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# Studies on the properties of epoxy resins cured with polythiourethanes

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**Abstract**

New mercaptan-terminated polythiourethanes were applied as curing agents for epoxy resin. The formulation studied consisted of a diglycidyl ether of bisphenol A epoxy resin, polythiourethane curing agent accelerated with primary or tertiary amine. The coating performance of the resins was tested by measurements of scratch resistance, pencil hardness, flexibility, adhesion and chemical resistance. The results show better properties of the polythiourethane-cured resin compared to standard epoxy formulation. It is observed that evaluation of the physico-mechanical and chemical resistance performance shows better results with the increased loading of polythiourethane hardener. In addition, polythiourethane hardeners revealed high reactivity toward curing of epoxy resins at low-temperature conditions (−10 °C). Polythiourethane-cured epoxy resins, thus stand as an effective surface coating material where high performance is needed in terms of physico-mechanical properties as well as chemical resistance.

*Keywords:* A. Epoxides; B. Metals; C. Lap shear; D. Cure; Polythiourethanes

## 1. Introduction

Epoxy resins are widely applied in structural adhesives, composites, moulding compounds and electrical laminates. They also play a dominant role in protective coatings mostly due to their outstanding performance in terms of chemical resistance, corrosion protection and excellent adhesion to many substrates. However, the epoxy systems are usually brittle materials having poor impact resistance and peel strength. Toughening can be achieved by flexibilizing the epoxy structure by the reduction of crosslink density or incorporating modifiers into adhesive, which lead to increased plastic deformation. Another approach to improving the toughness and flexibility of the cured resin without sacrificing its other useful properties is the application of suitable hardeners. It has long been recognized that the chemical nature of the curing agent can have a significant influence on the gel time and the physical properties of the epoxy, largely because it determines both the morphology and crosslink density of the growing network. The strength and toughness of the epoxy resin can be markedly affected by small changes in the curing agent. Several methods are available to toughen epoxy resins. These include using flexible hardeners and curing agents; using flexible, reactive diluents; blending with elastic polymers to achieve a single-phase, hybrid system or incorporation of a second phase of elastomeric particles into the epoxy resin matrix. For such purposes different polyamines, polyaminoamides and polymercaptan curing agents are used. This type of hardeners has an influence on the reactivity of the mixture and also has an impact on the physical and chemical properties of the product. An attraction of polymercaptan as hardeners, is their ability to cure epoxies rapidly at ambient temperature. The fast curing allows application at 0 to −20 °C. By using polythiols with high molecular weight even flexible polymers can be made. The addition of the polymercaptan acts as both an elastomeric modifier and a diluent for the epoxy resin. By reducing of the viscosity, these hardeners provide greater ease of mixing and application without solvent. Thiol groups (−SH) easily react with common metal surfaces, such as gold, silver, copper, and iron, to form sulfur–metal bonds [1]. Therefore, the epoxy–polymercaptan system was expected to improve not only bulk

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resin properties, but also corrosion resistance and adhesion. The use of polymercaptans as crosslinking agent in epoxy resins includes special compositions for coatings, adhesives or sealants, e.g. flame retardants, corrosion-resistant coatings or electrically conductive transparent films. The key limitation in the practical use of mercaptans as crosslinking agents is their odor, despite they have lower toxicity and are safer to handle than most other epoxy curatives.

In our previous papers, we have reported the synthesis and characterization of mercaptan-terminated polythiourethane hardeners for epoxy resins [2–3]. By converting dimercaptans into corresponding polythiourethane derivatives, we have succeeded in almost totally eliminating the unpleasant smell of thiol compounds. It was found that the incorporation of polythiourethane into epoxy resin enhanced the values of impact resistance and tensile strength. The curing characteristic and thermal behavior of the formulated curing mixtures indicate that epoxy/polythiourethane stoichiometry and thermal history during cure may greatly affect the curing mechanism and final properties of epoxy network. Prepared polythiourethane hardeners have an acceptable odor and give a perfectly homogeneous system with epoxy resin and have good storage stability with other coreactants like diamines.

The present work extends our studies on characterization of adhesion properties of epoxy/polythiourethane systems. In addition to the adhesive properties like lap shear strength and crosscut test, studies on the morphologies and chemical resistance of epoxy coatings are also presented in this paper. The thermal degradation behavior and the flame-retarding properties of these materials were studied. Further, the low-temperature curing reaction was also investigated.

## 2. Experimental

### 2.1. Materials

All materials used in this study were laboratory-grade chemicals and were used without any further purification. The commercially available epoxy resin (diglycidyl ether of bisphenol A) Epidian-5 having epoxide number of 0.487 was obtained from Organica-Sarzyna Inc., Poland. The viscosity of the resin is 23.9 N m$^{-2}$ s at 25 °C.

3,6-Dioxa-1,8-octanedithiol (DODT) (Fig. 1) was synthesized as reported in our previous paper [2,3]. The mercaptan-terminated polythiourethane hardeners DODT-TDI, DODT-HDI (Fig. 2) were synthesized according to our recent publication [2].

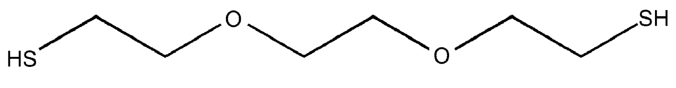

Fig. 1. Chemical structure of 3,6-dioxa-1,8-octanedithiol (DODT).

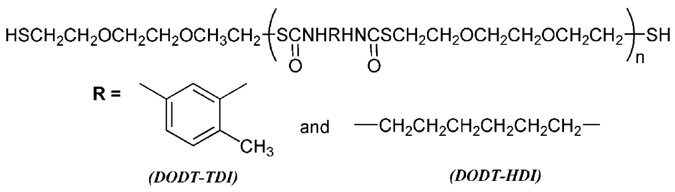

Fig. 2. Chemical structure of the polythiourethane hardeners.

### 2.2. Measurements

#### 2.2.1. Curing reactions and gel time measurement

Typically, a mixture of 5 g of epoxy resin and hardener was poured into a glass vial, and intensively stirred for 1 min with glass bar. To reduce viscosity of the resin, dioctyl phtalate was used as diluent in the low-temperature reactions. The gel time was determined according to EN ISO 179-1:2000, at temperatures of 25 and −10 °C. In this paper, gel times were the average of two samples. Curing compositions for all prepared cured epoxy systems are presented in Table 1.

#### 2.2.2. Spectroscopy characterization

The FTIR spectra were measured by BIORAD spectrophotometer in an air atmosphere. For the infrared measurements a small portion of the cured epoxy system was ground cryogenically to a fine powder, mixed with KBr powder and pressed into a pellet.

#### 2.2.3. Conversion of epoxy groups

The epoxy groups conversion was determined by the chemical analysis of the unreacted epoxy groups in swollen samples. The powder of the sample was suspended in a 1,4-dioxane for 8 weeks. The excess of HCl solution in dioxane was added to the swollen sample and after 24 h unbounded HCl was titrated with alcoholic solution of sodium hydroxide, using the potentiometric detection of the end-point. It is not possible to obtain quantitative and reproducible values of conversion due to the swelling conditions of the sample and the presence of unreacted active hydrogen from the curatives. The relatively low conversion observed for tested samples caused by their low swelling behavior, indicates that this procedure does not give face values. However, the results obtained by this method are proportional to the values quantitatively calculated from the FTIR spectra.

#### 2.2.4. Mechanical testing

For the preparing of test specimens, the mixed samples of epoxy resin and hardener were degassed for a few minutes under vacuum at room temperature to remove any trapped air bubbles. To crosslink the samples, the mixtures were poured into silicone-rubber mould and cured at temperatures of 25 and −10 °C.

The epoxy coatings were applied using a bar coater, the coating thickness was 0.4 mm. The coated substrates were cured for 3 days at room temperatures.

Table 1
Composition and curing characteristics of epoxy systems

| Comp. no. | Formulation of epoxy systems (phr)[a] | | | | Gel time (min) | | Conversion of epoxy groups (%) | |
|---|---|---|---|---|---|---|---|---|
| | Polythiourethane/ polymercaptane | TETA[b] | DMP-30[c] | Diluent (dioctyl phthalate) (phr) | 25 °C | −10 °C | 25 °C | −10 °C |
| 1 | HDI-DODT 10 | 4 | — | — | — | — | 56.9 | 51.2 |
| 2 | HDI-DODT 20 | 10 | — | 30 | 54 | 69 | — | — |
| 3 | HDI-DODT 20 | — | 4 | 30 | 36 | 171 | — | — |
| 4 | HDI-DODT 30 | 4 | — | — | — | — | 74.2 | 66.9 |
| 5 | HDI-DODT 50 | 4 | — | — | — | — | 81.9 | 74.3 |
| 6 | HDI-DODT 50 | 10 | — | 30 | 48 | 65 | — | — |
| 7 | HDI-DODT 20 | — | 4 | — | — | — | 86.1 | 75.6 |
| 8 | TDI-DODT 10 | 4 | — | — | — | — | 57.1 | 52.3 |
| 9 | TDI-DODT 20 | 10 | — | 30 | 21 | 43 | — | — |
| 10 | TDI-DODT 20 | — | 4 | 30 | 26 | 75 | — | — |
| 11 | TDI-DODT 30 | 4 | — | — | — | — | 74.2 | 68.5 |
| 12 | TDI-DODT 50 | 4 | — | — | — | — | 79.8 | 71.3 |
| 13 | TDI-DODT 50 | 10 | — | 30 | 9 | 35 | — | — |
| 14 | TDI-DODT 20 | — | 4 | — | — | — | 84.9 | 78.5 |
| 15[d] standard formulation | — | 15 | 2 | — | 68 | 30 h | 53.4 | 34.6 |
| 16 | DODT 20 | — | 4 | — | — | — | 69.6 | 48.9 |
| 17 | DODT 20 | 4 | — | — | — | — | — | — |
| 18 | DODT 30 | 4 | — | — | — | — | 80.3 | 63.5 |
| 19 | DODT 50 | 4 | — | — | — | — | — | — |
| 20 | DODT 30 | — | 6 | 30 | 21 | 38 | — | — |

[a] Phr, parts per 100 parts of epoxy resin.
[b] trietylenetetramine (TETA) was used as an accelerator.
[c] 3,4,6-tris(dimethylaminomethyl)phenol (DMP-30) was used as an accelerator.
[d] Dioctyl phtalate (30 phr) was used as diluent for gel time measurements.

The Charpy Impact Strength of the cured resin was determined according to EN ISO 179-1:2000. The dimension of unnotched specimens was approximately $80 \times 10 \times 4$ mm.

All these tests were performed at room temperature and at least seven specimens were tested and the average results were reported with the standard deviation.

Flexibility of the coatings was measured by standard test method for elongation of attached organic coatings with conical mandrel apparatus according to ASTM D 522-60 procedure.

Lap shear strength measurements were performed according to ASTM D-1002. Aluminum, steel, copper and polyamide substrates ($10.0 \times 2.5$ cm) were abraded with emery paper no. 60, ultrasonically degreased with acetone, rinsed with distilled water and dried with nitrogen gas before bonding. The average glueline thickness of the adhesives for all tests was controlled by the same spacer and was determined as 0.1 mm, with bond overlap of 12.5 mm.

Adhesion test on epoxy-coated metal (Al, Cu, steel) samples was carried out at 25 °C using the crosscut technique ASTM D 3359B. A crosscut was made with the help of utility knife on the coated surfaces deep to the metal substrate. At the crosscut, the blade of the knife was inserted under coating and with the levering action force was applied to chip off the coating. The chipped off area was observed under microscope to see the extent of removal of the coating from the substrate. The maximum number of adhesion was "5" and represented no detachment of crosscut squares. The minimum adhesive force "0" indicated complete detachment of crosscut squares.

The scratch resistance of the cured coatings was measured according to the pencil test ASTM D 3363. The coated panel was placed on a firm horizontal surface; the pencil was held firmly against the film at a 45° angle and pushed away in a smooth stroke with uniform pressure. The process was started with the hardest pencil and continued down the scale of hardness until the pencil used did not gouge or scratch the film. The range of pencil used in order of increasing hardness was as follows:

6B–5B–4B–3B–2B–B–HB–F–H–2H–3H–4H–5H–6H
Softer Harder

The morphology of impact fractured surfaces of epoxy resin was examined using Olympus optical microscope BX-40 equipped wit 50× long work distance objective (NA 0.5) and CCD camera. The reflective mode and magnification of 2500 times were used.

Table 2
Chemical resistance of epoxy coatings

| Comp. no.[a] | NMP[b] | | | | Toluene | | | | Ethanol 96% | | | | $H_2O$ | | | | NaOH 20% | | | | $H_2SO_4$ 30% | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1/4[c] | 1 | 3 | 6 | 1/4 | 1 | 3 | 6 | 1/4 | 1 | 3 | 6 | 1/4 | 1 | 3 | 6 | 1/4 | 1 | 3 | 6 | 1/4 | 1 | 3 | 6 |
| 1 | D | D | D | D | A | A | A | A | R | R | R | R | R | R | R | R | R | D | D | D | R | R | R | R |
| 4 | A | D | D | D | R | A | A | A | R | R | R | R | R | R | R | R | R | D | D | D | R | D | D | D |
| 5 | A | A | D | D | R | R | R | R | R | R | R | R | R | R | R | R | R | D | D | D | A | A | A | A |
| 7 | A | A | D | D | A | A | A | A | R | R | R | R | R | R | R | R | R | D | D | D | R | D | D | D |
| 8 | A | A | D | D | R | R | R | R | R | R | R | R | R | R | R | R | R | D | D | D | R | D | D | D |
| 11 | A | D | D | D | R | R | R | R | R | R | R | R | R | R | R | R | R | D | D | D | R | D | D | D |
| 12 | A | A | A | D | R | R | R | R | R | R | R | R | R | R | R | R | R | D | D | D | R | R | R | R |
| 14 | A | A | A | D | R | R | A | A | R | R | R | R | R | R | R | R | R | R | R | R | R | R | R | R |
| 15 | A | D | D | D | R | D | D | D | R | A | A | A | A | D | D | D | R | D | D | D | D | D | D | D |
| 16 | A | D | D | D | A | A | A | A | A | A | A | A | R | R | R | R | A | A | D | D | R | A | A | A |
| 17 | A | D | D | D | A | A | A | A | R | R | R | R | R | R | R | R | R | D | D | D | R | R | R | R |
| 18 | A | D | D | D | D | D | D | D | D | D | D | D | R | A | A | A | R | A | A | A | R | A | A | A |
| 19 | A | D | D | D | R | D | D | D | D | D | D | D | D | D | D | D | R | D | D | D | R | R | R | R |

R—resistant; A—attacked; D—destroyed.

[a] See Table 1.

[b] *N*-methyl pyrrolidone.

[c] The entries in this row are durations in months.

### 2.2.5. Chemical resistance

Chemical resistance tests of the coatings were performed by a method of exposing test specimens to liquid chemicals and evaluating the effects of such immersion, according to EN ISO 2812. Rectangular (4 × 2 cm), coated steel substrates were placed vertically into glass cylinders. Then the glass tubes were filled with test liquids to cover three-quarters of the height of the specimens and closed with stoppers. Test solutions included deionized water, dilute sulfuric acids, solution of sodium hydroxide, polar and nonpolar organic solvents: ethanol, *N*-methyl pyrrolidone, toluene. Storage occurred at 25 °C. The coatings were examined after 1 week, and then after 1, 3 and 6 months. Visual comparison was made with untreated samples and rated in three categories:

1. Resistant—slight changes that do not affect the protective capabilities of the coatings.
2. Attacked—changes that affect the protective capabilities of the coatings, e.g. blistering or underrusting.
3. Destroyed—severe damage of the coating, e.g. delamination or rust formation.

### 2.2.6. Thermal analysis

A Paulik–Paulik–Erdey system derivatograph was used to study the thermal stability. The derivatographic analysis was carried out in air using weighed portions of 90 mg at a heating rate of 7.9 $^{\circ}\mathrm{C\,min^{-1}}$ within the temperature range from 20 to 800 °C. The initial decomposition temperature (IDT) was determined with the temperature of onset weight loss of the sample. The maximum weight loss rate ($R_{\max}$) and the temperature at maximum rate of weight loss ($T_{\max}$) were taken from the peak values of the differential thermogravimetric thermograms.

The limiting oxygen index (LOI) test was performed according to the ASTM D 2836 specification. Test specimens bar of (80 × 10 × 4 mm) suspended vertically were ignited by Bunsen burner. The concentration of oxygen was raised if the specimen extinguished before 3 min or burning 5 cm of the sample length. The oxygen content was adjusted until the limiting concentration was determined.

## 3. Results and discussion

### 3.1. Chemical resistance of coatings

The poor chemical resistance of the common epoxy coatings is often stated as a major disadvantage hindering their commercial breakthrough. Their resistance regarding the different chemical agents depends on the type of resin as well as on the type and amount of hardener and also on the curing temperature. Table 2 summarizes chemical resistance comparison of all prepared epoxy coatings. Comparing the long-term chemical resistance of polythiourethane-cured epoxy coating and standard epoxy formulation clearly shows an advantage for the polythiourethane-based systems. Within the range of epoxy resin composition, the coating prepared from resin cured with standard amine hardeners (comp. 15) gives the lowest performance. The resistance of such composition is much inferior, especially against dilute sulfuric acid and distilled water. For both types of polythiourethane hardeners we can see the substantially higher resistivity for the resin with the higher concentration of curing agent. The reason seems to be connected with a higher content of thiol and thiourethane groups or with the high level of crosslinking. The polarity of the thiol and thiourethane groups serves to create high adhesive strengths and provides optimum chemical and solvent resistance.

The chemical inertness of the cured epoxy system is enhanced by the dense, closely packed structure of the resinous mass, which is resistant to solvent action. The effect of curing degree was observed especially in aromatic and polar solvents which have capacity to swell the material. In previous work which originated in our labs [2], it has been shown that crosslink density increased according to the percentage of polythiourethane hardener. The changes of swelling behavior are obviously proportional to the concentration of these hardeners. The high conversion of epoxy groups and the low swelling behavior observed for highly crosslinked materials result in improvement of the protective properties of the coatings. The resins with high degree of conversion contain a small amount of unreacted amine hardener. It is known that free amine hardeners remained in the coating make it less resistant for attack of water, solvent and other chemicals [4]. In the case of polythiourethane hardeners, a free amine that remains in condensed resin can react with diisocyanate-end derivatives liberated by the heat of reaction [2]. This gives less unreacted amine in the coating. The assumption of the influence of the unreacted amine on the chemical resistance can also be confirmed by the lower resistivities given by dimermercaptan (DODT)-cured coatings (comps. 16–19). It had been expected that the excellent chemical resistance of dimercaptan formulation could be incorporated in the epoxy systems but instead the effect was opposite. Especially poor acid resistance behavior of the film can be attributed to the fact that films were also composed of adduct of diamine and they were alkaline in nature. As a consequence, all samples were severely damaged by the sulfuric acid solution used for the test. Very poor alkali resistance of polythiourethane-cured coating can be attributed to the low hydrolytic stability of thiourethane and ether moieties. The results obtained for HDI-DODT and TDI-DODT hardeners were almost the same. The most pronounced difference was the worse resistivity of HDI-DODT-cured resins (comps. 1, 4, 5 and 7) against toluene and diluted sulfuric acid. These results support the conclusions made earlier. Higher resistivity of TDI-DODT-based coating (comps. 8, 11, 12 and 14) can be attributed to the formation of highly crosslinked system, by the more reactive TDI polymer, which additionally provide better conversion of amine [2].

### 3.2. Physico-mechanical properties of coatings

#### 3.2.1. Scratch resistance by pencil test

The scratch resistance of a coating refers to the hardest pencil that will not gouge the film. The pencil test was performed on each of the formulations to compare their relative scratch resistance values. The data compiled in Fig. 3 revealed that replacement of amine and dimercaptan hardeners by polythiourethanes enhances the scratch resistance of the epoxy resin. It is evident from these results that the more polythiourethane hardener was used to crosslink the epoxy, the stronger becomes the scratch resistance. These results correlated well with other mechanical properties and crosslink density of these materials presented before [2]. The higher impact resistances and tensile properties of the DODT-HDI-cured resin were explained by the flexible aliphatic spacer of HDI. Also the flexibilities, characterized by the elongation values, were improved by moving from the aromatic structures of the TDI-based hardeners, to the more aliphatic structures of the HDI materials. The high scratch resistance properties of resin cured with TDI-based polythiourethane can be attributed to the formation of highly crosslinked, rigid system by the more reactive TDI polymers. These assumptions were also confirmed by relatively high scratch resistance of the coating prepared in the presence of tertiary amine accelerator (comps. 7 and 14). As we reported earlier [2], the use of 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30) resulted in increasing the degree of conversion and crosslink density of the cured epoxy resin. A similar increase

| | Pencil Scratch Hardness | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition number[a] | 6B | 5B | 4B | 3B | 2B | B | HB | F | H | 2H | 3H | 4H | 5H | 6H |
| 1 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | | | |
| 4 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | | |
| 5 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | | |
| 7 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | |
| 8 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | |
| 11 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | |
| 12 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | |
| 14 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | |
| 15 | ▨ | ▨ | ▨ | ▨ | | | | | | | | | | |
| 16 | ▨ | ▨ | ▨ | ▨ | ▨ | ▨ | | | | | | | | |
| 17 | ▨ | ▨ | ▨ | | | | | | | | | | | |
| 18 | ▨ | ▨ | ▨ | ▨ | | | | | | | | | | |
| 19 | ▨ | ▨ | ▨ | ▨ | | | | | | | | | | |

[a] Numbering of resin composition according to Table 1.

Fig. 3. Pencil scratch hardness of epoxy coatings.

Table 3
Adhesive properties of epoxy systems

| Comp. no.[a] | Adhesion (cross-cut)[b] | | | Bending | | Lap shear strength (MPa) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Steel | Copper | Alum. | 1.4 in | 1.8 in | Steel | Copper | Alum. | Polyamide |
| 1 | 4 | 4 | 5 | Passes | Passes | 5.23 | 5.39 | 4.90 | 3.19 |
| 4 | 5 | 5 | 5 | Passes | Passes | 9.21 | 8.19 | 5.82 | 3.60 |
| 5 | 5 | 5 | 5 | Passes | Passes | 10.82 | 10.01 | 9.44 | 6.41 |
| 7 | 5 | 5 | 5 | Fails | Fails | 4.89 | 3.35 | 3.00 | 2.37 |
| 8 | 4 | 4 | 4 | Passes | Passes | 7.00 | 5.54 | 5.60 | 4.37 |
| 11 | 4 | 4 | 4 | Fails | Fails | 8.63 | 6.72 | 6.32 | 2.12 |
| 12 | 5 | 5 | 5 | Passes | Fails | 9.08 | 7.78 | 7.55 | 3.84 |
| 14 | 4 | 5 | 5 | Fails | Fails | 4.77 | 3.13 | 3.47 | 1.06 |
| 15 | 2 | 4 | 3 | Fails | Fails | 4.54 | 1.58 | 2.91 | 2.60 |
| 16 | 1 | 1 | 1 | Fails | Fails | 7.04 | 5.37 | 5.65 | 3.19 |
| 17 | 4 | 4 | 5 | Passes | Fails | 10.26 | 9.20 | 10.20 | 3.60 |
| 18 | 5 | 5 | 5 | Passes | Passes | 10.75 | 9.40 | 9.49 | 4.42 |
| 19 | 5 | 5 | 5 | Passes | Passes | 10.95 | 10.24 | 8.57 | 4.58 |

[a] See Table 1.
[b] Numbers from 0 to 5 represent increase of adhesive force.

in scratch resistance with increasing of crosslink density was reported by Lange et al. [5].

### 3.2.2. *Coating performance of the epoxy systems*

The coating performance characteristics of all compositions are presented in Table 3. From these data it has been found that the varnishes cured with polythiourethane hardeners give better adhesion than those produced with standard amine hardeners.

Flexibilizers in epoxy systems work by allowing material to deform under stress, they also improve peel and impact strength. However, improved flexibility will often result in the lowering of tensile strength. The bending test indicates that all the polythiourethane-cured resins are highly flexible due to the presence of flexible ether linkage. Flexibilities were improved by moving from the aromatic structures of the TDI-based hardeners (comps. 8, 11, 12 and 14), to the more aliphatic structures of the HDI material (comps. 1, 4, 5 and 7). These changes are in proportion to the concentration of a given polythiourethane. Flexibility measurement results are in good agreement with our preliminary research of the impact resistance of these systems [2].

Also, the dimercaptan-cured samples (comps. 17–19) demonstrated good flexibility, and when bent over a 1/4-in mandrel diameter, did not show any signs of cracking. For the samples 7, 14 and 16, cracking was evident through the entire thickness of coating. This may be due to increase of extent of crosslinking characteristic of all samples cured in the presence of DMP-30 accelerator [2].

The epoxy/polythiourethane system exhibits a better adhesion for copper and other metal surfaces as compared with standard epoxy system (comp. 15). These properties may be correlated to the polar groups of thiourethane and ether linkages which provide sufficient adhesion and toughness contributed by the thiourethane moiety. The –NH groups of thiourethane and urethane linkages can form hydrogen bonds both with the substrate and with the carbonyl oxygen atoms of the polymer itself [6]. Together with the ability of the reaction of thiol groups with common metal surfaces, this results into a well-adhered coating system.

As mentioned above, the application of DMP-30 increased crosslink density, produced strain in the films that lowered down the scratch hardness and adhesion force and introduced brittleness.

### 3.2.3. *Lap shear strength*

It can be seen from Table 3 that the lap shear strength of the adhesive using the polythiourethane and mercaptan hardeners is always higher than that of the composition using only the amine curing agents. The lap shear strength for all metal substrates increases with increasing content of both polythiourethane hardeners. However, these changes are particularly distinct for the more flexible chain of HDI-DODT hardener. Increase of the chain flexibility can reduce the concentration of internal stress and enhance the ability of the adhesive to inhibit the crack propagation [7]. Therefore, the lap shear strength will increase. Only polyamide substrates do not follow this trend, due to the adhesive failure of the bond. It must be noted that the surface of the polyamide substrates was virtually untreated. Much stronger bonds can be formed with various pre-treatments, e.g. potassium dichromate, sulfuric acid etch. In the case of metal substrates interaction of unreacted –SH groups of the dimercaptan-cured samples (comps. 16–19), with the metal surface exerting a strongly adhesive effect on the resin chains. For the samples cured with DMP-30 accelerator (comps. 7 and 14) shear strength decreased, because of the higher crosslink density and relatively low flexibility of the resin. The increased brittleness and impact sensitivity of these samples cause the weakening of the cohesive forces.

#### 3.2.4. Morphology of the fracture surface

The micrographs of the fracture surfaces of the epoxy specimens are shown in Fig. 4. It can be seen that the morphologies of the epoxy resin cured with polythiourethanes are quite different from those obtained with standard amine hardeners. The glassy fracture surface of the standard epoxy composition is smooth with uniform crack direction, Fig. 4a. This indicates brittle fracture which accounts for poor impact strength of this sample.

The micrographs of polythiourethane samples indicate that there are no separate phase domains and may indicate the formation of homogeneous intercrosslinked network of epoxy resin and polyurethane chains formed from diisocyanate derivatives freed by the heat of reaction. Their fracture surfaces show more branches resulting in higher strength. Further, smooth fractured surface was observed with decreasing polythiourethane content due to the flexibility and less brittle behavior imparted by polythiourethane Fig. 4b–d. This is in very good agreement with the impact resistance property of the polythiourethane-cured epoxy resins. It was found earlier that impact strength of the curing systems is greatly enhanced by the use of polythiourethane and closely related to the content of hardener [2].

### 3.3. Thermal properties and flame retardancy of the resins

High thermal stabilities over 300 °C and flame retardant properties are especially important for epoxy resins being utilized in the advanced technology, while associating with the surface mounting technology and lead-free soldering processes.

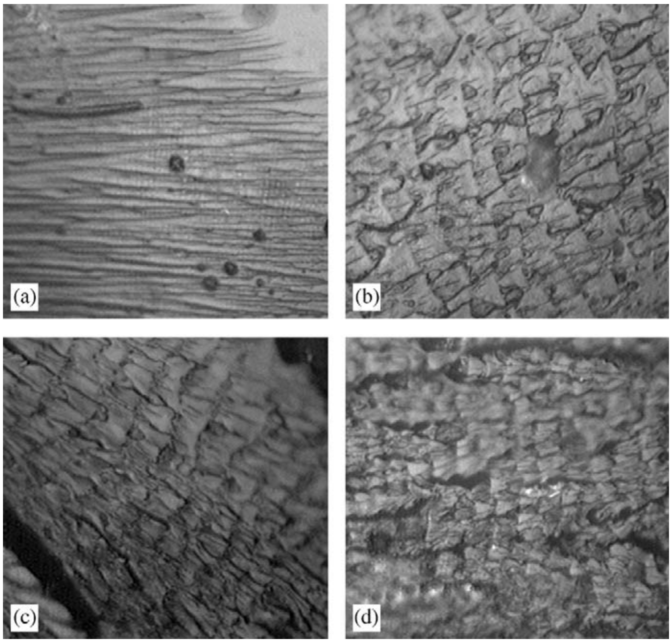

Fig. 4. Optical micrographs of the fracture surfaces for: (a) composition 15; (b) composition 1 (10 phr of HDI-DODT; (c) composition 4 (30 phr of HDI-DODT) and composition 5 (50 phr of HDI-DODT). Magnification of 2500 × .

The thermal studies of the polythiourethane-cured resins were carried out by thermogravimetric analysis. Fig. 5 shows thermal degradation behaviors of the epoxy resin cured with different amounts of polythiourethanes compared with the properties of samples cured with standard amine hardener. Test data are summarized in Table 4. The cured resins are thermally stable up to about 290–310 °C and involved two-step decomposition reactions. For both steps of decompositions, the $T_{\max}$ values are almost the same for all tested samples. Comparing the TGA curves of compositions 1, 5 and 8, 12, it is observed that the thermal stability of the resins, represented by IDT, $T_5$ and $T_{50}$ thermal stability indices, decreases with the increase of the polythiourethane content. The increased loading of this hardener results in an increase in the number of thiourethane and urethane linkages per unit chain of polymeric resin. As both of these moieties have low thermal stability, it is assumed that the increased loading of polythiourethane hardener is responsible for the decreasing of thermal stability. The pyrolysis of polymers involves a variety of reactions such as chain cleavage, rearrangement and decomposition of chain segments, crosslinking and branching reactions, etc. Looking at the small amount of residual weights, it can be presumed that all the cured samples were ultimately converted to low-molecular-weight substances. The thermal stability of the polythiourethane-cured epoxy resin is not superior to that of the amine-cured materials at low temperature; however, the char yields of the polythiourethane-cured epoxy at 800 °C are slightly higher than those prepared with standard hardeners. This phenomenon reveals that the polythiourethane-cured epoxy resins possess better thermal stability during high-temperature period. Increasing char formation can limit the production of combustible carbon-containing gases, decreases the exothermicity due to pyrolysis reactions, as well as inhibits the thermal conductivity of the burning materials [8,9]. Thus, a higher char yield can enhance the flame retardancy. The flame retardant properties of the obtained epoxy resins were examined by measuring the LOI, which is defined as the minimum fraction of $O_2$ in a mixture of $O_2$ and $N_2$ that will just support flaming combustion. The polythiourethane-cured samples have higher LOI than reference standard epoxy resin; however, their flame retardancy deteriorates with increasing the loading of the hardener. Such trend is in good agreement with the observed increasing char yield, and confirms the mechanism of improving the flame retardancy of the resins.

### 3.4. Low-temperature curing performance of the polythiourethane hardeners

Obtaining high reactivity and conversion as well as good physico-mechanical properties of the cured lower-temperature epoxy resin remains the challenge for majority of the common epoxy hardeners. The most important achievement

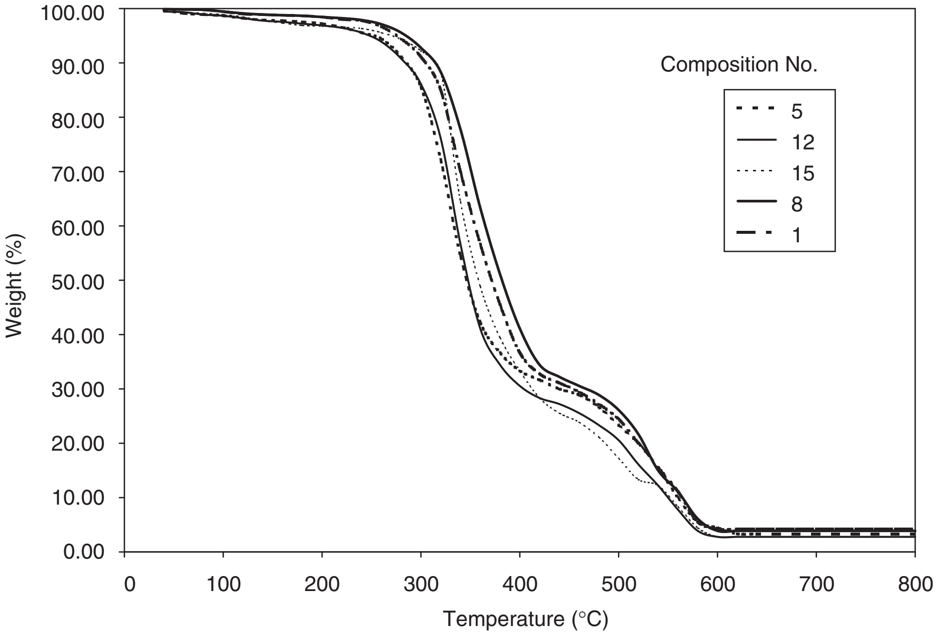

Fig. 5. TGA thermograms of cured epoxy resins.

Table 4
Thermal stability and flame retardancy data of the cured epoxy resins

| Comp. no.[a] | IDT[b] (°C) | | $T_5$ (°C) | $T_{10}$ (°C) | $T_{max}$[c] (°C) | | $R_{max}$[d] (mm) | | Char ratio at 800 °C (wt%) | LOI |
|---|---|---|---|---|---|---|---|---|---|---|
| | I | II | | | I | II | I | II | | |
| 1 | 290 | 490 | 270 | 302 | 330 | 540 | 33 | 10 | 4.2 | 34.8 |
| 5 | 284 | 485 | 240 | 275 | 330 | 540 | 38 | 8 | 3.3 | 31.5 |
| 8 | 305 | 500 | 280 | 305 | 340 | 540 | 30 | 11 | 3.9 | 32.8 |
| 12 | 300 | 480 | 240 | 280 | 330 | 550 | 45 | 8 | 3.1 | 29.2 |
| 15 | 310 | 490 | 260 | 305 | 330 | 550 | 45 | 8 | 2.8 | 27.1 |

[a] See Table 1.
[b] IDT—initial decomposition temperature.
[c] $T_{max}$—temperature of maximum rate of mass loss.
[d] $R_{max}$—maximum weight loss rate was taken from the peak values of the DTG chart.

of polymercaptan hardeners is curing at lower temperature compared to the other hardeners. To evaluate the usability of prepared hardeners for curing in low-temperature condition, the tests of curing reactions at −10 °C were carried out. The results strongly differentiate the low-temperature cure potential for conventional and polythiourethane hardeners. The gel times presented in Table 1 highlight the importance of polythiourethanes and mercaptans to enable low-temperature crosslinking reaction. These hardeners in contrast to standard amine curing agents (comp. 15) offer very high activity even at −10 °C. In order to estimate the degree of cure, the conversion of epoxide rings was determined by chemical analysis of the swollen resin. The small changes of conversion of epoxy groups for samples cured at low temperatures with polythiourethane hardeners (Table 1) provide a proof for our earlier proposed hypothesis [2], that the thiourethane moiety can react directly with the epoxy group with subsequent cyclization to an oxazolidone (Fig. 6). At the low-temperature conditions thiourethane dissociation is impossible, thus the free isocyanates cannot be the actual intermediates in the crosslinking process. A significant decreasing of the crosslink density of the resins cured at −10 °C with standard amine and mercaptan hardeners, connected with considerable deterioration of impact resistance (Fig. 7) seems to confirm such mechanism of crosslinking.

Additional evidences of the structural changes of the polythiourethane-cured epoxy systems under different thermal conditions were provided by IR measurements. The IR spectra of the DODT-TDI-cured system (comp. 11) at room temperature and −10 °C, are shown in Fig. 8. The presence of the peaks of urethane group at 1686–1640 and 1540–1518 $\mathrm{cm}^{-1}$ in the spectrum of the resin cured at room temperature, and their lack for the resin cured at −10 °C, seems to confirm that depending on the temperature conditions, the end product may also consist of crosslinked or uncrosslinked polyurethane chains. The free amine and hydroxyl groups remaining in the condensed resin provide adequate points for epoxy crosslinking by the diisocyanate-end derivatives liberated by the heat of reaction. Extremely reactive isocyanate groups are capable to react not only with the oxirane rings and hydroxyl groups present in the resin but also with any amine curing agents. The absence of the urethane absorption and characteristic absorption peak of oxazolidone at 1756 $\mathrm{cm}^{-1}$ in the spectrum of low-temperature cured sample gives further proof that dissociation of thiourethane moiety is not necessary in the crosslinking process. This indicates for the direct reaction of thiourethane unit with the epoxy group with subsequent cyclization to an oxazolidone (Fig. 6), so giving the advantage of high thermal and chemical stability [10]. For both spectra, the stretching band of epoxide groups at 921 $\mathrm{cm}^{-1}$ still remained, the intensity peaks were further confirmed by a quantitative measurement of the degree of curing.

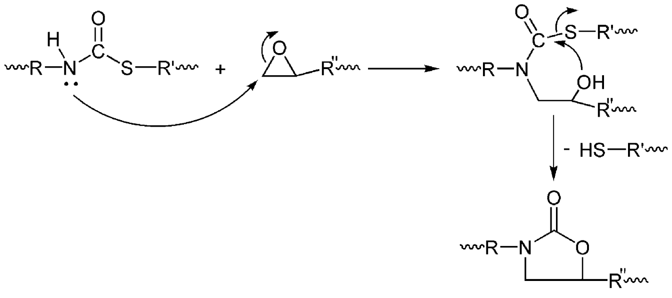

Fig. 6. Reaction of the thiourethane moiety with the epoxy group.

Future work will include coating properties of the low-temperature cured formulation as well as their mechanical and chemical resistances at low-temperature conditions.

## 4. Conclusions

From this work, it can be concluded that polythiourethanes hardeners can be utilized successfully for the curing of epoxy resins. It was observed that evaluation of physico-mechanical and chemical resistance performance shows better results with the increased loading of polythiourethane hardener. Aromatic ring of TDI-based polythiourethane introduces rigidity in the polymer resin and causes the deterioration of physico-mechanical properties. Also, the application of DMP-30 accelerator gives to much crosslinking, thus adhesion and chemical resistance of such compositions are worsened.

The chemical resistance data showed that the polythiourethane-cured resins have very good chemical resistance in all test media. The increased number of polar groups in polythiourethane-based coating material imparts very good adhesion of the resin to the metal substrate as compared to the common epoxy systems. Excellent adhesion of these materials, contributes to the good chemical resistance properties of the coatings, which in interacting with various chemicals, does not allow the corrosive ions penetrate through coating framework. In spite of deteriorating of the thermal stability of the cured resin, polythiourethane hardeners have an efficient effect on levelling up the flame retardancy of the epoxy systems. The char yield has been correlated to denote the flame retardancy.

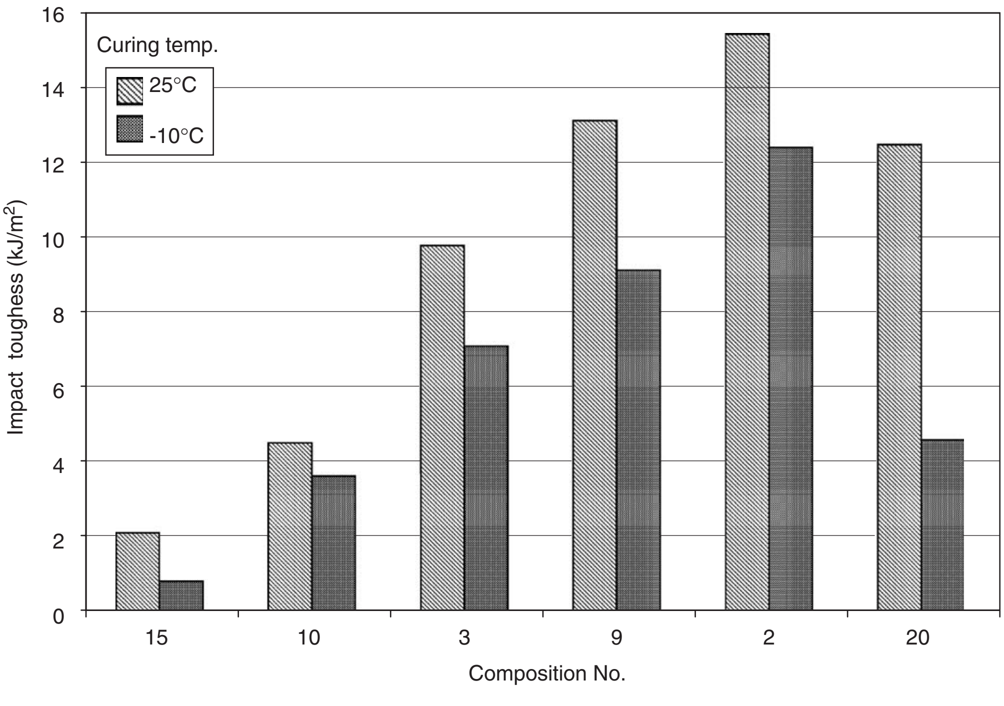

Fig. 7. Effect of different curing thermal conditions on impact resistance of epoxy resins.

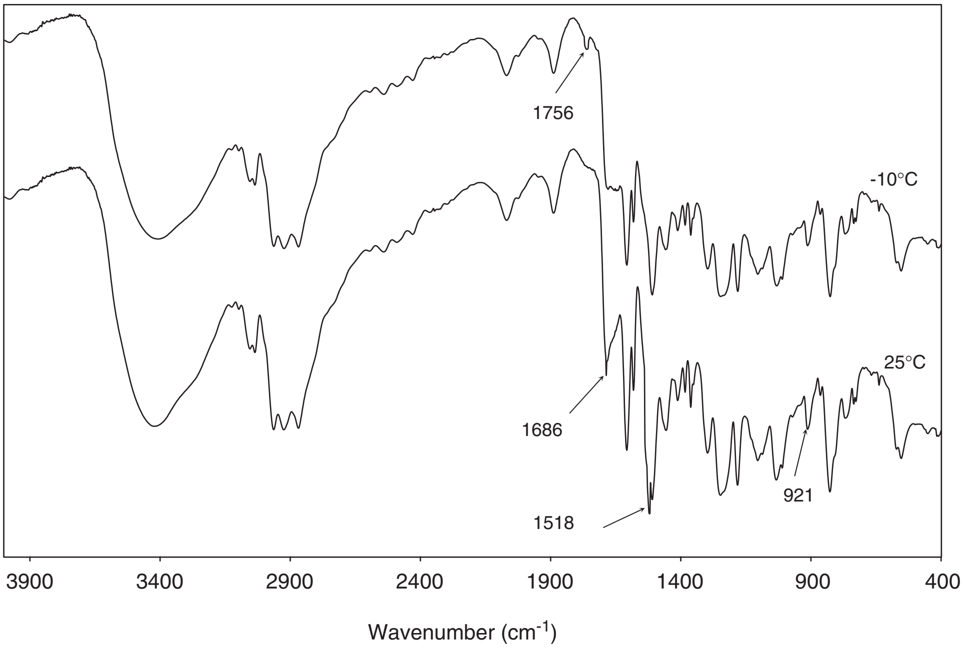

Fig. 8. FTIR analysis of the epoxy systems cured with DODT-TDI at different thermal conditions.

Described epoxy/polythiourethane systems will gain interest in a wide range of applications because of their excellent properties, including adhesion to various substrates, resistance to chemicals, solvents and water, hardness and toughness. The predicted major applications for such systems include adhesives, binder for composite, and especially plastic, steel and other metal coatings for normal, as well as low-temperature processing.

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