Study on the synthesis of tetraglycidyl 4,4’-diamino-3,3’-chlorodiaminodiphenyl methane and application as an adhesive for flame-retardant cover and solid propellant rod

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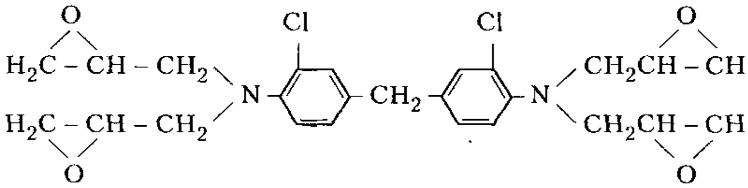
ABSTRACT

Tetraglicidyl 4,4'- diamino 3,3'- chlorodiaminodiphenyl methane was synthesized by a two-stage process. The first stage involved the addition polymerization reaction and the second stage involved the hydrochloride group reduction reaction. The synthesized product was measured, analyzed for technical parameters and compared with foreign samples using IR, ^1H NMR and ^{13}C NMR spectra. The results showed that the physicochemical characteristics and spectral structure of the studied product were equivalent to foreign samples of the same type. The applicability was evaluated by manufacturing OKZMS adhesive used as an adhesive for the flame-retardant cover and solid propellant rod for good adhesion quality, meeting the requirements.

Keywords: EXD; Solid propellant rod; Flame-retardant cover; Diameter X; Epichlorohydrin; Adhesive.

1. INTRODUCTION

Tetraglycidyl 4,4'-diamino-3,3'-chlorodiaminodiphenyl methane (commonly referred to as EXD resin) has the molecular formula:



EXD is a chlorine-containing epoxy resin classified as a specialized epoxy resin due to its unique properties. Its molecular structure contains four glycidyl functional groups, which, upon reaction with curing agents (typically multifunctional amines), form a robust cross-linked network. Consequently, after curing, the adhesive exhibits excellent thermo-mechanical strength, high moisture resistance, and strong resistance to oxidative agents, along with low flammability. Owing to these superior characteristics, EXD resin is widely applied in the production of high-performance structural adhesives requiring exceptional mechanical and thermal stability, as well as in moisture and oxidation-resistant coatings. In the field of weapon systems manufacturing, EXD serves as a key component of OKZMS adhesive, acting as a bonding agent between the flame-retardant cover and composite solid propellant rod [1].

Currently, imported EXD adhesive is still required for bonding the solid propellant rod to the flame-retardant cover. In fact, the amount of this adhesive used is not much, while if it is imported, it must be purchased in large quantities, which will cause waste and be unnecessary. Therefore, researching and manufacturing the EXD adhesive with the aim of proactively supplying when needed is a necessary task with high applicability.

Information on EXD adhesive synthesis methods remains limited. However, in principle, three approaches can be considered [2-7]: first, the epoxidation of unsaturated compounds to prepare epoxy derivatives of cyclic hydrocarbons and epoxy rubbers; second, the polymerization or copolymerization of unsaturated monomers containing epoxy groups to produce high-molecular-weight epoxy resins; and third, the synthesis of epoxy resins based on the reaction between proton-donating compounds (bearing active hydrogen atoms), such as multifunctional phenols, alcohols, or amines, with epichlorohydrin, followed by dehydrochlorination to generate epoxy groups. For EXD, which requires a liquid epoxy resin with relatively low molecular weight, only the third method meets the desired specifications. Consequently, this study presents findings on the synthesis of EXD adhesive via the reaction between [4,4'-methylene-bis-(ortho-chloroaniline)] (commonly referred to as diamet X) and epichlorohydrin. The resulting EXD adhesive was subsequently evaluated for its applicability as an adhesive for bonding flame-retardant cover to a composite solid propellant rod.

2. EXPERIMENT

2.1. Chemicals

- Diamet X type P of China;
- Epyclohydrin, type Sigma of USA;
- NaOH, type AR of China;
- Acetone, a type of AR of China;
- Acetic acid, type AR of China;
- Double-distilled water;
- Sodium hydroxide, type AR of China;
- Phenolphthalein indicator, 25 g bottle, PA;
- Standard tube of HCl 0.1N;
- $AgNO_3$, type PA;
- Standard tube of $AgNO_3$ 0.1N;
- Potassium chromate indicator.

2.2. Experimental methods

2.2.1. Synthesis of the EXD adhesive

The EXD was synthesized in a 2000 mL three-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. A reaction mixture consisting of 555 g of epichlorohydrin (6 mol) and 267 g of diamet X (1 mol) was introduced. Initially, diamet X was dissolved in epichlorohydrin. When the reaction mixture was heated to 80 °C with stirring, a polyaddition reaction between diamet X and epichlorohydrin occurred. After 12 hours of stirring at 80 °C, the reaction mixture was transferred to a 3000 mL beaker placed in a water bath at 80 °C. Then, 2000 mL of water at 80 °C was added, stirred for 30 minutes, allowed to settle, and the water layer was decanted. A second wash was performed with 2000 mL of hot water at 80 °C for 15 minutes. After the washing step, the beaker was left to settle, and the water was decanted again. The remaining reaction mixture was transferred back into a 2000 mL three-necked round-bottom flask, followed by the dropwise addition of 1000 mL of 20% alkaline solution. The mixture was stirred for 30 minutes at 60 °C to dehydrochlorinate. After the complete addition of the alkaline solution, the reaction mixture was further stirred for another 30 minutes at 60 °C. Upon completion, the entire solution was transferred to a 3000 mL beaker, allowed to settle, and the alkaline waste layer was decanted. The crude product was then washed twice with 2000 mL of hot water at 60 °C for 15 minutes each time. After hot-water washing, the mixture was neutralized with 10% acetic acid solution while maintaining the temperature at 60 °C, followed by two additional washes with hot water at 60 °C and a final wash with water at room temperature. The semi-finished product was then dissolved in toluene and washed twice with water. The organic phase (toluene layer) containing the desired product was separated and subjected to vacuum distillation at a pressure of 10 - 20 kPa and a temperature of 120 °C for 6 hours, yielding approximately 300 g of product (the corresponding product efficiency reaches approximately 71%).

The reaction mechanism is presented as a diagram in figure 1.

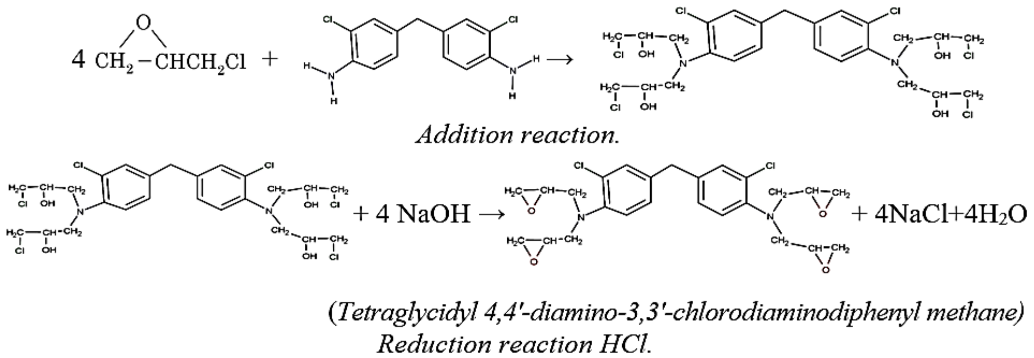


Figure 1. *General diagram of the reaction mechanism to form epoxy product EXD.*

2.2.2. Methods for evaluating product quality

a) Analysis of the technical specifications of EXD adhesive

The external appearance and kinematic viscosity were examined according to GOST 10587-84; the epoxy group content was tested according to GOST 12497-78; the volatile content was analyzed according to GOST 22456-77; and the chloride ion content and saponifiable chloride ion content were determined according to GOST 22457-90 [8].

b) Infrared spectroscopy analysis

Infrared (IR) spectra were recorded at room temperature over the range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}.

c) ^{1}H NMR and ^{13}C NMR spectroscopy analysis

The research samples were analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy in acetone solvent using tetramethylsilane (TMS) as the internal standard. The ^{1}H NMR signals indicate the number and position of hydrogen atoms in the main chain, while the ^{13}C NMR signals reflect the number and types of carbon atoms in the molecule.

2.2.3. Methods for evaluating the application of EXD adhesive

The application potential of EXD adhesive as a bonding agent for flame-retardant cover to composite solid propellant rod was evaluated by preparing OKZMS adhesive (formulation provided in the transferred technical documentation). The viscosity of the OKZMS adhesive was tested by the VZ-2,4,6 viscometer, serial number 170309 of Russia. The OKZMS adhesive was used to bond the flame-retardant cover to the composite solid propellant rod. Proceed to make the sample and then test the adhesion strength through the tensile testing device as described in reference [11]. A tensile strength result that causes adhesive separation but is not less than 8 kG/cm^2 is considered acceptable.

3. RESULTS AND DISCUSSION

3.1. Results of the analysis of the technical specifications of EXD adhesive

An analysis of several technical specifications of EXD synthesized by the research team (EXD-VN) was conducted and compared with the Russian sample. The results are presented in table 1.

Table 1. *Results of the analysis of technical specifications of EXD-VN and the Russian sample.*

No.	Technical specifications	EXD (VN)	ЭХД (Nga)	Requirements (TY 2225-607-1131395-2003)
1	Appearance	A viscous liquid with a lemon-yellow color	A viscous liquid with a lemon-yellow color	A viscous liquid with a lemon-yellow color
2	Epoxide group content, %	27.9	26.11	26.2 - 30.0
3	Volatile content, %, not more than	0.72	0.90	1.0
4	Chloride ion content, %, not more than	0.012	0.031	0.035
5	Saponifiable chloride ion content, %, not more than	0.47	0.58	1.4
6	Kinematic viscosity at 50 °C, Pa.s, not more than	6.46	32.3	7.0

Table 1 shows that the technical specifications of the EXD adhesive synthesized by the research team all meet the requirements of standard TY 2225-607-1131395-2003 [9] and are comparable to the Russian sample. For the Russian sample, the viscosity parameter is higher than the required specification. This can be explained by the fact that the Russian sample has been stored for a long time, affected by the storage environment causes the adhesive to thicken, which leads to an increase in its viscosity.

3.2. Results of infrared spectrum analysis

To evaluate the quality of the product after synthesis, the infrared (IR) spectroscopy of the sample EXD, which was synthesized by the research group, was analyzed and compared with the sample ЭХД of the Russians. The results are shown in figure 2 and figure 3, respectively.

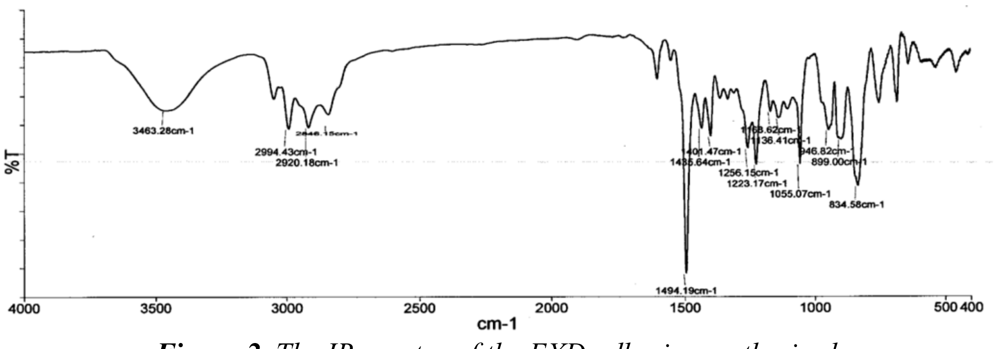


Figure 2. *The IR spectra of the EXD adhesive synthesized.*

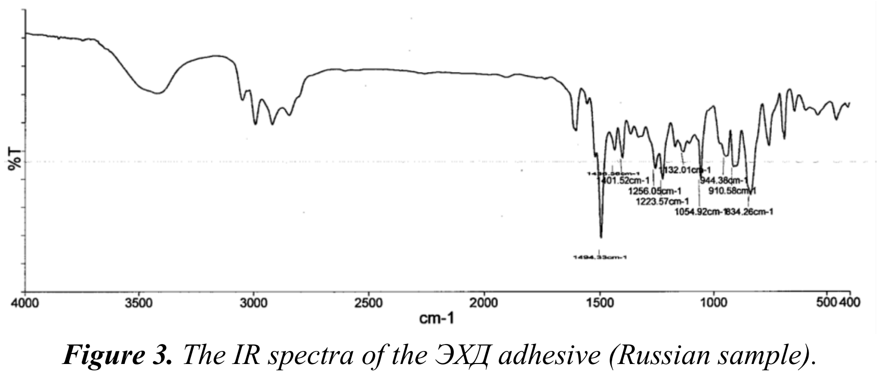


Figure 3. *The IR spectra of the ЭХД adhesive (Russian sample).*

Figure 2 and figure 3 show that at the absorption peak position of 3500 cm^{-1}, a broad band characteristic of the stretching vibration of the OH bond appears; at 3050 and 2994 cm^{-1}, peaks characteristic of the stretching vibration of aromatic hydrocarbon C–H bonds are present; at 2820 cm^{-1}, a peak characteristic of the stretching vibration of CH_2 groups in epoxy units is observed; at 1600, 1494, and 1435 cm^{-1}, peaks characteristic of the stretching vibration of the –C=C–C–C– bonds of the aromatic ring are present; at 1401 cm^{-1}, a peak characteristic of CH_2 groups adjacent to the epoxy group is detected; at 1255, 1225, 1168, 1135, and 1055 cm^{-1}, peaks characteristic of the symmetric stretching vibrations of C–O–C bonds in epoxy groups and C–N bonds are observed; at 944 and 910 cm^{-1}, peaks corresponding to the asymmetric stretching vibrations of C–O–C bonds within epoxy groups appear, indicating the presence of epoxy groups in the molecular structure; at 834 cm^{-1}, a peak characteristic of the symmetric stretching vibration of C–O–C and C–Cl bonds is present; at 750 cm^{-1}, peaks characteristic of straight-chain CH_2 groups and C–Cl bonds are found; and at 685 cm^{-1}, peaks characteristic of cyclic CH groups (broad and weak) are observed. The vibration region between 850-750 cm^{-1} corresponds to C–Cl bonds and overlapping absorption bands. The obtained data confirm that the epoxy groups are located in the range of 1260-830 cm^{-1}, with the 834 cm^{-1} peak being influenced by C–Cl bonds.

A comparison of the IR spectra of the Russian ЭХД adhesive and the EXD adhesive synthesized by the research group shows a high degree of similarity.

3.3. Results of nuclear magnetic resonance (NMR) spectroscopy analysis

The nuclear magnetic resonance spectrum of the sample EXD, which was synthesized by the research group, was analyzed and compared with the sample ЭХД of the Russians. The results are shown in figure 4 and figure 5, respectively.

^{1}H NMR spectrum:

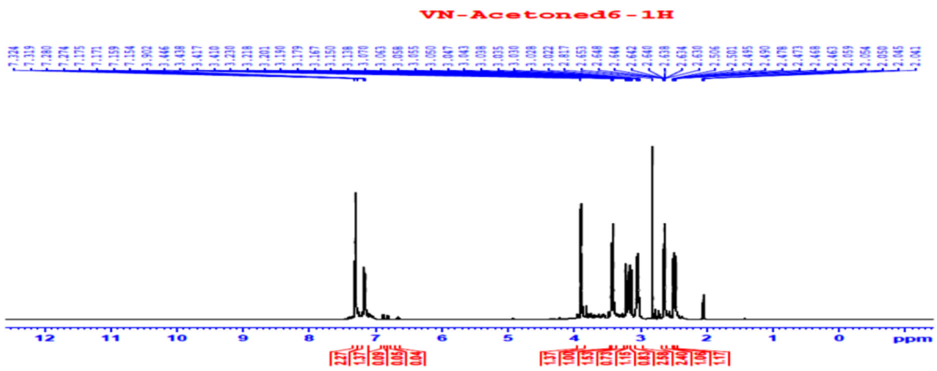


Figure 4. *The ^{1}H NMR spectra of the EXD adhesive synthesized.*

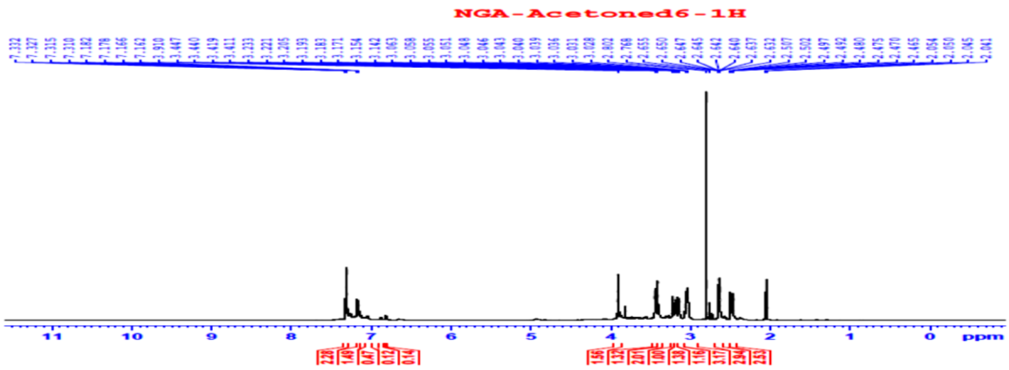


Figure 5. *The ^{1}H NMR spectra of the ЭХД adhesive (Russian sample).*

Figure 4 and figure 5 show that spectral signals related to protons in aromatic rings (marked in the spectrum at approximately δ = 7.32 ppm, 7.27 ppm, and 7.19 ppm) are observed. The peak at δ = 3.9 ppm corresponds to the CH_2 protons attached to the carbon atom linking two aromatic rings. Three peaks at δ = 3.42 ppm, δ = 3.19 ppm, and δ = 3.32 ppm correspond to CH_2 and CH protons adjacent to epoxy groups. Six irregular peaks at δ = 3.05 ppm and δ = 2.64 ppm correspond to CH_2 groups in epoxy units. The absorption peak at approximately δ = 2.5 ppm is characteristic of protons in –OH groups. The prominent peak at δ = 2.8 ppm is attributed to the solvent (acetone) used to dissolve the adhesive during sample preparation.

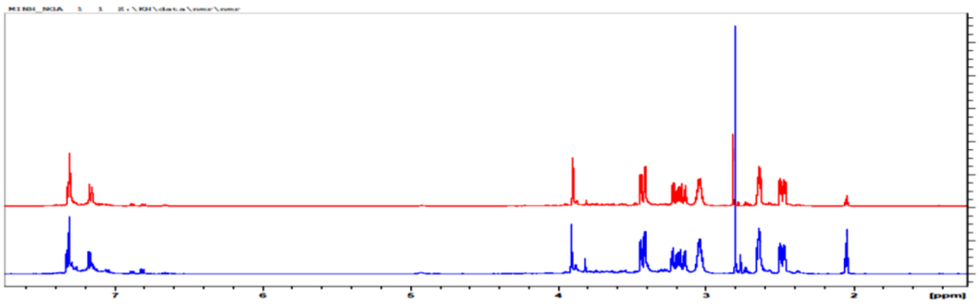


Figure 6. *Comparison of the ^{1}H NMR spectra of the EXD/ЭХД (our research) and the Russian sample.*

Figure 6 shows that the ^{1}H NMR spectra of the Russian ЭХД adhesive and the EXD adhesive synthesized by the research group exhibit a high level of similarity.

^{13}C NMR spectrum:

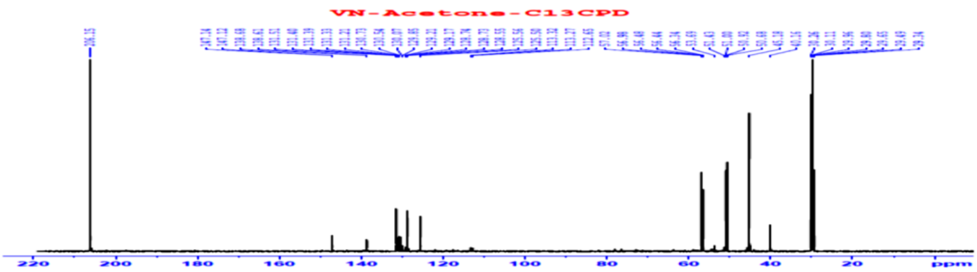


Figure 7. *The ^{13}C NMR spectra of the EXD adhesive synthesized by the authors.*

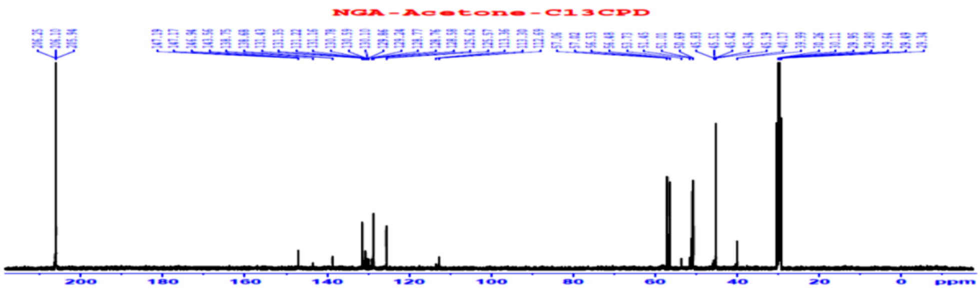


Figure 8. *The ^{13}C NMR spectra of the ЭХД adhesive (Russian sample).*

In the ^{13}C NMR spectrum, resonance signals of carbon atoms in the molecule are present. Aromatic carbon atoms appear in the range of δ = 147.1-125.5 ppm. Carbon atoms in CH and CH_2 groups are found in the δ = 57-40 ppm range. Specifically, the region δ = 56.5-57 ppm corresponds to CH carbons in epoxy groups, while δ = 50.7-51 ppm corresponds to CH_2 carbons in epoxy groups. The signal at δ = 45.2 ppm is associated with CH_2 carbons adjacent to epoxy groups, and the signal at δ = 40 ppm corresponds to CH_2 carbons connecting two aromatic rings.

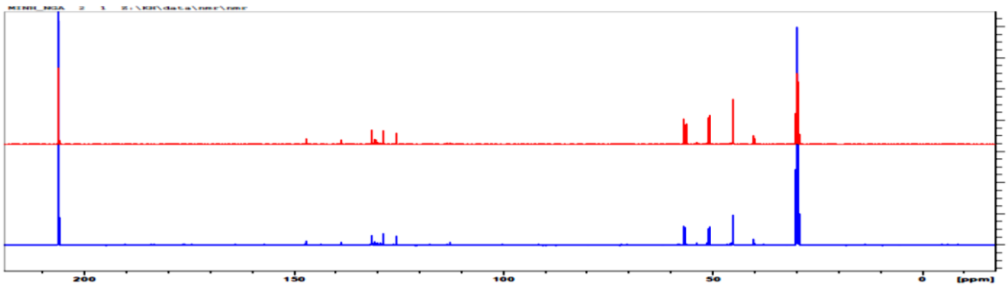


Figure 9. *Comparison of the* ^{13}C *NMR spectra of the EXD/ЭХД (our research) and the Russian sample.*

Figure 9 shows that the ^{13}C NMR spectra of the Russian ЭХД adhesive and the EXD adhesive synthesized by the research team are highly similar.

3.4. Application of EXD adhesive as a binder for fireproof cover and solid propellant rod

3.4.1. The manufacturing of OKZMS adhesive and viscosity analysis

Due to the operational requirements of the cruise missile engine, the composite solid propellant rod must burn in a controlled geometric pattern, initiating ignition from the front face while preventing combustion along the lateral surface. To meet this requirement, the rod is encapsulated by a flame-resistant cover applied to its outer surface. The adhesion between this cover and the solid propellant rod is achieved using a specialized adhesive. This adhesive must exhibit high bonding strength, chemical compatibility with the propellant components (avoiding structural degradation, decomposition, or undesirable by-product formation), resistance to aging during storage and usage, and simplicity in the coating process. Among various candidates, the EXD adhesive is one of the adhesives that meet the stated requirements.

Based on the original formulation of the OKZMS adhesive, the authors manufactured the adhesive according to the material components given in table 2.

Table 2. *Components of OKZMS adhesive and viscosity specifications of adhesive material.*

No.	Technical specifications	Standard [10]	Content, (%)
1	CKH-10KTP-liquid rubber	STP 07521506-130E-2002	33.59
2	EXD (VN) epoxy adhesive	TY 2225-512-00203521-94 (TY 2225-607-11131395-2003)	9.24
3	M-phenylene diamine	GOST 5826-78	0.06
4	P-803 technical carbon	GOST 7885-86	6.72
5	Ethyl cellosolve	GOST 8313-88	50.39
6	The viscosity according to VZ-246, 4 mm at 20 ± 0,5 °C, s, not more than	170	

The manufacturing of OKZMS adhesive was conducted by the research team with a list of laboratory equipment available.

After preparation, the OKZMS adhesive was stabilized in a thermostatic chamber at 20 °C for 12 hours, then its viscosity was tested by the VZ-2,4,6 viscometer, serial number 170309 of Russia. The results are shown in table 3.

Table 3. *Viscosity test results of OKZMS adhesive prepared with EXD adhesive.*

No.	Parameters	Viscosity test results		
		Time 1	Time 2	Time 3
1	Test of temperature, °C	20.1	19.9	20.2
2	Viscosity, s	110	113	100

Table 3 shows that the viscosity of the OKZMS adhesive used by the EXD adhesive, which was synthesized by the research team, meets requirements, not more than 170 seconds.

3.4.2. Preparation of solid propellant samples and adhesion testing

Proceed to spray adhesive onto the inner surface of the flame-resistant covers using the adhesive spray equipment. The flame-resistant covers were then dried in an air environment for 48 hours.

Solid propellant paste was prepared following the formulation provided in table 4.

Table 4. *Components of solid propellant for adhesion strength evaluation.*

No.	Components	Content,%
1	Ammonium perchlorate	71.5
2	Aluminum powder	13.0
3	CKH-10-KTP rubber	9.85
4	ED-20 Epoxy	2.0
5	Dioctyl sebacate	1.9
6	Lead (II) oxide	0.25
7	1,1- Diethyl ferrocene	1.4
8	Lecithin	0.1

Solid propellant paste was then cast into a flame-resistant cover and dried under specified conditions. The solid propellant rods and flame-resistant covers were bonded with an OKZMS adhesive layer. The products were divided into aged and non-aged conditions for comparison.

The procedure for aging the samples was conducted as follows: firstly, the solid propellant rods were dried at a temperature of + 60 °C for 79 days. Secondly, the aging samples were continuous run for four cycles at 20 °C → 50 °C → 20 °C → 0 °C. At each temperature was maintained for 24 hours. Finally, the aging samples were run one cycle at - 20 °C → 0 °C → - 20 °C → - 50 °C. At each temperature was maintained for 24 hours.

After aging/non-aging, the samples were cut into sections and machined into specific shapes and dimensions as described in reference [11]. Adhesion strength was measured by a tensile testing device at a pulling speed of 3.0 ± 0.5 mm/min with a minimum load of 250 N and a measurement error not exceeding 3%. Test results showed that the adhesion strength for aged and non-aged samples was approximately 8.5 ± 0.5 kG/cm² and 9.5 ± 0.5 kG/cm², respectively. Both values met the requirement, not less than 8 kG/cm².

It can be seen that the adhesive strength of the aged samples is reduced compared to the non-aged samples, but it still meets requirements. This shows that even under harsh conditions, the OKZMS adhesive in general and the EXD adhesive in particular are still effectively preventing diffusion of components in the solid propellant, such as plasticizers and catalysts like 1,1-diethyl ferrocene, without swelling or significant loss of adhesion. Therefore, it can be concluded that the EXD adhesive synthesized by the research team fully meets the required specifications.

4. CONCLUSIONS

Tetraglycidyl 4,4'-diamino 3,3'-chlorodiaminodiphenyl methane (EXD) was successfully synthesized via the reaction between diamet X and epichlorohydrin in the presence of an alkaline agent, following a two-step process: a copolymerization reaction in the first step, followed by a dehydrochlorination in the second step. The intermediate product was then washed with water and neutralized with acetic acid. Distillation and extraction of the product into toluene solvent. The product was evaluated based on technical specifications and compared with the Russian reference product using spectroscopic methods, including IR, ^{1}H NMR and ^{13}C NMR. The results show that the physicochemical and spectral characteristics of the EXD adhesive, which was synthesized by the authors, were comparable to the Russian product. The product has been applied in manufacturing OKZMS adhesive, which is used as a bonding agent for the flame-retardant cover and solid propellant rod. The adhesion strength test shows that the quality of adhesive meets the requirements, including aged and non-aged samples.

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TÓM TẮT

Nghiên cứu tổng hợp tetraglixidin 4,4'-diamino-3,3'-clodiaminodiphenyl metan ứng dụng làm chất kết dính giữa vỏ chống cháy và thỏi nhiên liệu rắn hỗn hợp

Tetraglixidin 4,4'- diamino 3,3'- clodiaminodiphenyl metan đã được tổng hợp theo quá trình gồm hai giai đoạn. Giai đoạn thứ nhất, thực hiện phản ứng cộng trùng hợp và giai đoạn thứ hai, thực hiện phản ứng khử nhóm hydroclorua. Sản phẩm sau tổng hợp được tiến hành đo đạc, phân tích các chỉ tiêu kỹ thuật và khảo sát đối chứng với mẫu của nước ngoài bằng các loại phổ hồng ngoại IR, phổ cộng hưởng từ ^{1}H NMR và phổ ^{13}C NMR. Kết quả cho thấy, các đặc trưng hóa lý và cấu trúc phổ của sản phẩm nghiên cứu đều tương đương với mẫu cùng loại của nước ngoài. Đánh giá khả năng ứng dụng thông qua việc chế tạo keo OKZMS sử dụng làm chất kết dính cho lớp vỏ chống cháy và thỏi nhiên liệu rắn hỗn hợp cho chất lượng bám dính tốt, đạt yêu cầu đề ra.

Keywords: EXD; Thỏi thuốc phóng rắn; Vỏ chống cháy; Diamet X; Epiclohydrin; Chất kết dính.