1), DGEBA/DDM/VR (2), and DGEBA/DDS/VR (3) have not been observed here. DGEBA/DDM/ESR phase inversion is completed in a very narrow range of rubber content (between 30 and 35 percent). The morphology of continuous rigid DGEBA matrix and rubbery particles at 30 percent rubber changes into continuous rubbery phase with rigid DGEBA particles at 35 percent rubber content. Obviously, the phase inversion in DGEBA/DDM/ESR follows a different mechanism from the other three types of formulations. It proceeds practically without DGEBA partition in the rubbery particles.

Further increase of the rubber content leads to the formation of two-phase thermosets with continuous rubbery phase and randomly distributed small DGEBA rigid particles.

CONCLUSION

Homogeneous formulations of DGEBA epoxy resin and DDM diamine containing liquid rubber, based on epoxidized soybean oil and DDM diamine, form two-phase epoxy thermosets. Phase inversion is completed in a very narrow range of intermediate rubber content (30 - 35 wt percent).

ACKNOWLEDGEMENT

The authors would like to thank SCAQMD and U.S.A.I.D. for their financial support.

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(1) Frischinger, I.; Dirlikov, S. Polym. Mater. Sci. Eng. 1993, 69 (in press). (2) Frischinger, I.; Dirlikov, S. Polym. Mater. Sci. Eng. 1993, 69 (in press). (3) Frischinger, I.; Dirlikov, S. Polym. Mater. Sci. Eng. 1993, 69 (in press).

Table I. Morphology and Particle Size Distribution for DGEBA/DDM/ESR Formulations.

Thermoset Formulation	Morphology	Dispersed Phase	Particle Size Microns
DGEBA/DDM	homogeneous		
DGEBA/DDM/ESR(10)	homogeneous		
DGEBA/DDM/ESR(15)	two phase	soybean	0.1 - 0.5
DGEBA/DDM/ESR(20)	two phase	soybean	0.1 - 0.4
DGEBA/DDM/ESR(30)[a]	two phase	soybean	0.1 - 0.8
DGEBA/DDM/ESR(35)[a]	two phase	DGEBA	3 - 5
DGEBA/DDM/ESR(50)	two phase	DGEBA	1 - 2
DGEBA/DDM/ESR(60)	two phase	DGEBA	0.5 - 1
DGEBA/DDM/ESR(70)	homogeneous		
ESR[b]	homogeneous		

[a] Phase Inversion occurs between 30 and 35 percent of ESR.
[b] Neat cross-linked soybean rubber

Figure 1. SEM Micrograph of the Fracture Surface of DGEBA/DDM/ESR(15) Specimen.

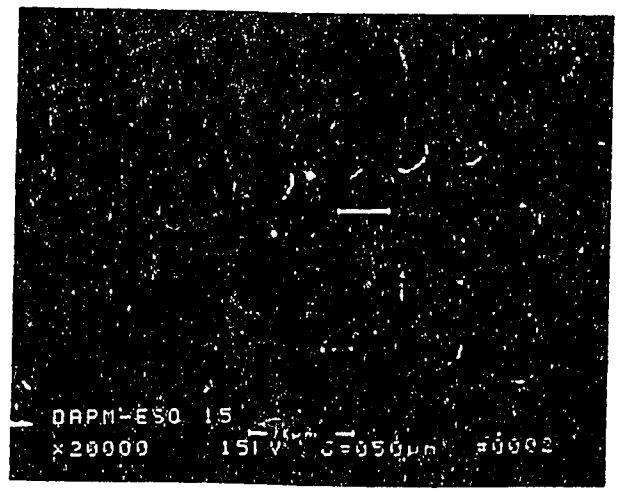

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Figure 2. SEM Micrograph of the Fracture Surface of DGEBA/DDM/ESR(20) Specimen.

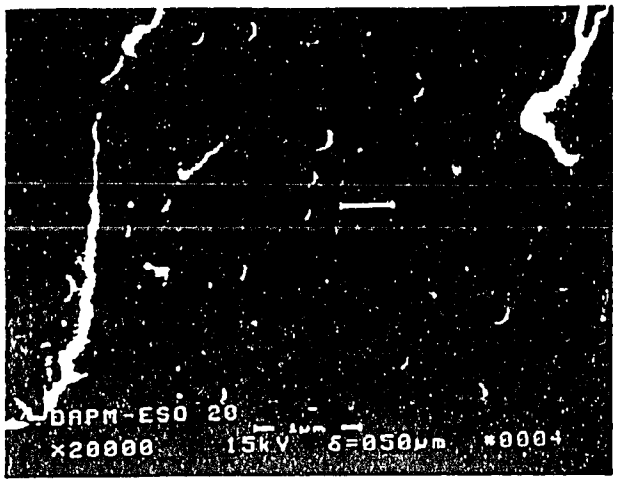


Figure 3. SEM Micrograph of the Fracture Surface of DGEBA/DDM/ESR(30) Specimen.

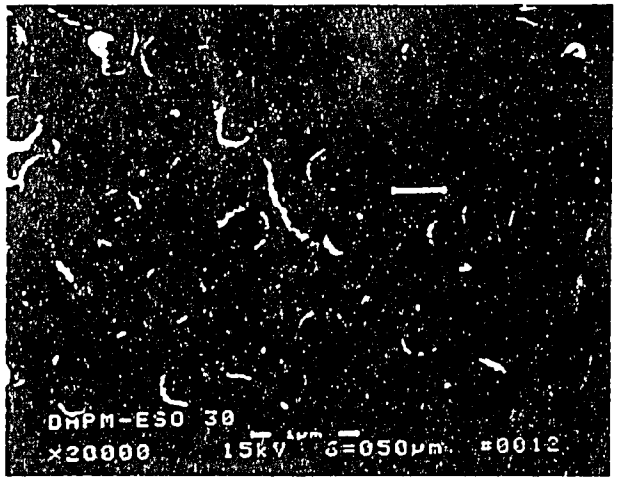


Figure 4. SEM Micrograph of the Fracture Surface of DGEBA/DDM/ESR(35) Specimen.

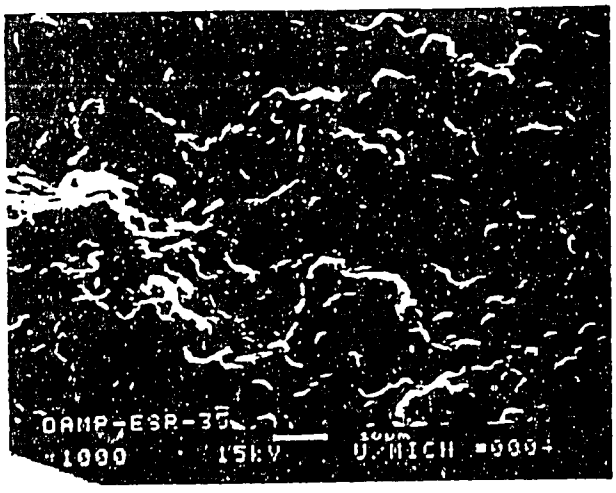


Figure 5. SEM Micrograph of the Fracture Surface of DGEBA/DDM/ESR(40) Specimen.

Figure 6. SEM Micrograph of the Fracture Surface of DGEBA/DDM/ESR(60) Specimen.

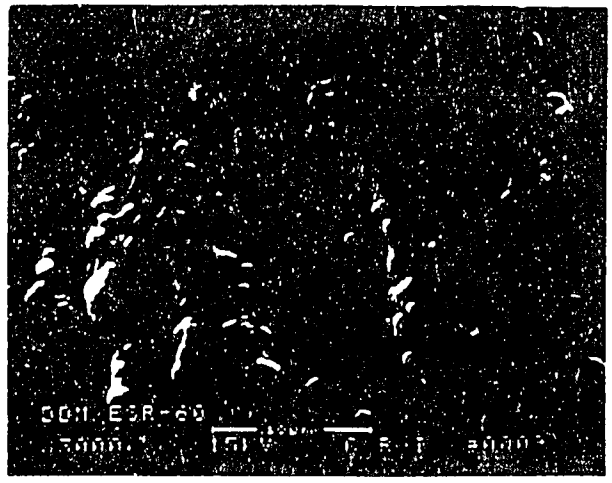
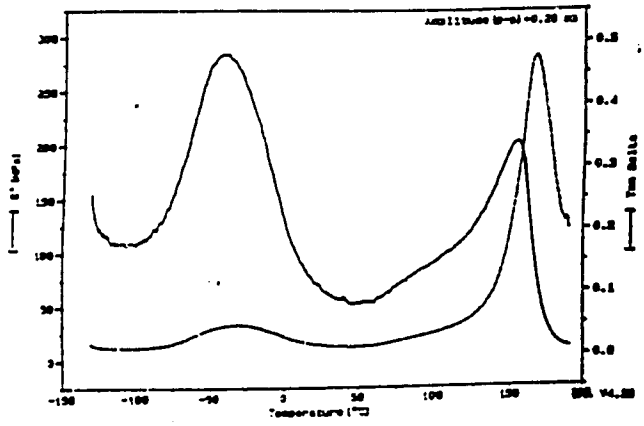


Figure 7. DMA Temperature Dependence of the Dynamic Loss (Flexure) Modulus, E" (Solid Line) and Tan Delta (Dashed Line) of DGEBA/DDM/ESR(20) Specimen.



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TWO-PHASE EPOXY THERMOSETS THAT CONTAIN EPOXIDIZED TRIGLYCERIDE OILS[1]

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ABSTRACT

Homogeneous mixtures of diglycidyl ether of bisphenol A epoxy resin and commercial diamines that contain an epoxidized triglyceride oil form, under certain conditions, two-phase thermosetting materials that consist of a rigid epoxy matrix and randomly distributed small rubbery "vegetable" particles (0.1 - 5 microns). These two-phase thermosets have excellent toughness, better than CTBN-modified epoxies, low water absorption and very low ionic (sodium and chlorine) content. In comparison to the unmodified thermosets, the two-phase epoxies exhibit slightly lower glass-transition temperature and Young's moduli; their dielectric properties do not change. The epoxidized soybean oil is avalable at a price ($0.53/lb) below that of the commercial epoxy resins and CTBNs and it appears to be very attractive for epoxy toughening on an industrial scale.

INTRODUCTION

Recently, it was found out that homogeneous mixtures of diglycidyl ether of Bisphenol A (DGEBA) epoxy resins and commercial diamines containing epoxidized triglyceride oils form two-phase interpenetrating epoxy thermosets under certain conditions (2). Their morphology, particle size, and phase inversion depend on the nature of the epoxidized vegetable oil and the diamine used for their preparation. The two-phase epoxy thermosets, especially those based on the commercially available inexpensive epoxidized soybean oil ($0.53/pound), appear to be very attractive for different industrial applications. In the present paper, their potential application for toughening commercial epoxy thermosets and coatings is described.

EXPERIMENTAL

The initial materials as well as the preparation of liquid rubbers, based on epoxidized triglyceride oils and final two-phase interpenetrating thermosets have been described in detail in the previous paper (2). The epoxy morphology and transition temperatures were determined by scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA), respectively, as also described in Ref. 2.

[1]Excerpted with permission from Ref. 1. Copyright 1994 American Chemical Society.

Fracture Toughness

Single-edge-notched (SEN) specimens with approximate dimensions of 100mm long x 12.7mm width x 6.7mm thick were machined from castings (3). A sharp crack was introduced into the specimen by the strike of a razor blade, previously chilled in liquid nitrogen, with a rubber mallet. The tests were carried out with a three-point bending assembly, which was monitored by a servohydraulic materials testing machine (Instron 1331) with a span of 50.8 mm and a piston rate of 2.54 mm/s. A computer interface controlled the machine and recorded the data. An HP model 310 computer was programmed to calculate the critical stress intensity factor, K_{IC}, using the following relation (4):

$$K_{IC} = Y \frac{2 P S \sqrt{a}}{3 t w^2}$$

where: P is the critical load for crack propagation in N,
S is the length of the span in mm,
a is the crack length in mm,
w is the width in mm,
t is the thickness in mm,
Y is the non-dimensional shape factor given by:

$$Y = 1.9 - 3.07 (a/w) + 14.53 (a/w)^2 - 25.11 (a/w)^3 + 25.80 (a/w)^4$$

The following relationship, which holds in case of Linear-Elastic-Fracture Mechanics (LEFM) under plane strain conditions, was used for determination of the fracture energy, G_{IC}:

$$G_{IC} = \frac{(1 - \nu^2)(K_{IC})^2}{E}$$

where ν is the Poisson ratio and E is the elastic or Young's modulus. At least 8 specimens of each formulation were used for determination of average fracture energy G_{IC}.

Uniaxial Tensile Test

Dog bone bars with dimensions of 6" x 0.5" x 1/8" (152mm x 12.7mm x 3.5mm) were cut with a high speed router and their external surface polished with very fine aliminium oxide sandpaper 220 (3M). A screw-driven Instron (model 1185), equipped with an extensometer for determination of the longitudinal strain and a computer interface type 4500 series, was used at a stroke of 60 mm/min.. At least ten specimens of each formulation were used for determination of their average tensile properties at room temperature.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out on DuPont Thermal Analyzer 2100 instrument with DSC model 2910 over the temperature range from -130° to +200°C at a heating rate of 2°C/min.

Water Absorption

Maximum water absorption was determined on rectangular specimens with approximate dimensions of 45mm x 7.8mm x 3.5mm which were predried in a vacuum oven at 60°C to constant weight and then kept in boiling water for 3 to 4 weeks until saturation (e.g. to constant weight).

Dielectric Properties

Dielectric constant and dissipation factor were measured at 1 MHz and room temperature on specimens with 3" x 3" x 1/8" dimensions on a Genrad 1687 B Digibridge equipped with an LD-3 cell and by using the two-fluid method (air and DC-200, 1 cs).

Sodium and Chlorine Content

Sodium and chlorine content were determined by Galbraith Analytical Laboratories, Inc. (Knoxville, TN). Paint Research Associates (Ypsilanti, MI) confirmed sodium content by analysis with Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

PROCEDURES AND FORMULATIONS

The initial materials: DGEBA, 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), vernonia, and epoxidized soybean oil have been described in detail in the previous paper (2), together with the procedures for preparation of liquid rubbers and final cure of two phase thermosets.

Three types of formulations have been evaluated in the present study: DGEBA/DDM/VR(x), DGEBA/DDM/ESR(x), and DGEBA/DDS/ESR(x). Vernonia (VR) and epoxidized soybean (ESR) liquid rubbers were prepared from DDM and the corresponding oils. The DGEBA/DDM/VR(x) thermosets were obtained from initial homogeneous stoichiometric mixtures of DGEBA and DDM modified by vernonia rubber. The content of the liquid rubber (x) was varied between 0 and 100 weight percent. X equal to 0 corresponds to neat DGEBA/DDM thermoset, whereas, x equal to 100 is pure vernonia rubber. Analogous abbreviations are used for the other two types of formulations.

TOUGHENING COMMERCIAL EPOXY RESINS

A small amount of discrete rubbery particles with an average size of several microns, randomly distributed in a glassy, brittle epoxy thermoset is known to dissipate a part of the impact energy, thus improving crack and impact resistance without significant deterioration of other properties (5,6).

The epoxy toughness is usually achieved by separation of a rubbery phase with a unimodal particle size distribution from the matrix during the curing process. Different reactive liquid rubbers, based on low molecular weight carboxy- or amino- terminated oligomers of butadiene and acrylonitrile (CTBN and ATBN), are usually used for the formation of the rubbery phase. Low molecular

weight amino-terminated (methyl)siloxanes offer other alternatives. However, some of these oligomers are quite expensive.

Epoxidized triglyceride oils such as vernonia, epoxidized soybean, and linseed oils provide new opportunities. Epoxidized triglyceride oils react with commercial diamines to form epoxy resins which are elastomers at room temperature with low glass transition temperatures in the range of -70°C to 0°C, depending on the nature of the amine used for their curing. Epoxidized soybean rubber, therefore, was evaluated for toughening commercial epoxy resins. For this purpose, DGEBA/DDM and DGEBA/DDS formulations were toughened by the addition of 10, 15, 20 and 30 percent of epoxidized soybean liquid rubber. The resulting thermosets consist of a rigid DGEBA matrix and small "soybean" rubbery particles (Table I). Their morphology is discussed in detail in the previous paper (2).

Table I. Average range of "soybean" particle size distribution of the rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR thermosets

Thermoset Formulation	Particle size microns
DGEBA/DDM/ESR(10)	no phase separation
DGEBA/DDM/ESR(15)	0.1-0.5
DGEBA/DDM/ESR(20)	0.1-0.4
DGEBA/DDM/ESR(30)	0.1-0.8
DGEBA/DDS/ESR(10)	1-2
DGEBA/DDS/ESR(20)	1-5
DGEBA/DDS/ESR(30)[a]	1-17
DGEBA/DDS/ESR(30)[b]	5-10, 100-200

[a] Tensile specimens
[b] Fracture toughness specimens

Glass Transition Temperature (T_g)

The transition temperatures were determined by DMA from the temperature dependence (maximum) of their tan delta (Table II).

The glass transition temperatures of the neat DGEBA/DDM and DGEBA/DDS thermosets are observed at 190° and 185°C respectively. Both exhibit also beta-relaxations at lower temperatures: -30° and -35°C, respectively. The pure epoxidized soybean rubber (ESR), cured under the same conditions in the absence of DGEBA/diamine component, shows a glass transition temperature of -25°C by DSC.

The two-phase DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations exhibit two transitions at higher and lower temperatures. The higher temperature transitions in the range of 145° to 190°C have been

assigned to the T_g of their DGEBA matrices. T_g gradually decreases with an increasing amount of soybean liquid rubber due to plasticization of the DGEBA rigid matrix. As previously discussed (2,3), the nonpolar soybean rubber has higher solubility in less polar DGEBA/DDM than in the more polar DGEBA/DDS matrix. The plasticization phenomenon, therefore, is more pronounced for the DGEBA/DDM/ESR formulations. The depression of the glass transition temperature of their matrices is about 25°C at 15% to 20% of soybean rubber content, and almost 45°C at 30% loading. The less miscible two-phase DGEBA/DDS/ESR formulations exhibit smaller depressions; 15°C at 10% soybean liquid rubber to approximately 25°C at 30% loading.

Table II. DMA lower and higher temperature transitions of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations

Thermoset Formulation	Transition °C[a]	°C[b]
DGEBA/DDM	-30	190
DGEBA/DDM/ESR(15)	-35	161
DGEBA/DDM/ESR(20)	-33	165
DGEBA/DDM/ESR(30)	-39	145
DGEBA/DDS	-35	185
DGEBA/DDS/ESR(10)	-45	168
DGEBA/DDS/ESR(20)	-43	166
DGEBA/DDS/ESR(30)	-30	161
ESR[c]	-25	

[a] The lower transition temperature corresponds to an overlap in the glass transition temperature of the rubbery particles and the beta-transition of the DGEBA matrix
[b] Glass transition temperature of the DGEBA matrix
[c] Determined by DSC

The lower temperature transitions of the DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations, observed in the range of -30°C to -45°C, are assigned to an overlap of the glass transition temperature of the ESR rubbery particles and the beta-transition of their matrix. In general, the glass transition temperature of the rubbery particles in the two-phase thermosets corresponds to that of the pure ESR rubber. This indicates that the rubber phase in these two-phase thermosets does not contain a significant amount of the DGEBA component and is formed by practically pure soybean rubber.

Fracture Toughness

The fracture toughness, in terms of stress intensity factor, K_{IC} and fracture energy, G_{IC}, is given in Table III. The fracture surfaces of both formulations DGEBA/DDM/ESR and DGEBA/DDS/ESR show extensive

particle cavitation as shown in (2), which is the main toughening mechanism.

A better toughening effect, which gradually increases at a higher soybean rubber content, is observed for the DGEBA/DDM/ESR formulations. It is probably due to the plasticization phenomenon which occurs at a larger scale for these formulations (2). The "soybean" component, which acts as a plasticizer of the matrix, improves its toughness.

A smaller improvement of the fracture toughness and an optimum toughening effect at 20% "soybean" content is observed for the DGEBA/DDS/ESR formulations. The DGEBA/DDS/ESR(30) specimens at 30% soybean liquid rubber, which were used here for determination of fracture toughness, have a bimodal particle size distribution which is characteristic for the beginning of phase inversion phenomena (2). At this point the physico-mechanical properties start to deteriorate rapidly and we observe lower fracture toughness.

Table III. Stress intensity factor, K_{IC} and fracture energy, G_{IC} of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations

Thermoset Formulation	K_{IC}, $MPa.m^{1/2}$	G_{IC}, J/m^2
DGEBA/DDM	0.75	175
DGEBA/DDM/ESR(10)[a]		
DGEBA/DDM/ESR(15)	1.24	564
DGEBA/DDM/ESR(20)	1.33	802
DGEBA/DDM/ESR(30)	1.40	1008
DGEBA/DDS	0.75	145
DGEBA/DDS/ESR(10)	1.09	374
DGEBA/DDS/ESR(20)	1.19	596
DGEBA/DDS/ESR(30)	0.54	145
DGEBA/DDS[b]		162
DGEBA/DDS/CTBN(10)[b]		242

[a] This formulation does not phase separate due to better miscibility of its two phases (2). Its fracture toughness has not been determined
[b] Ref. 7

In summary, the soybean liquid rubber significantly improves the fracture toughness of commercial highly crosslinked, brittle DGEBA/DDS and DGEBA/DDM epoxy thermosets. This toughening effect is due to both rubber toughening due to particle cavitation and enhanced ductility of the matrix through plasticization (2).

Tensile Properties

Young's moduli were determined from the corresponding tensile stress/strain curves as an average value of several independent measurements (Table IV). In contrast to fracture toughness, where DGEBA/DDS/ESR(30) specimens with a bimodal particle size distribution were used, all tensile specimens used in this study, had a unimodal distribution (Table I). It is difficult to reproduce the exact morphology of DGEBA/DDS/ESR(30). This formulation is very close to its phase inversion point and small deviation of the experimental conditions leads to different morphologies.

As expected, the elastic moduli gradually decreased with the increasing soybean fraction. Linear relationships can approximately fit for both types of DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations and a slight deviation is observed only at a higher content of soybean rubber. The tensile properties of the DGEBA/DDS/ESR formulations, however, decrease faster with the increasing soybean content than that of DGEBA/DDM/ESR.

Table IV. Young modulus, E of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations

Thermoset Formulation	E MPa
DGEBA/DDM	2840
DGEBA/DDM/ESR(10)[a]	
DGEBA/DDM/ESR(15)	2410
DGEBA/DDM/ESR(20)	1950
DGEBA/DDM/ESR(30)	1720
DGEBA/DDS	3420
DGEBA/DDS/ESR(10)	2810
DGEBA/DDS/ESR(20)	2100
DGEBA/DDS/ESR(30)	1780
DGEBA/DDS[b]	3360
DGEBA/DDS/CTBN(10)[b]	3000

[a] This formulation does not phase separate and its tensile properties have been determined
[b] Ref. 7

Water Absorption

High water absorption is another major disadvantage of commercial epoxy resins in addition to their poor fracture toughness. The maximum water absorption was determined by placing predried samples in boiling water until constant weight was achieved. Although the results are somewhat lower than expected, the water absorption of both formulations decreases gradually and linearly with the

increasing soybean content (Table V).

Obviously, the highly hydrophobic long fatty chains of the epoxidized soybean oil reduce the water absorption of its epoxy thermosets. As expected, the DGEBA/DDS/ESR formulations at different soybean liquid rubber contents have a higher water absorption than the corresponding DGEBA/DDM/ESR formulations, due to the more polar character of DDS in comparison to DDM.

Table V. Maximum water absorption of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations

Thermoset Formulation	Water Absorption %
DGEBA/DDM	2.42
DGEBA/DDM/ESR(15)	2.22
DGEBA/DDM/ESR(20)	2.00
DGEBA/DDM/ESR(30)	1.62
DGEBA/DDS	3.61
DGEBA/DDS/ESR(10)	3.33
DGEBA/DDS/ESR(20)	3.13
DGEBA/DDS/ESR(30)	2.80

Dielectric Properties

The introduction of epoxidized soybean oil, with its long aliphatic chains, was expected to lower simultaneously the dielectric constant and dissipation factor of the commercial epoxy resins, despite the formation of free hydroxyl groups by the opening of its epoxy rings. Surprisingly, the dielectric properties of both types of formulations do not change with the increasing content of soybean liquid rubber (Table VI).

Table VI. Dielectrical properties of pure DGEBA/DDM and DGEBA/DDS thermosets and their rubber-modified DGEBA/DDM/ESR and DGEBA/DDS/ESR formulations

Thermoset Formulation	Dissipation Factor	Dielectrical Constant
DGEBA/DDM	0.033	3.78
DGEBA/DDM/ESR(15)	0.035	3.78
DGEBA/DDM/ESR(20)	0.036	3.77
DGEBA/DDM/ESR(30)	0.037	3.77
DGEBA/DDS	0.025	3.95
DGEBA/DDS/ESR(20)	0.033	3.88

Sodium and Chlorine Content

A requirement for the application of epoxy resins in the electronics industry is their low ionic content, often below 10 ppm, especially for sodium and chlorine ions. Electronics grade epoxy resins are more expensive due to the additional purification procedure needed to lower their ionic content.

The epoxidized soybean oil without any purification has a very low content of sodium and chlorine of below 5 ppm (Table VII). This is due to its hydrophobic nonpolar molecular structure lacking free hydroxyl or carboxyl groups. Thus, epoxidized soybean rubber is especially suitable for the toughening of epoxy resins for electronics applications.

Table VII. Ionic content and bulk price of epoxidized soybean oil (ESO), vernonia oil (VO), and CTBN

	ESO	VO	CTBN[a]
Sodium, ppm	4.2	4.3	380
Chlorine, ppm	<5.0	906	952
Price, $/lb	0.53	[b]	2-2.50

[a] Hycar[R] CTBN 1300 x 16 (B.F. Goodrich Chemical Co.)
[b] Not industrially produced

Epoxidized Soybean Liquid Rubber v.s. CTBN

We also compared the effect of the epoxidized soybean liquid rubber with that of CTBN (Hycar[R] CTBN 1300 x 16, a product of B.F. Goodrich Chemical Co.) which is commonly used for epoxy toughening. The introduction of 10% CTBN liquid rubber into a DGEBA/DDS epoxy resin produces similar two-phase thermosets with CTBN rubbery particles (about 5 microns). The fracture energy of the unmodified DGEBA/DDS thermoset increases from G_{IC} = 162 J/m^2 to G_{IC} = 242 J/m^2 in the presence of 10% CTBN, that is with ΔG_{IC} = 80 J/m^2, whereas its Young modulus simultaneously decreases from E = 3360 MPa to E = 3000 MPa (7). Our unmodified DGEBA/DDS thermoset exhibits similar fracture toughness (G_{IC} = 145 J/m^2) and Young's modulus (E = 3420 MPa) (Table III and IV). The introduction of 10% soybean liquid rubber, however, more than doubles its fracture energy from G_{IC} = 145 J/m^2 to G_{IC} = 374 J/m^2 (Table III), that is with ΔG_{IC} = 229 J/m^2, whereas the Young modulus decreases from E = 3420 MPa to a slightly lower value of E = 2810 MPa (Table IV). The soybean liquid rubber appears to have better toughening effect than CTBN.

Another advantage of the epoxidized soybean rubber is its low sodium and chlorine content (an important characteristic for electronics applications) in contrast to that of the carboxy-terminated CTBN (Table VII).

The carbon-carbon double bonds of the butadiene monomeric units of CTBN undergo a variety of cross-linking reactions at higher temperature (>100°C). As a result, the rubber toughening effect of CTBN rapidly deteriorates during a prolong exposure of its two-phase epoxy thermosets at higher temperature. Improved toughness at higher temperature requires a rather expensive hydrogenation of CTBN. Epoxidized soybean oil and its rubbers do not have carbon-carbon double bonds. Better weathering, isothermal stability, and toughness at higher temperature are expected for their two-phase epoxy thermosets.

Epoxy thermosets that contain liquid rubbers based on epoxidized triglyceride oils are also environmentally friedly. The oil undergoes rapid enzymatic degradation to carbon dioxide and water by hydrolysis followed by Knoop and Krebs cycles.

Finally, epoxidized soybean oil is industrially produced and available at about 50 cents per pound, a price below that of CTBN (in the range of $2.25 - $2.50 per pound) and DGEBA (about $1.50 per pound). It makes the toughening of commercial epoxy resins by epoxidized soybean oil very attractive for commercial applications in large scale.

STRESS RESISTANT TWO-PHASE EPOXY COATINGS

These two-phase epoxy thermosets are also attractive for preparation of crack- and stress-resistant coatings (1). In order to evaluate their morphology and physico-mechanical properties, model two-phase interpenetrating epoxy coatings, based on a DGEBA/DDM stoichiometric formulation modified by the addition of 5, 10, 15, 20, 30, and 50 weight percent vernonia liquid rubber were studied (Table VIII). Below 20 percent rubber, they consist of a rigid DGEBA matrix and randomly distributed small "vernonia" rubbery particles (0.2 to 1.0 micrometer). Phase inversion is observed in the range of 20 to 30 percent rubber. Above 30 percent rubber, the thermosets consist of continuous "vernonia" rubbery phase and small rigid DGEBA particles (0.4 to 1.0 micrometer).

Initial results show that similar two-phase interpenetrating epoxy coatings based on epoxidized soybean rubber can be obtained.

These coatings have excellent physico-mechanical properties and appear to be suitable for container applications (1). This in situ approach for zero VOC two-phase (epoxy) coatings is an attractive alternative to the core-shell reactive latex technology.

DISCUSSION

Further research indicates that the introduction of vernonia oil in other formulations such as urethanes (a mixture of methylenediphenylene diisocyanate and 1,10-decanediol) also results into two-phase thermosets under similar conditions.

In general, initial homogeneous formulations based on two components with different polarity and different reactivity and a suitable curing agent are expected to undergo phase separation by a two-stage (condensation) polymerization. In the formulations discussed above, the commercial epoxies (and urethanes) are the polar components with very fast cure rates. As these formulations cure at lower temperature (first stage), they form the rigid phase. At this stage, the hydrophobic epoxidized triglyceride oil (or rubber), which is the nonpolar component and has a slow cure rate, phase separates and forms a liquid phase. The liquid phase cures later at a higher temperature (second stage) with the unreacted curing agent (diamine, etc.) to form the rubbery phase.

Similar two-phase thermosets have been prepared via two-stage addition polymerization as reported recently by Widmaier and coworkers (8) for two component formulations based on methyl methacrylate (or butyl acrylate) and diallyl carbonate of Bisphenol A.

CONCLUSIONS

Epoxidized triglyceride oils and especially epoxidized soybean oil, which is commercially available at a low price, are very attractive for preparation of two-phase interpenetrating epoxy thermosets. Two potential industrial applications have been evaluated: toughening commercial epoxy resins and preparation of stress resistant coatings.

Thermosets with DGEBA matrix and "soybean" rubbery particles have excellent toughness without deterioration of other physico-mechanical properties. Epoxidized soybean liquid rubber is environmentally friendly and has a better toughening effect, lower ionic content, lower price, and probably improved weathering than CTBNs.

Stress and crack resistant two-phase epoxy coatings, especially those with a continuous rubbery phase and rigid DGEBA particles, are suitable for coil and container applications. This in situ approach for preparation of coatings with two-phase morphology is an attractive alternative to hard-core/soft-shell and soft-core/hard-shell reactive latex technology.

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Table VIII. Morphology and physico-mechanical properties of DGEBA/DDM/VR coatings

Coating Formulation	Particle size (microns)	Impact resistance[a] Direct	Reverse	Hardness Rocker	Pencil	Adhesion[b]	Flexibility
DGEBA/DDM	Homogeneous	70	50	50	>8H	5B	[c]
DGEBA/DDM/VR(5)	[d]	70	40	46	>8H	5B	[c]
DGEBA/DDM/VR(10)	0.3-1.2	90	80	45	5H	5B	[c]
DGEBA/DDM/VR(15)	0.2-1.0	150	150	50	5H	5B	•
DGEBA/DDM/VR(20)	0.5-47[f]	150	160	38	3H	5B	•
DGEBA/DDM/VR(30)	1-27[f]	>160	>160	41	H	5B	•
DGEBA/DDM/VR(50)	0.4-1.0	>>160	>>160	21	H	5B	•
VR	Homogeneous	>160	>160	8	6B	5B	•

[a] in in.lb (1 in.lb = 0.01152 kg.m)
[b] 5B corresponds to 100% adhesion
[c] passed maximum but failed minimum diameter
[d] not studied by SEM
• passed maximum and minimum diameter
[f] phase inversion

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