

PAPER • OPEN ACCESS

## Effect of benzotriazolyl fragments on properties of thermoreactive benzotriazolylsuccinimides

To cite this article: D M Mogonov *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **320** 012046

View the [article online](#) for updates and enhancements.



**IOP | ebooks™**

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the **collection** - download the first chapter of every title for free.

# Effect of benzotriazolyl fragments on properties of thermoreactive benzotriazolylsuccinimides

**D M Mognonov<sup>1</sup>, I A Farion<sup>1</sup>, O V Il'ina<sup>1</sup>, O Zh Ayurova<sup>1</sup> and V N Kornopol'tsev<sup>1</sup>**

<sup>1</sup> Baikal Institute of Nature Management SB RAS, Ulan-Ude, 670047, Russia

E-mail: fariv@mail.ru

**Abstract.** An effect from the introduction of the benzotriazolyl fragments into the structure of thermoreactive resins based on benzotriazols and molar excesses of hexamethylene-bis-maleimide was revealed. A change of thermal characteristics and improving mechanical properties and adhesion of the cured thermally glue layers to the surfaces of metallic samples made of Steel-3 were found. Such a conclusion was made from the data of the thermal analyzes and mechanical testes, when compared the samples made of both 'pure' hexamethylene-bis-maleimide and the ones containing benzotriazolyl fragments.

## 1. Introduction

The atom-save technologies (atomic effectiveness) in a synthesis of different organic compounds are one of the priority directions in chemistry and chemical industry. The addition reactions are the ones in which the  $\pi$ -electron deficient double bond of the maleimide heterocycle is involved, for example, Michael nucleophilic addition [1, 2], the Diels-Alder cyclization across a  $\pi$ -addition [3, 4], photo addition [5, 6], the 'ene' reactions [7, 8], and the reactions of the (co-)polymerization across the double bond [9, 10]. In these abovementioned cases, the processes of a preparation of the substances occur without evolving condensation by-products; this makes such processes favorable in the point of view of ecology (green chemistry).

Early, we synthesized a number of thermoreactive benzotriazolylimide oligomers with the end-capped maleimide groups. Basic attention was paid to a synthesis and investigation of model low-molecular compounds, as well as to a study of an opportunity to utilize such oligomers as binders for laminate glassy plastics and as agents structuring linear polybenzimidazoles with the formation of polymer networks [11]. At the same time, the investigation on effect from an introduction of the benzotriazolyl fragments into a structure of oligobenzotriazolylimides did not carry out. Hence, the aim of this work was the synthesis of thermoreactive oligobenzotriazolylimides based on bisbenzotriazols and a molar excess of hexamethylene-bis-maleimide (GMBMI) as aliphatic bismaleimide, the comparative analysis of their thermal properties as well as the physic-mechanical characteristics of the glue joints made of them.



## 2. Models and Methods

### 2.1. Equipment and investigation methods

The NMR  $^{13}\text{C}$  and  $^1\text{H}$  spectra were run using a «Bruker-DXR500» spectrometer at 100 and 500 MHz, respectively in DMSO- $\text{d}_6$  solution. The inner standards were signals of the  $^{13}\text{C}$  isotopes at  $\delta$  39.7 ppm or ones of  $^1\text{H}$  at  $\delta$  2.5 ppm. The TG, DTG and DSC analyses were run using a «STA 449C Jupiter®» thermal analyzer of the «NETZSCH Gerätebau GmbH» manufacturer. The melting points were determined using a «IA 9100» apparatus or from the DSC endotherms. The strength properties of glue joints were determined using a «Instron-3367» bursting machine according to ISO 13445:2003.

### 2.2. Reagents and solvents

Isopropyl alcohol of “chemical pure” grade was used as received. GMBMI of the Kharkov plant of chemical reagents was purified by double crystallization from isopropyl alcohol in the presence of activated charcoal (m.p. 147.2 °C, according to DSC). Isophthalic acid was supplied from ‘Sigmaaldrich’ and purified by the vacuum sublimation (m.p. 346–347 °C). Glass fiber cloth was annealed at 500–600 °C to remove a lubricant. 5,5'-bis-benzotriazol methane (BBTM) and 5,5'-bis-benzotriazol oxide (BBTO) were prepared according to the methods described in the work [11].

### 2.3. Oligomers syntheses

Oligomers 1–4 were prepared according to our method developed early in the work [11] with some modifications.

**Oligomer-1 ( $n = 4$ ).** In a Wood’s alloy bath preheated up to 170 °C with a temperature regulator, a fluoroplast cap was placed and thermostatically controlled for 3–5 min. Next, 0.2075 g (0.0012 mol) of sublimed isophthalic acid was firstly placed and then mixture of 5.5258 g (0.020 mol) GMBMI and 1.2513 g (0.005 mol) BBTM was placed. After that, bath temperature was increased up to 220–225 °C, with being mixed simultaneously fused blend by a fluoroplast stick, and this fused blend was stood at this temperature for 1–1.5 min until it became clear. After, melted reaction product was rapidly cooled down to room temperature; this was accompanied by crystallization of it. According to the DSC data, melting point is 131.6–135.6 °C.

**Oligomer-2 ( $n = 4$ ), oligomer-3 ( $n = 3$ ) and oligomer-4 ( $n = 3$ )** were prepared in a similar manner. Loadings of monomers for oligomer-2 were GMBMI 5.5258 g (0.020 mol) and BBTO 1.2612 g (0.005 mol). According to DSC, melting point is 130.8–134.8 °C. Loadings of monomers for oligomer-3 were GMBMI 4.144 g (0.015 mol) and BBTM 1.2513 g (0.005 mol). According to DSC, melting point is 131.3 °C. Loadings of monomers for oligomer-4 were GMBMI 4.144 g (0.015 mol) and BBTO 1.2612 g (0.005 mol). According to DSC, melting point is 129.6–132.9 °C.

### 2.4. Making glue joints

The metallic plates with the dimensions of  $2 \times 6 \text{ cm}^2$  made of steel-3, copper and brass were cleaned with sandpaper followed by wiping with a wet filter paper. Next, the plates were soaked into 9M  $\text{H}_3\text{PO}_4$  for three days. After that, the surfaces of the plates were rinsed with distilled water and dried. A thin layer of binder was applied by melting powder of oligomer or GMBMI directly on the bonded area of the plate with the dimensions of  $1 \times 2 \text{ cm}^2$ . Next, after a solidification of the layer of binder, the upper plate was overlapped with the bottom one so that the overlapped area matched that of the layer of binder. If necessary, a prepreg made of the glass-fiber cloth permeated with binder could be placed between the plates. To make the glue joint, the plates were gradually heated in an oven from room temperature up to 220 °C with maintaining at this temperature for 6 or 12 h and at specific pressure of 0.4 MPa. After cooling, the glue joints were tested for the shear strength.

### 3. Results and Discussion

#### 3.1. Syntheses of oligomers and proving their structures

Oligomers were synthesized by an interaction of three- or fourfold molar excess of GMBMI with BBTM or BBTO in melt (Figure 1) according to the method developed by us [11] with some modifications.

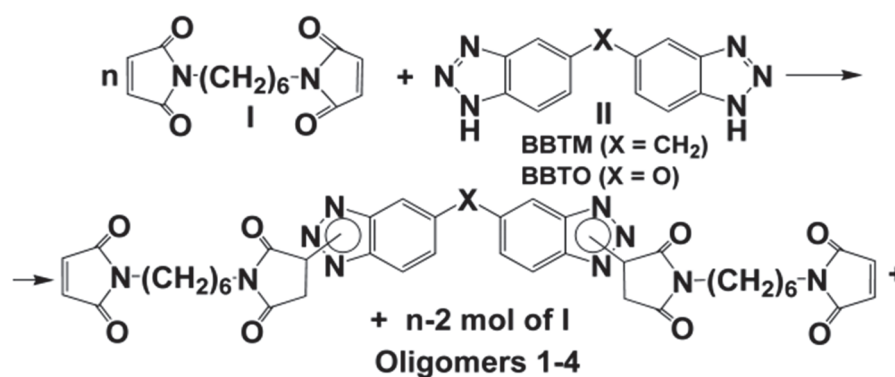


Figure 1. Scheme of oligomers synthesis.

According to the  $^1\text{H}$  NMR spectrum, oligomer-1 is blend of 2 mol of GMBMI and the product of addition of 2 mol of GMBMI to 1 mol of BBTM. Such a conclusion was proved by a ratio of the integral intensities of the peaks of the maleimide (6.99 ppm, s, 22H) and  $\alpha$ -protons (3.40 ppm, t, 32H) of the hexamethylene residue, which is 0.70; the theoretical ratio of quantities of these protons is 0.75. In addition, the spectrum contains the following peaks (ppm): 1.44 (d, 35H) and 1.20 (s, 34H) for the  $\beta$ - and  $\gamma$ -protons of the hexamethylene residue, 7.10–8.30 (m, 12H) for the aromatic protons.  $^1\text{H}$  NMR spectra of oligomers 2-4 possess a similar pattern. That is, the addition of 2 mol of GMBMI to 1 mol of bisbenzotriazole occurred in the all of the cases.

The  $^{13}\text{C}$  spectrum of oligomer-1 has the intensive resonance peaks of the  $\alpha$ -,  $\beta$ - and  $\gamma$ -carbons of the hexamethylene residue at  $\delta$  36.81, 27.60 and 25.43 ppm, respectively. The aliphatic carbons of the succinimide cycle give the low-intensity signals at  $\delta$  34.95 ( $\underline{\text{C6}}$ ),  $\sim 56$  и  $\sim 64$  ( $\underline{\text{C7}}$ ) ppm, and the maleimide olefinic carbons,  $\underline{\text{C2}}$  and  $\underline{\text{C3}}$ , resonate at  $\delta$  134.23 ppm. Owing to the low content, the aromatic and succinimide carbons result in the very low-intensity signals. The signal at  $\delta$  170.84 ppm is due to the  $\underline{\text{C1}}$  and  $\underline{\text{C4}}$  maleimide carbonyl carbons; while the low-intensity signals at  $\delta$  172.56 and 173.69 ppm are due to the  $\underline{\text{C8}}$  and  $\underline{\text{C5}}$  non-equivalent carbonyl carbons of the benzotriazoly succinimide residue.  $^{13}\text{C}$  NMR spectra of oligomers 2-4 possess a similar pattern. The assignment of peaks in the  $^1\text{H}$  and  $^{13}\text{C}$  spectra of all of oligomers was done according to the data from the spectroscopic investigations of model benzotriazoly succinimide compounds [11].

Thereby, one can conclude about the exhaustive interaction of BBTM and BBTO with a molar excess of GMBMI across the nucleophilic addition of the nitrogen atoms benzotriazoly residues to the  $\pi$ -electron deficient double bonds of maleimide cycles with the formation of succinimides. That is, it has been evidenced that benzotriazoly fragments include in the structure of oligomers.

#### 3.2. Thermal properties of oligomers

According to TG (air, 5 grad/min) (Figure 2) the initial weight loss observes in the temperature interval of 150–250  $^{\circ}\text{C}$  at both all oligomers and GMBMI and is 4.8–10.3%; this phenomenon connects with the GMBMI sublimation after melting. After cross-linking, the GMBMI sublimation ends in all of cases. The intensive thermooxidative destruction in air (Figure 2) at all of oligomers begins with at about 400–420  $^{\circ}\text{C}$  and ends completely at about 620–630  $^{\circ}\text{C}$ .

According to DSC (air, 5 grad/min) (Figure 3) the maximums of the melting endotherms of oligomers are in the interval of 129.6–135.6 °C. The melting endotherms of oligomers 1 and 2 are split onto two peaks; this may be due to the presence of two kinds of compounds in their composition (see Figure 1). In the case of oligomers with the lower content of GMBMI, the peak at the more high temperature either is absent (oligomer-3) or reveals as the low-intensity one (oligomer-4). The exotherms appropriating the homopolymerization (curing) across the double bonds of oligomers, unlike the appropriate exotherm of GMBMI with the maximum at 188.4°C, are very wide and reveal at above 180 °C.

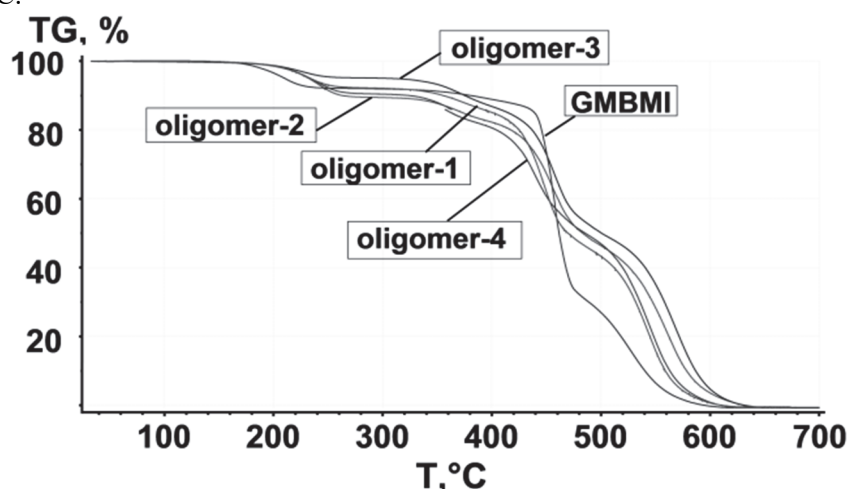


Figure 2. TG curves of oligomers and GMBMI.

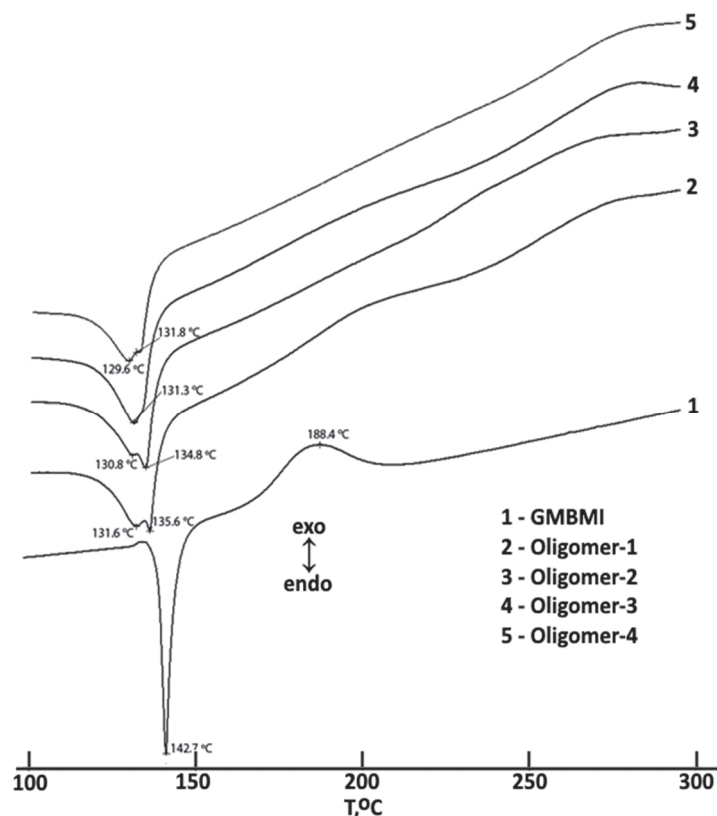


Figure 3. DSC of GMBMI and oligomers.

This phenomenon of the exotherms widening at oligomers may be explained by their lower rate of the homopolymerization across the double bonds due to the possible inhibitory influence of isophthalic acid and the structure of oligomers themselves. The analogous effect of the exotherms widening and, as sequence, the deceleration of the rate of the thermal polymerization (curing) due to the change of a bismaleimide structure were pointed out in the work [12]. In view of technology of making composite materials, such a phenomenon is favorable because a time of molten state of oligomers (melt viability) increases. The lower rate of homopolymerization (curing) is proposed to promote that the heat generated in this process has a time to dissipate without causing local overheating of the material and the resulting mechanical stresses. All of this has to improve the physic-mechanical properties composites based on such oligomers.

### 3.3. Study of glue joints

The glue joints of the samples were studied for the shear stress ( $\sigma$ ) according to ISO 13445:2003, where metallic plates were overlapped with each other in an appropriate area, and the shear load was parallel to a glue joint. Data are summarized in Table 1.

**Table 1.** Properties of glue joints based on oligomers and GMBMI.

Glue binder	Plate material <sup>b</sup>	Time of curing, $\tau_{\text{cur}}$ , h <sup>c</sup>	$\sigma$ , MPa
Oligomer-1	Steel-3	12.0	14.6
(one-layered prepreg <sup>a</sup> )	Copper	12.0	0.9
GMBMI	Steel-3	12.0	6.7
(one-layered prepreg <sup>a</sup> )	Copper	12.0	1.0
	Brass	12.0	0.4
Oligomer-1	Steel-3	6.0	14.2
Oligomer-2	Steel-3	6.0	23.7

<sup>a</sup> Glass fiber cloth impregnated with binder agent was sandwiched between plates;

<sup>b</sup> Surface was processed with  $\text{H}_3\text{PO}_4$ ;

<sup>c</sup> At 210–220°C.

As seen from Table 1, the strength of the joint from glue binder based on oligomer-1 is equivalent approximately for all of the plates made of steel-3 both in case of using the glass fiber cloth prepreg ( $\tau_{\text{cur}}$  12 h,  $\sigma$  14.6 MPa) and without the prepreg at the lesser curing time ( $\tau_{\text{cur}}$  6.0 h,  $\sigma$  14.2 MPa). If the one-layered prepreg impregnated with GMBMI was sandwiched between the steel-3 plates, then  $\sigma$  was approximately two times less, that is, 6.7 MPa. An attempt to make glue points based on GMBMI without a prepreg was unsuccessful; this can be explained by a brittleness of cured GMBMI along with the lower adhesion of it to a metallic surface. The best result,  $\sigma$  23.7 MPa, was achieved with oligomer-2, when the steel-3 plates were glued without a prepreg at  $\tau_{\text{cur}}$  6.0 h.

## 4. Conclusion

When bisbenzotriazoles interact with a molar excess of GMBMI across the nucleophilic addition of the nitrogen atoms of the benzotriazolyl fragments to the  $\pi$ -electron deficient double bond of the maleimide cycles, the addition products of two mol of GMBMI to one mol of bisbenzotriazoles form. In this case, the bisbenzotriazolyl residues are included into the structure oligomers, which contain, besides such addition products, the excess of GMBMI that does not take part in the reaction.

Based on the comparative analyses of data from the thermal tests of the samples of GMBMI and oligomers, one can conclude that the presence of the benzotriazolyl fragments in the structure such

oligomers decreases slightly temperature of the onset of the thermal destruction in oxidative atmosphere (air), when compared with 'pure' GMBMI. This phenomenon is proposed to be due to the decrease of the polymer network density. In the same time, the rate of their thermal destruction is lesser, probably, due to the thermal destruction of the benzotriazolyl residues with evolving inert nitrogen. The presence of the products of the addition of two mol of GMBMI to one mol of bisbenzotriazols decreases, according to DSC, melting points due to the eutectic formation; the melting endotherms become bimodal, and the exotherms due to the thermal homopolymerization across the double bonds become very wide.

Based on the comparative analyses of data from the mechanical tests of the glue joints, one can conclude that the introduction of the bisbenzotriazolyl fragments into the structure of thermally polymerized oligomers containing the aliphatic hexamethylene residues improves noticeably the physic-mechanical properties of the glue joints between the metallic plates compared with 'pure' GMBMI.

### Acknowledgments

This work was carried out in Baikal Institute of Nature Management according to the government assignment framework.

### References

- [1] Mather B D, Viswanathan K, Miller K M and Long T E 2006 *Prog. Polym. Sci.* **31** 487–531
- [2] Belbekhouche S, Guerrouache M and Carbonnier B 2016 *Macromol. Chem. Phys.* **217** 997–1006
- [3] Kloxin C J, Scott F, Adzima B J and Bowman C N 2010 *Macromolecules* **43** 2643–53
- [4] Schatz J, Brendgen T and Schühle D 2008 *CHEC-III* **3** 931–74
- [5] Rivas K, Vargas F, Aguiar G, Torrealba A and Machado R 1997 *J. Photochem. Photobiol. A* **104** 53–8
- [6] Musa Y and Stevens M P 1972 *J. Polym. Sci. A-1* **10** 319–27
- [7] Cunningham I D, Brownhill A, Hamerton I and Howlin B J 1997 *Tetrahedron* **53** 13473–94
- [8] Chandran M S, Robert T M, Sunitha K, Mathew D and Nair C P R 2015 *Des. Monomers Polym.* **18** 210–21
- [9] Ouchi M, Terashima T and Sawamoto M 2009 *Chem. Rev.* **109** 4963–5050
- [10] Drobny J G 2013 *4 - Electron Beam Processes. Ionizing Radiation and Polymers Principles, Technology and Applications.* (Norwich: William Andrew Publishing. Elsevier) p 83–99
- [11] Farion I A, Mognonov D M, Il'ina O V and Bal'zhinov S A 2012 *J. Appl. Polym. Sci.* **126** 1797–1807
- [12] Ninan K N, Krishnan K and Mathew J 1986 *J. Appl. Polym. Sci.* **32** 6033–42