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HEAT- AND FIRE-RESISTANT COMPOSITION BASED ON N, N'-(4,4'- DIPHENYLMETHANE) BISIMIDOMALEIN-1,2,3,4-TETRACHLOROCYCLOHEXA-1,3-DIENE-5,6-DICARBOXYLIC ACID AND EPOXY RESIN ED-20

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A new adhesive composition based on epoxy resin ED-20 and N, N′-(4,4′-diphenylmethane) bismaleimide-1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid was obtained. Its properties have been studied and it has been found that it possesses high physical and mechanical characteristics. It operates effectively in a temperature range from -80 to +96°C without forming cracks, making it suitable as a heat-resistant adhesive for bonding photo-, optical, and semiconductor components in devices with photosensitive elements. Additionally, the obtained adhesive composition based on N, N′-(4,4′-diphenylmethane) bismaleimide-1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid and epoxy resin ED-20 is used for sealing and pouring in the manufacture of the above-mentioned devices and appliances.

1. Introduction

The need to create heat-resistant and non-combustible polymers is associated with the development of electronics, electrical engineering, aerospace and other industries [1]. The development of modern microelectronics would be unthinkable without the creation of special polymers that possess fire resistance, heat resistance, as well as high elasticity and solubility in organic solvents. However, at present, all commercial polyimides have significant drawbacks:

a) The traditional method of obtaining polyimides is primarily based on a two-stage process, with the second stage of this process typically implemented through thermal cyclization [2, 3];

b) insolubility of polyimides in traditional organic solvents, which complicates their processing into a product

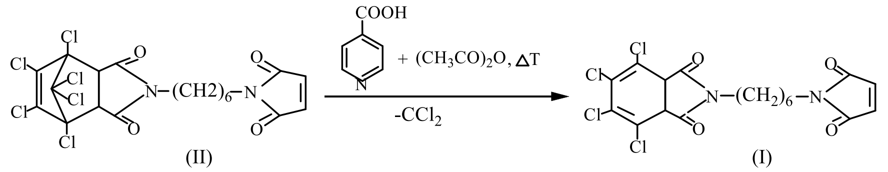
In order to eliminate such individual disadvantages of polyimide polymers, attempts have been made to modify their structures. Special attention was paid to the development of halogen-containing polyimides, whose composition and specific structure of the elementary units create the possibility of partially, and sometimes completely, eliminating the aforementioned drawbacks.

Few works are devoted to the synthesis and development of chlorinated polyimides. However, it is known [4–6] that halogen-containing polyimides with a specified spatial structure are perspective compounds for obtaining monomers containing imide rings, as well as various functional groups. Such monomers are capable of undergoing polycondensation reactions with other bifunctional monomers, leading to the formation of flame-resistant and heat-resistant polymeric materials that can withstand abrupt changes in temperature [7-9].

Based on the above, we have developed a method of obtaining chlorinated cyclic bisimidodienes suitable for their application as fire- and heat-resistant adhesives for bonding of separate elements of photographic, optical and semiconductor devices. The selection and application of such adhesives and sealants for cooled photovoltaic elements in photo materials is a rather complex task [10].

At present in photodetectors for bonding of optical elements silicon-organic polyurethane composites UK-1 and UK-2 are used. The operating temperature range for compound UK-2 is from +80 to -80°C, while for UK-1 it is from +80 to -60°C [11]. However, for bonding a germanium carrier substrate with an optical plate made of Cd×Hg Te (CMT), the adhesive, in addition to being effective at low temperatures, must have high adhesion strength and chemical resistance to a range of aggressive environments (acids, bases, various solvents), as well as mechanical strength against detachment.

The aim of the work was to obtain an adhesive composition that meets the properties mentioned above. The present article is devoted to the synthesis of N, N'-(4,4'-diphenylmethane) bismaleimide-1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid prepared according to the scheme:



This reaction was carried out by heating bisimide (II) in dimethylformamide (DMF) medium in the presence of the acceptor isonicotinic acid and acetic anhydride. The obtained imidodiene is used as a modifier of ED-20 epoxy resin to produce an adhesive composition.

2. Experimental part

N,N'-(4,4'-diphenylmethane) bisimidamalein-1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid (I) was synthesized as follows:

0.01 mol of N,N'-(4,4'-diphenylmethane) bisimidamalein-1,4,5,6,7,7,7-hexachlorobicyclo-[2.2.1.1]-hept-5-ene-2,3-dicarboxylic acid was dissolved in 50 ml of DMF. The mixture was stirred until a homogeneous mass was formed. Then,10 ml of acceptor (a mixture of isonicotinic acid and acetic anhydride - 1:1 molar ratio) was added to the mixture. The reaction proceeded exothermically with temperature increase up to 45-50°C. After the temperature decreased to 20°C, the mixture was heated for an additional 2 hours at 120°C. Then, the mixture was poured into ice-cold water while stirring. The resulting precipitate was filtered through a Schott filter, recrystallized from isopropyl alcohol, and dried at 60°C. The yield of the product was 75%. T_m 135°C, R_f 0.58. In the UV spectrum, a peak at 285 nm was observed, characteristic of a diene system. The obtained bisimide (I) is a white powdery product. M=548. Formula: $C_{25}H_{14}Cl_4N_2O_4$. Calculated %: C 54.74, H 2.55, Cl 25.91, N 5.10. Found %: C 54.17, H 2.41, Cl 25.01, N 4.98.

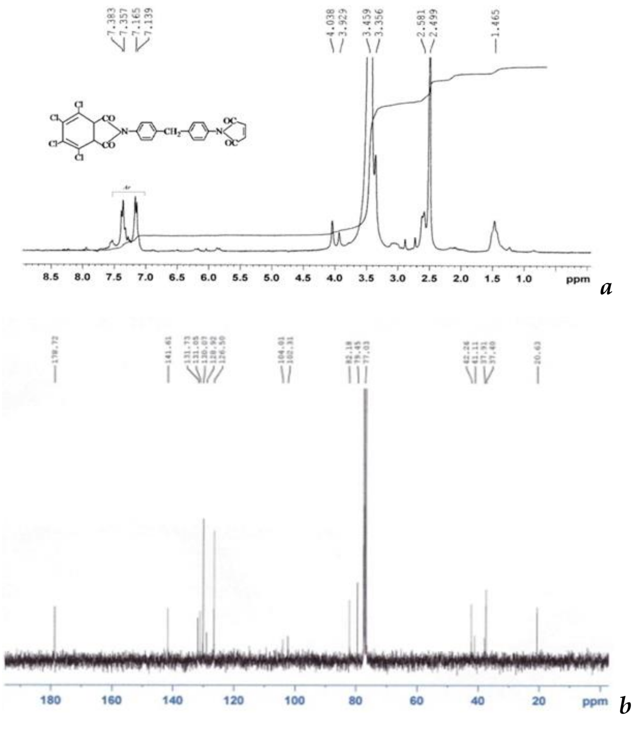


Figure 1. NMR ^{1}H *(a)* and ^{13}C *(b)* spectra of N,N'-(4,4'-diphenylmethane) bismaleimide-1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid

The structure of N,N'-(4,4'-diphenylmethane) bisimide of 1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid (1) has been confirmed by ^{1}H and ^{13}C NMR and IR spectra [12, 13]. The signals of the protons were identified as follows from the 1H NMR (BRUKER-Fourier 300.18 MHz, acetone-d6, δ): 1.46 (triplet, CH), 2.58, 2.49 (CH_2), 3.45, 3.56 (singlet, 4H, CH), 3.92 (singlet, CH_2), 3.92 (singlet, 6H), 4.03 (singlet, 2H, CH_2), 7.38, 7.35, 7.16-7.13 (6H, CH, Ar). The 13C NMR signals are: 20.63 (CH), 37.40 (CH_2), 79.45 (Cl-C-C), 104.01 (Cl-C-Cl), 126.50, 128.92, 131.05, 131.73, 141.61 (C, Ar), 130.07 (C-Cl), 178.72 (C=O).

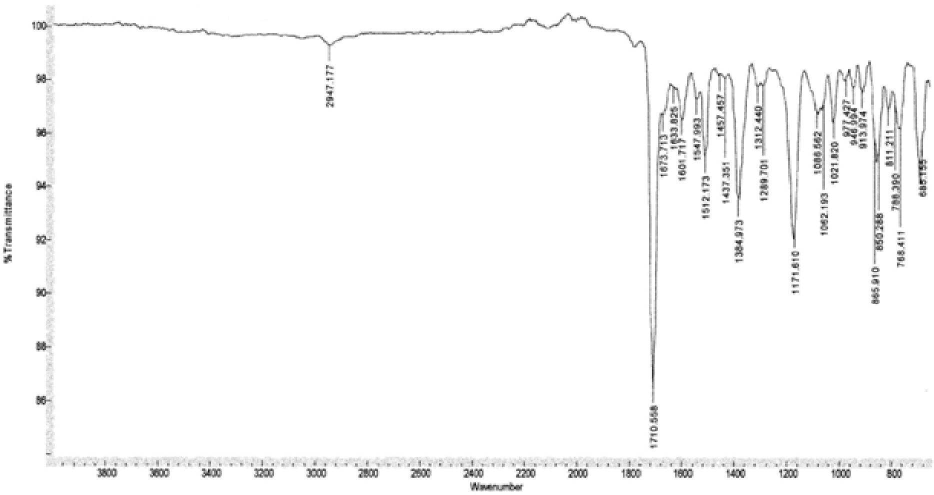


Figure 2. IQ spectrum of N, N'-(4,4'-diphenylmethane) bismaleimide-1,2,3,4-tetrachlorocyclohexa-1,3-diene-5,6-dicarboxylic acid

In the IR spectrum, characteristic absorption bands were observed for the C=C bond at 1601 cm^{-1}, for the imide rings at 1710 cm^{-1}, and for the C-Cl bond at 685 cm^{-1}.

The adhesive epoxy composition was prepared at the following ratios of components; (mass fraction): ED-20-(80 and 90); modifier (I) - (10 and 20) hardener PEPA -8.

For the preparation of the composition, industrial resin ED-20 (GOST 10587-63) was used, which contains 18% epoxy groups.

Modification of ED-20 was carried out as follows: to 80 or 90 mass fraction of ED-20 was added 20-10 mass fraction of modifier (I) and stirred for 30-35 minutes at 90-95° C to obtain a homogeneous mass, then the mixture was cooled to 20° C and 8 mass fraction of polyethylene polyamine hardener (PEPA) was added as a hardener under stirring. The mixture was then vacuumed to remove air bubbles and applied to the photosensitive elements and the CMT (CdxHg Te) substrate or poured into a mold for curing and bonding for 48 hours at room temperature To determine the physical and mechanical parameters, the samples were made in the form of spatulas with the size of 80×7×5 mm and thickness of 2 mm. The performance of the samples was evaluated based on the results of at least three parallel determinations.

3. Results and discussion

The obtained adhesive composition was tested for bonding optical plates of CMT with a germanium carrier substrate.

The composition of the adhesive composition and test results are given in the table 1.

Table 1. Composition and parameters of the adhesive composition

Component names and parameters	**ED-20 without modifier**	**Composites**	
		I	**Known**
Amount of ED-20, parts	100	90	90
Amount of modifier (I), parts	–	10	10
Amount of curing agent PEPA, parts	8	8	8
Vicat softening point, °C	138	195	180
Brinell hardness, MPa	5.48	13.7	14
Resistance to uniform direct pull, MPa			
at 20°C	–	1120	–
at 50°C	–		
Impact strength, MPa	–	24.5	–
Adhesive strength, MPa	82	200	210
Water absorption, (48 h.) %	0.69	Absent	absent
Crack formation after 72 temperature gradient cycles from -80 to +96°C	cracks	Does not form cracks	can't withstand subzero
Degree of curing, %	96	98	temperatures
Curing time, h.	24	24	98
Chemical resistance in 50% H_2SO_4 solution at 20-60°C (after 24 h. exposure)	–	13.5	24 –
Chemical resistance in 50% NaOH solution at 20-60°C (after 24 h. exposure)	–	13.2	–

The study of resistance to temperature change of the adhesive composition showed that the adhesive compound is workable at the temperature of liquid nitrogen and at repeated temperature changes from minus 80 to plus 120 °C during repeated thermocycling.

From the results of the study, it can be seen that the obtained adhesive composition has high tensile strength (9.02-9.72 MPa) and adhesion strength (1.47-1.86 MPa), at temperatures ranging from -80 to +96 °C. The quality of adhesion after 72 hours of thermocycling does not change. High frost resistance of the adhesive composition is due to the presence of double bonds in the polymer chain.

In addition, it is shown that bonded samples of CMT optical plates with germanium substrate are resistant to aggressive environments and moisture for 48 hours.

Thus it has been established that the obtained adhesive composition based on ED-20 and compound (I) is workable in the temperature range from minus 80 to plus 96 °C and can be used for gluing optical parts to photosensitive elements, as well as for sealing and casting semiconductor devices.

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