New Materials, Compounds and Applications
Vol.7, No.1, 2023, pp.15-22

SYNTHESIS OF DIESTERS OF BIS-ADDUCTS OF ROSIN WITH ETHANEDITHIOL AND THEIR USE IN THE COMPOSITION OF POLYVINYL CHLORIDE AS A PLASTICIZER

Matanat S. Pirguliyeva*

Sumgait State University, Sumgait, Azerbaijan

Abstract. In the paper the corresponding diesters have been synthesized and characterized by the interaction of rosin and ethanedithiol adducts with aliphatic alcohols. Their compatibility is investigated with PVC by establishment of the critical dissolution temperature of PVC. The obtained diesters of bis-adducts of rosin and ethanedithiol (EDT) are tested as PVC plasticizers and some properties of compositions with their use are investigated. The thermal stability of the obtained diesters is studied by the method of thermogravimetric analysis. Some physical-mechanical properties of compositions are studied on the basis of PVC using the obtained dialkyl esters of rosin adducts with EDT. It is established that the obtained results have values close to the characteristics of compositions obtained by the standard plasticizer dioctyl phthalate (DOPh).

Keywords: *polyvinyl chloride, rosin, ethanedithiol, adduct, plasticizer, composition.*

Corresponding Author: *Matanat Pirguliyeva, Sumgait State University, Baku str.,1, AZ5008, Sumgait, Azerbaijan, e-mail: sdtk-1959@mail.ru*

Received: *18 November 2022;* ***Accepted:*** *2 February 2023;* ***Published:*** *17 April 2023.*

1. Introduction

One of the main methods of the polymer modification is the method of plasticization by introduction of various additives, so-called plasticizers, into the polymer composition. Such method of plasticization leads to an improvement of the elasticity and frost resistance of the material, decreases the viscosity of the system and thereby, improves the rheological properties of the compositions (Chu *et al.*, 2021; 2022).

The esters of organic (mainly, phthalic) and inorganic acids, oil-polymer resins, vegetable oils (linseed, cotton, castor, sunflower), oil-refining products, etc. have found the greatest use as plasticizers (Chu *et al.*, 2021; 2022; Ma *et al.*, 2021).

Among the products of vegetable origin, the rosin derivatives are of interest as plasticizers (Song *et al.*, 2020; Arrieta *et al.*, 2017; Jia *et al.*, 2019). The use of rosin as a plasticizer in its pure form is not of interest due to the availability of carboxyl groups in its molecule, which give it acidity. For reduction of the rosin acidity, it is esterified with monoatomic and polyatomic alcohols. The diacid esters obtained in this way are used as plasticizers.

The addition reaction of ethanedithiol to rosin carried out by us led to the preparation of the compound containing sulfur atoms as a sulfide bond (compound **1)** in

How to cite (APA):
Pirguliyeva, M.S. (2023). Synthesis of diesters of bis-adducts of rosin with ethanedithiol and their use in the composition of polyvinyl chloride as a plasticizer. *New Materials, Compounds and Applications, 7(*1), 15-22.

its molecules. This compound by interaction with aliphatic alcohols has been then converted into alkyl esters (compounds **2(a-d)**).

2. Experimental part

Synthesis of diesters of rosin bis-adduct with ethanedithiol

The synthesis of diesters has been carried out as follows: a solution containing 10 ml of the concentrated H_2SO_4 in 150 ml of the corresponding alcohol was placed in a three-necked flask equipped with a mechanical stirrer, a thermometer and a reflux condenser in an inert gas current. 0.025 mol of adduct **1** was added to the heated solution. The mixture was boiled until a homogeneous solution was obtained. The process was controlled on change of the acid number of the reaction mass. The total reaction time was 6-8 hours. The reaction mixture was poured into 500 ml of cold water; the forming product was separated and washed until a neutral medium was reached.

In this method, the corresponding diesters of diacids (compounds **2(a-d)**) have been obtained from aliphatic alcohols (C_2H_5OH; C_4H_9OH; $C_6H_{13}OH$; $C_8H_{17}OH$).

Making of compositions on the basis of PVC and diesters of bis-adducts of rosin

The compositions on the basis of PVC have been made according to the following formulation: PVC of mark C-7058-M – 100 mass p.; diesters of diacids (compounds **2 (a-d)**) as plasticizers – 40 mass p.; mixture of stabilizers – barium stearate (1.5 mass p.) and calcium stearate (1.5 mass p.); stearic acid (as a lubricant) – 0.25 mass p. Initially, the components of the composition were thoroughly mixed, then gelatinized, keeping the compositions in a drying box at 80°C for 20-40 min. The samples were subjected to rolling at 150°C for 15 min., and then pressed for 3 min. at 170-180°C and press pressure of 15.0 MPa. The obtained plates with a thickness of 1.0-1.75 mm were kept at room temperature for 48 hours. Also, for comparison of physical-mechanical parameters, the samples were made using a well-known plasticizer – dioctyl phthalate (DOPh) as a standard.

The critical dissolution temperature (CDT) was determined on the methodology described in work (Mazitova *et al.*, 2022).

The hydrolytic stability of the compounds **2(a-d)** was determined at 100°C for 24 h. The process was carried out in an ampoule, where an equal quantity (on 2.5 g) of ester (compounds **2(a-d)**) and water was placed. According to the found value of the hydrolysis rate constant, the hydrolytic stability of the compounds **2(a-d)** was determined.

The physical-chemical characteristics of diacid diesters were determined by finding the acid number and saponification number (GOST 8728-88. Plasticizers. Technical specifications).

Determination of the acid number. The content of carboxyl groups and acid number was determined on the methods described in the literature (Toroptseva *et al.*, 1972).

The acid number (AN) is characterized by the quantity of KOH (in mg) necessary for neutralization of the carboxyl groups contained in 1 g of the analyzed substance. AN was calculated according to the formula:

$$AN = \frac{(V_1 - V_2)F \cdot 0.00561 \cdot 1000}{g}$$

where 0.00561 – titer 0.1n. of KOH solution, g/ml;

V_1 – volume of 0.1 n. KOH solution consumed for titration of the working sample, ml;

V_2 – volume of 0.1 n. KOH solution consumed for titration of the control sample, ml;

g – sample weight, g.

The saponification number (SN) was determined by reverse titration of the excess of potassium hydroxide remaining after hydrolysis of the ester groups contained in the sample. The saponification number was calculated according to the formula:

$$SN = (V_{blank} - V_{titer}) \cdot 56.1 \cdot C_{HCl} \cdot m_{sample}$$

where V_{blank} – the volume of hydrochloric acid solution used for titration of the blank sample, ml;

V_{titer} – the volume of hydrochloric acid solution used for titration of the analyzed sample;

C_{HCl} – molar concentration of hydrochloric acid solution;

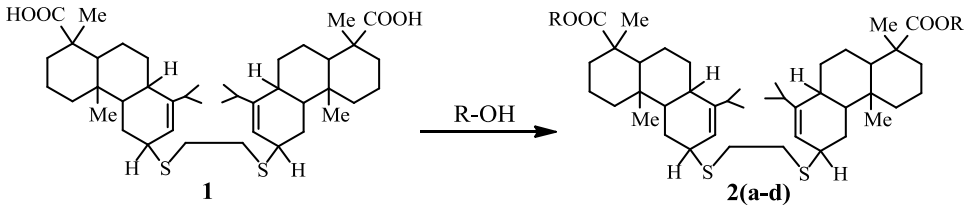
m_{sample} – sample weight, g.

3. Results and discussion

It was known that the esterification reaction is equilibrium. However, the use of a catalytic quantity of H_2SO_4 in this reaction and the removal of water from the reaction zone formed as a result of esterification makes this process non-equilibrium. In this case, the reaction proceeds under non-equilibrium conditions with the removal of water from the reaction zone.

The rosin adducts with ethanedithiol have been obtained by addition of ethanedithiol to rosin in the presence of the initiator azo-*bis*-isobutyronitrile at 343K with the ratio of rosin: ethanedithiol = 2:1, according to the methodology described in work (Pirguliyeva, 2015).

The interaction of rosin adduct and ethanedithiol with alcohols occurs according to the scheme shown below:



1 **2(a-d)**

R= C_2H_5 (a) ; C_4H_9 (b) ; C_6H_{13} (c) ; C_8H_{17} (d)

The composition and structure of the obtained adduct **1** have been established by data of IR spectroscopy and elemental analysis.

In the IR spectra of these compounds, the characteristic absorption bands in the field of 1700-1680 cm^{-1}, attributed to valence vibrations of the carbonyl group and the

absorption bands characteristic for the carboxyl group at 3300 cm^{-1} are observed. The appearance of the weak absorption band in the field of 2510-2600 cm^{-1} indicates the availability of $–CH_2–S–$ bond in the obtained adducts.

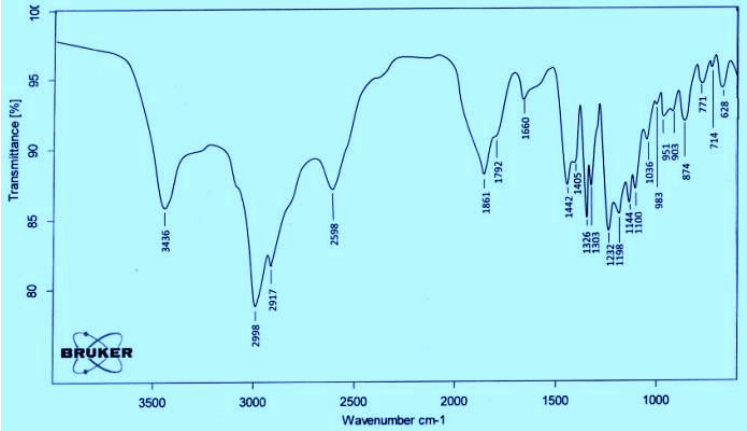


Fig. 1. IR spectrum of the esterification product of adduct **1** with butanol (compound **2b)**

In the IR spectra of esterification products, the disappearance of the absorption bands characteristic for –OH carboxyl group at 3300 cm^{-1}, and the appearance of the absorption bands of alkyl groups in the field of 2800-3100 cm^{-1} is observed. The absorption bands characteristic for the carbonyl group in the ester fragment undergo the displacement and are appeared at 1792-1861 cm^{-1}. The vibration of –C–O–C- group is appeared by a group of bands in the field from 1100 to 1232 cm^{-1}.

For estimation of the suitability of dialkyl esters of rosin adduct with EDT (compounds **2(a-d)**) as plasticizers, some of their properties have been investigated.

First of all, for synthesized esters **2(a-d)**, their compatibility with PVC has been determined using the capillary method. In this case, it was found that within 3 h the forming spot has a diameter of 12-13 mm, while during testing a standard plasticizer DOPh, the spot diameter corresponded to 14 mm. Then the solubility of PVC in the synthesized dialkyl esters was determined, for which the critical dissolution temperature (CDT) of PVC in the synthesized diesters was determined and compared with CDT of the alkyl diesters of other dicarboxylic acids, for example, diesters of glutaric acid (Merzlikina *et al.,* 1982). The compounds **2(a-d)** have lower values of CDT (415-426K) in comparison with other alkyl esters of aliphatic dicarboxylic acids of a similar structure (CDT = 448K), which indicates good compatibility of these compounds with PVC and, consequently, their good plasticizing ability.

In Table 1 some properties of the synthesized adducts **2(a-d)** are presented.

Analyzing the data in Table 1, it can be seen that the synthesized esters **2(a-d)** on physical-chemical parameters meet the requirements for plasticizers for polymer materials and, consequently, can be used as such ones. These plasticizers are not dissolved in water, consequently, the process of their migration and washing from the finished product is excluded.

The thermal stability of the investigated compounds was found on increase of the acid number during the heating of the samples at temperature 180°C (Fig.2).

In practice, the thermal stability is often characterized by a temperature, at which the substance loses 5, 10 and 50% of the initial mass at a constant heating rate. For

comparison of the thermal stability of the obtained esters **2(a-d)** the mass losses of samples were determined by the method of TGA at temperature rise with a constant rate 5°C/min. In Fig.3 the mass loss curves of the synthesized esters **2 (a, c and d)** are shown.

Table 1. Physical-chemical characteristics of dialkyl esters of rosin adduct and ethanedithiol

Indices	Dialkyl ethers of bis-adducts of rosin with ethanedithiol				
	2a	**2b**	**2c**	**2d**	**DOPh**
Coloration on the iodometric scale, J_2/10cm^3	20	18	6–7	3	0.5
A.N., mg KOH/g	0.2	0.15	0.10	0.10	0.10
Saponification number, mg KOH/g found calculated	 147.3 148.5	 137.1 138.3	 128.8 129.3	 119.6 121.0	 287.1 287.2
Volatile content, % (at 100ºC for 6 h)	0.3	<0.3	<0.3	0.2	0.3
Solubility in water	insoluble	insoluble	insoluble	insoluble	insoluble
Flash temperature in an open crucible (GOST 4333-2014)	170	173	177	178	169
Compatibility with PVC (capillary method), mm	19	12	11	11	14

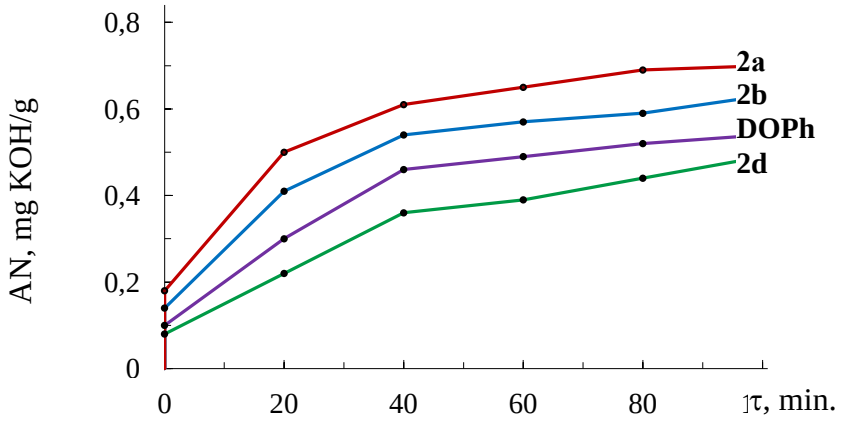


Fig. 2. Thermal stability of dialkyl esters of rosin adduct with ethanedithiol (compounds **2(a-d)**)

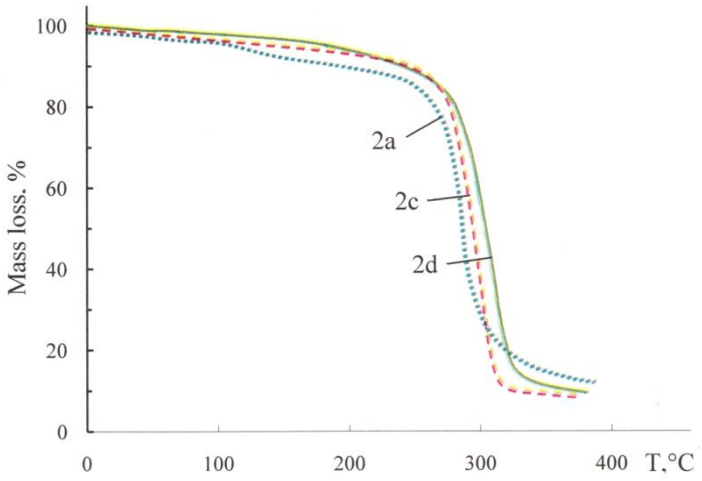


Fig. 3. TGA curves of dialkyl esters of rosin adduct with EDT (ethyl ether (**2a**); hexyl ether (**2c**); octyl ether (**2d**))

It follows from the mass loss curves that the compound **2a** loses 5 and 10% of the mass at temperatures 160 and 185°C, respectively. The losses of 50% of the mass occur at temperature 300°C. Consequently, the obtained data indicate satisfactory thermal stability of the synthesized compounds. As follows from Figure 3, the thermal stability of dialkyl esters (compounds **2(a-d)**) with increase of chain length of the acid residue increases and changes in the following series:

$$C_8H_{17}O > C_6H_{13}O > C_4H_9O > C_2H_5O$$

The ability of the plasticizer to dissolve the polymer has been stipulated by many factors, including the chemical nature of the polymer and solvent, MW of the polymer, the flexibility of the macromolecule chain, the phase state, the packing density of macromolecules, the heterogeneity of the chemical composition of the polymer chain, the availability and frequency of the spatial network, the dissolution temperature (King *et al.*, 2020). These factors complicate the process of swelling, plasticization and dissolution, and also the methods of their investigation. The reactivity of plasticizers and polymers is evaluated on the solubility parameters δ, the values of which are calculated on energy increments for separate atoms and groups of atoms (Anilova & Voynova, 1983).

The data obtained on tensile strength, specific elongation at break and modulus of elasticity at 100% deformation, as well as frost resistance are presented in Table 2.

As follows from the data in Table 2, the obtained test results of PVC compositions using dialkyl esters of rosin adduct with EDT on physical-mechanical parameters have close values with indices obtained for compositions made with use of a standard plasticizer DOPh. However, the dialkyl esters of the rosin adduct proposed as plasticizers have the important advantage in comparison with DOPh that they have been synthesized using natural raw materials – rosin. In comparison with the well-known plasticizer DOPh, the proposed compounds show better compatibility with PVC. Since the synthesized dialkyl esters are insoluble in water and have sufficiently high molar masses in comparison with DOPh, the migration and their washing from the product are completely excluded.

Table 2. Physical-mechanical properties of the compositions on the basis of PVC and dialkyl esters of rosin adduct with EDT – compounds **2(a-d)**

Indices	Compositions with the use of adducts-plasticizer				
	2a	**2b**	**2c**	**2d**	**DOPh**
Critical dissolution temperature, ºC	142	147	145	153	158
Tensile strength, MPa	23.4	22.5	21.3	22.2	19.0
Specific elongation at break, %	210	230	220	240	250
Frost resistance, °C (on GOST 5960-72)	-55	-60	-53	-55	-50
Thermal stability at 180°C, min	63	69	67	72	69
Volatile, % (100°C, 1 h under vacuum)	0.28	0.27	0.23	0.18	0.31
Water resistance for 1 day (50×0,5)	0.27	0.25	0.27	0.23	0.29
Migration to polyethylene at 80ºC, % 24 h 72 h	 6.21 7.02	 6.71 6.97	 7.02 7.36	 5.93 6.12	 67.0 72.0

4. Conclusion

On the basis of rosin adducts with ethanediol and aliphatic alcohols (ethyl, butyl, hexyl and octyl) in the presence of sulfuric acid as the catalyst, the corresponding diesters used then as plasticizers for PVC have been synthesized and characterized.

It has been revealed that the synthesized esters show good compatibility with PVC and therefore their exudation from the composition during long-term storage is not observed. The found values of the hydrolysis rate constants characterizing the hydrolytic stability of the compounds **2(a-d)** varied in the range from $1{,}2\cdot10^{-3}$ to $5{,}6\cdot10^{-3}$mol/l·min^{-1}.

The thermal stability of the obtained diesters has been determined by the method of thermogravimetric analysis. It has been established that they posssess thermal stability up to 553K. It has been revealed that with increase of the chain length of the acid residue, the thermal stability of diesters increases.

The study of the physical-mechanical properties of the obtained compositions on the basis of PVC and dialkyl esters of rosin adduct with ethanedithiol showed that the obtained results have close values with characteristics of the compositions made using a standard dioctyl phthalate DOPh plasticizer.

References

Anilova, A.V., Voynova, S.K. (1983). Plasticizers for PVC on the basis of adipic acid. *Plastmassy*, *2*, 55-56.

Arrieta, M.P., Samper, M.D., Jiménez-López, M., Aldas, M., & López, J. (2017). Combined effect of linseed oil and gum rosin as natural additives for PVC. *Industrial Crops and Products*, *99*, 196-204.

Chu, H.Y., Li, H.B., Sun, X.Y., & Zhang, Y.W. (2021). Synthesis and application of eleostearic acid based plasticizer. *Green Materials*, *10*(4), 146-153.

Chu, H.Y., Li, H.B., Sun, X.Y., & Zhang, Y.W. (2021). Synthesis of biomass-based plasticizer with excellent durability for high transparent polyvinyl chloride film. *Journal of Vinyl and Additive Technology*. https://doi.org/10.1002/vnl.21851

Chu, H.Y., Li, H.B., Sun, X.Y., & Zhang, Y.W. (2022). Synthesis of biomass based plasticizer from linoleic acid and cardanol for preparing durable PVC material. *Journal of Polymers and the Environment*, *30*(8), 3270-3278.

Jia, P., Ma, Y., Zhang, M., Hu, L., & Zhou, Y. (2019). Designing rosin-based plasticizers: effect of differently branched chains on plasticization performance and solvent resistance of flexible poly (vinyl chloride) films. *ACS omega*, *4*(2), 3178-3187.

King, R., Grau-Bové, J., & Curran, K. (2020). Plasticiser loss in heritage collections: Its prevalence, cause, effect, and methods for analysis. *Heritage Science*, *8*(1), 1-17.

Ma, Y., Kou, Z., Jia, P., & Zhou, J. (2021). Effect of benzene ring and alkane chain contained bio-based plasticizers on the plasticizing performance of polyvinyl chloride films. *Chemical Papers*, *75*, 5515-5521.

Mazitova, A.K., Aminova, G.K., & Vikhareva, I.N. (2022). Development of new ecologically safe plasticizers. *SOCAR Proceedings*, 3, 114-119.

Merzlikina, V.P., Kirillovich, V. I., Monakhova, G. V., & Moisa, Yu N. (1982). Frost-resistant plasticizers for PVC on the basis of glutaric acid. *Khimicheskaya promyshlennost*, 3, 15-19.

Pirguliyeva, M.S. (2015). Sulfur–containing epoxide compounds on the basis of rosin – stabilizers for PVC. In *Collection of materials of XII Numanov readings State and prospects of development of organic chemistry in the Republic of Tajikistan*, 11-13.

Song, F., Jia, P., Xia, H., Zhang, M., Hu, L., & Zhou, Y. (2020). Rosin-derived poly (vinyl chloride) plasticizer: Synthesis, structure, and properties. *Journal of Vinyl and Additive Technology*, *26*(2), 180-186.

Toroptseva, A.M., Belogorodetskaya, K.V., & Bondarenko, V.M. (1972). *Laboratory workshop on chemistry and technology of macromolecular compounds*. Leningrad, Chemistry, *416*.