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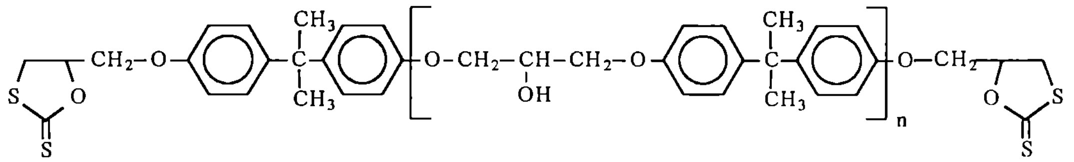
Studies on the properties of epoxy-oxothiolane resins

RAPID COMMUNICATION

Summary — *Bis*-1,3-oxothiolane-2-thione resins (Scheme 1) were prepared in the reactions of commercial low-*M* epoxy resins, Epidian 5 and Epidian 6, with carbon disulfide. Compositions including Epidian 5 or 6 and various amounts (5, 10, 20, 30 or 40 wt. %) of oxothiolane resins as additives were prepared and cured with piperidine. Mechanical properties such as bending, compressive, tensile and impact strengths were determined. Water absorbency, combustibility and thermal stability were also determined. Addition of 5 to 10 wt. % of sulfur-containing resin was found to improve mechanical strength by 15% (Fig. 1) and thermal stability by 35°C (Table 3, Fig. 3).

Key words: *bis*-1,3-oxothiolane-2-thione resins, epoxy-oxothiolane compositions, mechanical properties, water absorbency, combustibility, thermal stability.

Among the numerous methods of chemical modification of epoxy resins there are also techniques involving synthesis of sulfur analogs [1]. So far carbon disulfide has not been used to modify epoxy resins, although reactions with carbon dioxide have been studied [2]. As recently reported [3], *bis*-oxothiolane-2-thione resins



Scheme 1. *Bis*-1,3-oxothiolane-2-thione resin

(Scheme 1) have been obtained in the reactions of commercial-grade low-molecular-weight epoxy resins, Epidian 5 and Epidian 6, with carbon disulfide.

The new method developed to modify epoxy resins [4] allows di-oxothiolane resins to be selectively prepared in an easy and effective way. The resins obtained were characterized by elemental analysis, spectroscopic and chromatographic methods and their structures were confirmed. The behavior of oxothiolane resins was examined in the curing and thermal degradation reactions. The stable five-member oxothiolane ring was found to be less reactive than the starting epoxy resins [5]. Pure uncured oxothiolane resins and resins cured with hexahydrophthalic anhydride, piperidine and triethylenetetraamine revealed a lower thermal stability than that of epoxy resins. Nevertheless, owing to the properties of 5-substituted-1,3-oxothiolane-2-thione rings [6, 7], oxothiolane resins could be considered as additives. They could be applied as antioxidants, stabilizers and plasticizers for epoxy composites.

In this work we prepared mixed epoxy-oxothiolane compositions, cured them with piperidine, and finally determined the physical, mechanical and thermal properties of the polymeric materials achieved.

EXPERIMENTAL

Materials

Epidian 5, Epidian 6 and triethylenetetraamine (hardener Z-1, TETA, ZCh Organika-Sarzyna, Nowa Sarzyna) were commercial-grade materials. Pure-grade piperidine was Merck's reagent. All materials were used without any additional purification.

Bis-1,3-oxothiolane-2-thione resins were synthesized on the basis of Epidian 5 (Ep5-S) and Epidian 6 (Ep6-S) as described elsewhere [3, 8].

Preparation of compositions

A series of compositions consisting of Epidian 5 or Epidian 6 and different amounts (Table 1) of oxothiolane resins as additives were prepared by mixing liquid epoxy resins with solid oxothiolane resins at 70°C for 1 hour.

T a b l e 1. **Contents of epoxy-oxothiolane compositions**

Amount of oxothiolane resin, wt. %	
Ep5-S	Ep6-S
5	5
10	10
20	20
30	30
—	40

Curing conditions

Each epoxy-oxothiolane resin was cured with piperidine (6 wt. %, based on resin) for 4 hours at 80°C and post-cured for 24 hours at 100°C. Curing with triethylenetetraamine (10 wt. %, based on resin) was performed at room temperature for 24 hours. Additionally, samples were annealed at 100°C for 24 hours.

Measurements

Flexural (ISO 178-1975), compressive (ISO 604-1973) and tensile (ASTM D 638-77) strengths were determined by means of a ZWICK 1445 testing machine. Impact resistance (method of Schob-Nitsche-Salewski, DIN 51-230) was established with a DYNSTAT equipment. Water absorbency was evaluated according to ISO 62-1980. Thermal stability (ISO 7111-1987) was measured by using a NETZSCH TG 209 thermogravimetric analyzer, operated in the dynamic mode at a heating rate of 10°C/min. The conditions were: sample mass, ~4.0 mg; atmosphere, argon; and temperature range, 30—600°C. Flammability was determined by using the oxygen index method. Oxygen index measurements were performed on a standard test equipment according to the procedure described in ASTM D 2863-74.

RESULTS AND DISCUSSION

As compared with the properties of unmodified epoxy resin, small amounts (≤20 wt. %) of oxothiolane resins used as additives were found to improve the strength of epoxy-oxothiolane compositions. With the higher value of the modulus of elasticity, the tensile strength of the compositions was also higher by up to 10% than that of epoxy resins. The compressive strength of the materials composed of 10 wt. % and 20 wt. % of sulfur containing resins increased by 20%. Analogously, the small amount of sulfur modifiers increased the modulus of elasticity and improved the flexural strength by 10%; in relation to epoxy resins cured with triethylenetetraamine, the improvement reached even 50% (Fig. 1).

It was found that also the impact resistance of the systems containing 5 wt. % and 10 wt. % of oxothiolane

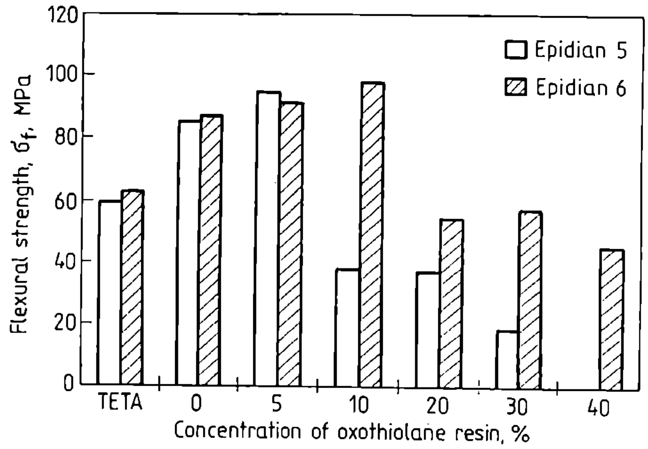


Fig. 1. Flexural strength σ_f in relation to concentration of oxothiolane resins; TETA — epoxy resins cured with triethylenetetraamine

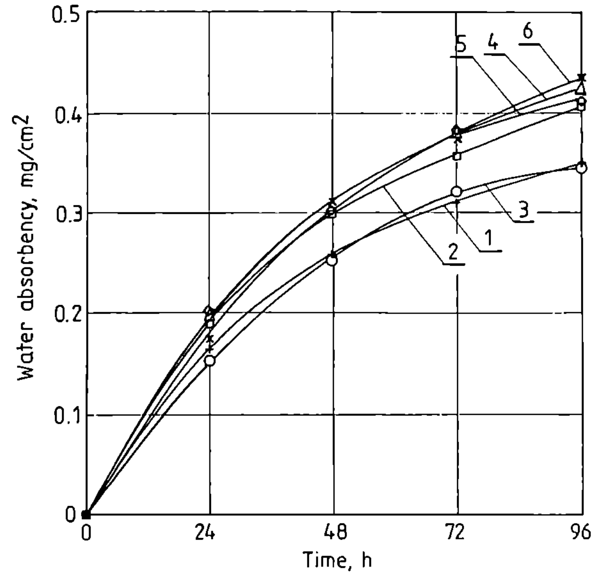


Fig. 2. Water absorbency of epoxy-oxothiolane compositions prepared on the basis of Epidian 5 versus time; 1 — Epidian 5 cured with triethylenetetraamine, 2 — Epidian 5 cured with piperidine, 3 — composition containing 5 wt. % of Ep5-S, 4 — composition containing 10 wt. % of Ep5-S, 5 — composition containing 20 wt. % of Ep5-S, 6 — composition containing 30 wt. % of Ep5-S

resins was higher than the impact resistance of Epidian 5 and Epidian 6 cured with triethylenetetraamine and piperidine. Water absorbency of the mixed systems and of the pure epoxy materials was found to be comparable or slightly higher in the epoxy-oxothiolane systems. The difference in water absorbency between the compositions studied was max. 0.1 wt. %. Of the compositions prepared on the basis of Epidian 5 (Fig. 2), the system containing 5 wt. % of oxothiolane resin Ep5-S had the lowest water absorbency.

The fire behavior studied in terms of the oxygen index showed the mixed compositions to exhibit thermal resistivity at the same level (or slightly worse) as that of the epoxy resins cured with triethylenetetraamine and piperidine. The composition prepared with Epidian 5 and 10 wt. % of Ep5-S was even less combustible than Epidian 5 cured with piperidine (Table 2).

Table 2. Results of measurements of oxygen index

Composition	Oxygen, %	
	Epidian 5	Epidian 6
Epidian cured with TETA	23.1	23.1
Epidian cured with piperidine	22.5	26.1
5% Ep-S	21.0	22.4
10% Ep-S	23.2	22.5
20% Ep-S	20.5	22.4
30% Ep-S	18.5	21.3
40% Ep-S	—	18.5

As already reported, pure uncured oxothiolane resins and resins cured with hexahydrophthalic anhydride, piperidine and triethylenetetraamine exhibit lower thermal stability than epoxy resins. Nevertheless, a small amount of the oxothiolane additives was found to result in the initial decomposition temperature increased by 35°C (Table 3, Fig. 3) in the composition consisting of Epidian 6 and 5 wt. % of Ep6-S. In analogy to mechanical strength, the systems containing more than 10 wt. % of oxothiolane resins have poorer thermal properties.

Table 3. Initial decomposition temperature (IDT) and char residue of Epidian 6 and mixed epoxy-oxothiolane compositions cured with piperidine

Resin	IDT, °C	$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	Char residue, %
Epidian 6	294.6	346.0	364.0	398.1	18.20
5% Ep6-S	329.2	371.4	392.8	421.9	8.58
10% Ep6-S	319.3	363.4	381.3	412.0	9.18
20% Ep6-S	296.4	343.5	360.5	389.6	3.04
30% Ep6-S	246.0	324.7	341.4	370.5	4.90
40% Ep6-S	234.1	315.5	333.2	361.5	11.07

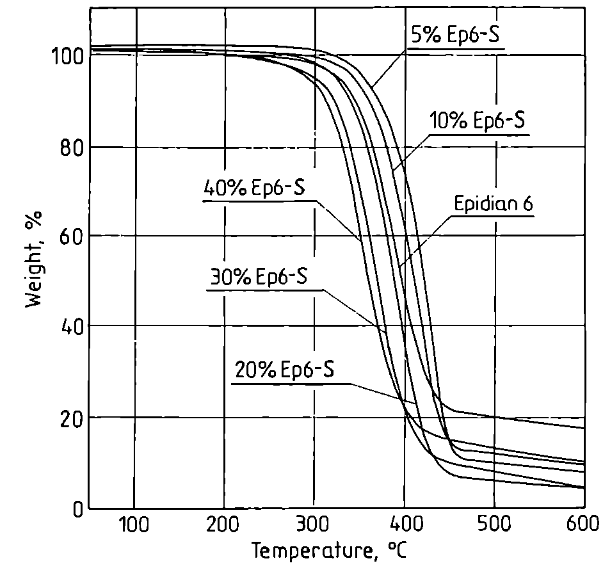


Fig. 3. Thermogravimetric analysis of Epidian 6 and mixed epoxy-oxothiolane compositions cured with piperidine

CONCLUSION

The results of our investigation show the oxothiolane resins to be applicable as additives to modify the properties of epoxy resins. Apart from the applications of 5-substituted-1,3-oxothiolane-2-thiones described in the literature, we have found that even small amounts of sulfur containing resins (5—10 wt. %) improve the mechanical strength of epoxy resins by 15% and increase their thermal resistivity by 20—35°C. However, the higher contents (above 10 wt. %) of oxothiolane resin in the composition give rise to a visible deterioration of the properties. This effect needs a detailed study, which is now in progress.

ACKNOWLEDGMENT

This work was financially supported by the Polish State Committee for Scientific Research (KBN), Grant No 3/T09B/05113.

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Received 17 IV 2000.