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The Effect of the Structure of the Alcohol Component on the Plasticizing Ability of the Ester of Aliphatic Dicarboxylic Acid

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Abstract: Esters of aliphatic dicarboxylic acids are promising plasticizers of polyvinyl chloride due to their low toxicity and high biodegradability. Plasticized PVC materials containing them are characterized by high frost resistance and heat resistance. In this regard, esters of adipic acid and alkoxyated alcohols with various structures have been obtained. The influence of alcohol structure on the plasticizing ability of ether has been determined. A theoretical assessment of the plasticizing effect of diesters in relation to PVC was performed based on the calculation of Hansen solubility parameters. For this purpose, the thermodynamic compatibility of adipates with PVC was investigated. The processability of esters in the composition of PVC compositions was studied according to the values of the critical temperature of dissolution of PVC. The intervals of transition of plastics from a glassy to a highly elastic state, as well as the depression of the glass transition temperature of compounds containing adipates, were determined. Rheological characteristics of PVC compositions based on the obtained adipates were investigated. It is shown that the chemical structure of the alcohol group determines the important technological and operational characteristics of esters in the composition of polymer materials.

Keywords: adipate; frost resistance; alkoxyated alcohol; plasticizer; polyvinyl chloride; polymer; ester; compatibility; manufacturability; efficiency



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1. Introduction

Esters of aliphatic dicarboxylic acids are widely used in various spheres of human activity [1–6]. This class of compounds is most commonly used in engineering. Compounds containing an ester group in the structure are used as lubricating oils, solvents, components of liquid fuels, and cosmetic ingredients. In recent years, dicarboxylic acid esters for thermal energy storage have attracted increasing attention due to their ease of production, different temperatures and solving the problems of fatty alcohols, which are potential TES materials [5]. About 90% of plasticizers are esters, for example, adipates, azelates, citrates, benzoates, orthophthalates, terephthalates, sebacates and trimellitates [7–9].

Of particular interest are the esters of adipic acid and sebacic acid. Oils and plasticizers based on dicarboxylic acid esters are characterized by oxidative and thermal stability, good biodegradability and moderate production costs [10,11].

According to expert data, the global plasticizer market will increase from USD 17 billion in 2022 to USD 22.5 billion in 2027 [12]. Currently, the share of non-phthalate plasticizers is 35% [13]. Among the diester plasticizers, phthalates occupy more than 80% of the market. Due to the retrotoxicity of phthalates for animals and humans, some of them have been banned for widespread use. Over the past 25 years, the plasticizer industry has invested

more than EUR 6 billion in research and development to expand the range of these additives to ensure sustainable development, product safety and cost reduction [14,15].

As an alternative to phthalates, a wide range of compounds are being investigated, including biologically based plasticizers from renewable resources [16–19].

Bioplasticizers are substances with a low molar mass, produced on a biological basis or from plant products such as vegetable oils, sugar cane or plants containing starch. Epoxy esters based on vegetable oils have been studied as bioplasticizers, including soybean, linseed and tall oil, as well as citrates, stearic acid, lactic acid, glycerol esters, isosorbide, glycidylglycerin, rosin acid, tartaric acid esters and starch [20–23].

The use of biologically based plasticizers is currently very relevant. Bioplasticizers have great potential to replace and limit the use of traditional plasticizers and play an important role in the modern market. The demand for bio-based plasticizers of this kind is growing rapidly. The volume of the global bioplasticizer market in 2023 was estimated at USD 2.92 billion [24]. The average annual growth rate (CAGR) is 8.39%. Bioplasticizers have significant potential to replace phthalates in personal care products, food packaging, medical devices and toys. Typically, relatively expensive raw materials are required for the production of biologically based plasticizers.

Alternative plasticizers are aliphatic esters of adipic, azelaic and sebacic acids. The use of these additives is currently widespread on an industrial scale, due to their low toxicity and excellent operational and technological characteristics, such as frost resistance and thermal stability. Research work on the search for and study of new esters of aliphatic dicarboxylic acids has shown the effectiveness of their use in PVC compounds to improve mechanical and thermal properties [25–28]. Therefore, there is a need for further research to expand the range of these esters, since there is a greater demand for them in the plastic industry.

2. Materials and Methods

2.1. Materials

Industrial samples of suspension polyvinyl chloride supplied by Bashkir Soda Company Caustic JSC (Sterlitamak, Russia) were used as a matrix. It is characterized by a Fikentscher constant in the range of 58–70. The plasticizer dioctyl phthalate (DOP) was supplied by JSC Kamtex-Khimprom (Perm, Russia). Its main characteristics are its acid number (mg KOH/g) ≤ 0.07 , saponification number (mg KOH/g) ≤ 289 , mass fraction of volatile substances (%), no more) of 0.1 and flash point ($^{\circ}\text{C}$) ≥ 205 . The stabilizer tribasic lead sulfate (TBLS) was produced by Baerlocher GmbH (Ingolstadt, Germany): appearance—powder; lead content (%)— 89 ± 2 ; pH—7.0–7.5; solidity (%)—at least 95. Calcium stearic acid stabilizer (CaSt) was produced by the HIMSTAB company (Mytishchi, Russia). Its main characteristics are as follows: acid number (mg KOH/g)—no more than 2; calcium content (%)—within the range of 6.4–7.5; calcium oxide content (%)—within the range of 9.0–10.5. Adipic acid is a white crystalline compound. The mass fraction of the basic substance (%) is not less than 99.8; the melting point is 152.3°C . Butoxyethanol is a colorless transparent liquid. The mass fraction of the main substance (%) is not less than 99.5; the density at 20°C (g/cm^3) is within the range of 0.900–0.904; the mass fraction of water (%) is not more than 0.1; the mass fraction of acids (in terms of acetic acid, %) is not more than 0.005; the boiling point at 760 mm Hg ($^{\circ}\text{C}$) is within the range of 169–172. Phenoxyethanol is a colorless transparent liquid. The mass fraction of the basic substance (%) is not less than 99.5; the density is $1.105\text{--}1.110\text{ g}/\text{cm}^3$ (20°C); the melting point is -2°C ; the boiling temperature is 247°C . Butoxypropanol (1-butoxypropan-2-ol) is a clear liquid with a faint odor. The content of the basic substance (%) is not less than 99.0; the acidity in the conversion to acetic acid (%) is not more than 0.02; the water content (%) is not more than 0.10; the density is $0.874\text{--}0.881\text{ g}/\text{L}$.

2.2. Synthesis Methods

For the synthesis of esters of dicarboxylic acids and ethoxylated alcohols, estimated amounts of dicarboxylic acid, alcohol and catalyst were loaded into a circular chemical reactor equipped with a reverse refrigerator with a Dean–Stark trap, a thermometer and a magnetic stirrer. The reaction was carried out at the boiling point of the reaction mass until the calculated amount of water was released through the Dean–Stark nozzle. At the end of the reaction, the vessel containing the reaction mixture was cooled. Isolation of the target ether was carried out depending on the aggregate state of the resulting plasticizer. Upon receipt of liquid products, the esterification was washed alternately with a 5% alkali solution, water and a saturated sodium chloride solution. These were drained with freshly calcined sodium sulfate. When solid target esters were obtained, a certain amount of ethanol was added to the flask with the reaction mixture and decanted. The sediment was dried.

2.3. Sample Preparation

To create prototypes using the developed plasticizers, all components of the composition were mixed in a laboratory two-stage mixer (Polimermash, St. Petersburg, Russia) for 60 min. For testing, samples of PVC compounds were prepared in the form of rigid and plastic films. PVC films were produced on two-roll “SCAMEX” extrusions (SCAMEX, Crosne, France) at temperatures in the range of 165–175 °C for 5–10 min, depending on the composition. Pressed samples were obtained from rolled PVC films using a hydraulic press.

2.4. Methods of Analysis

The determination of acid and ester numbers of plasticizers was carried out by titration of an alcoholic solution of the tested product with a solution of potassium hydroxide using phenolphthalein as an indicator.

The refractive index (n) of esters was determined using an IRF-22 refractometer (“Ecros-Analytics”, St. Petersburg, Russia).

The density of esters was determined using a general-purpose densimeter.

The determination of the mass fraction of volatile substances was carried out based on the degree of evaporation of the components of the substance. Fourier spectroscopy (KBr tablets) performed according to the standard procedure was used to analyze the IR spectra of synthesized products. Absorption spectra were recorded in the range of 450–3700 cm^{-1} using a Fourier spectrometer FTIR-8400S (Shimadzu, Kyoto, Japan) at room temperature. The resolution was 4 cm^{-1} , and the number of scans was 20.

The dynamic mechanical analysis (DMA) method was used to evaluate the effect of plasticizers on the segmental mobility and temperature transitions of plasticized PVC. The studies were carried out on the NETZSCH DMA-242 device (NETZSCH Group, Selb, Germany) in the stretching mode in a temperature range from −80 to +100 °C with a frequency of 1 Hz in an atmosphere of nitrogen supplied at a rate of 100 mL/min. During the analysis, changes in the complex modulus of elasticity were recorded with an increase in the temperature of the polymer sample. The sensitivity of the method to segmental movements makes it possible to determine the temperature transitions of a polymer sample at a given frequency over a wide temperature range. Measurements were performed at least three times for each sample. A systematic error cannot be determined for this test method, as there is no acceptable control sample. The experimental conditions were the same for all the studied samples: the heating rate, the loading frequency, the type and flow rate of the purge gas, and the position of the heat pump.

The melt fluidity was studied on the IIRT-AM device (LLC “ROSS” Moscow, Russia) in a temperature range from 160 to 180 °C by capillary viscometry. The value of the melt flow index (MFI) corresponds to the mass of the polymer in grams that comes out of the capillary (capillary length—8 mm; diameter—2.09 mm) of the device in 10 min at a certain temperature and pressure. MFI measurements for PVC compositions were carried out at a load of 49 N and a predetermined temperature of 160–180 °C. A quantity of 4–5 g of the

PVC composition under study was injected into the device and heated to a predetermined temperature. Then, the capillary was opened to allow the melt of the composition to flow out under pressure.

To measure the MFI parameter, at least five extrusion segments of the composite were used, cut off at equal time intervals. The mass of the cooled extrusion segments was measured with an error of no more than 0.0001 g. The value of the MFI parameter was calculated using the appropriate Formula (1):

$$\text{MFI (g/10 min)} = 600 \text{ m/t} \quad (1)$$

where m is the average mass of extruded segments, in g, and t is the time interval between two consecutive cutoff segments, in s.

3. Results and Discussion

By esterification of dicarboxylic acids with alkoxyated alcohols according to the method described earlier, the following were obtained: dibutoxyethyl adipate (DBEA), diphenoxyethyl adipate (DPEA) and dibutoxypropyl adipate (DBPA) [29] (Table 1). The yield of diesters was 86.9% or more.

Table 1. The structure of alkoxyated adipates.

Ester	Structural Formula
Dibutoxyethyl adipate (DBEA)	
Diphenoxyethyl adipate (DPEA)	
Dibutoxypropyl adipate (DBPA)	

The duration of synthesis is significantly influenced by the presence of a benzene ring in the structure of phenoxyethanol, which is associated with steric difficulties during reaction. As a result, the synthesis time of phenoxyester increased. The synthesis time of dibutoxypropyl adipate slightly exceeded the synthesis time of dibutoxyethyl adipate, which was probably also due to the branched structure of the alcohol used—1-butoxypropane-2-ol.

The characteristics of the esters obtained are given in Table 2.

Table 2. The main characteristics of dicarboxylates.

Indicators	DBEA	DPEA	DBPA
Acid number, mg KOH/g	0.15	0.2	0.16
Ester number, mg KOH/g	321	289	298
Molecular weight, calculated	346	386	374
Mass fraction of volatile substances, %, no more	0.7	0.5	0.6
Yield, %	87.5	86.9	87.0
Reaction time, min	150	180	165
Maximum reaction temperature, °C	130	150	138

The obtained adipic acid diesters were characterized by low acid number values and mass fractions of volatile substances, which are critically important indicators in the production of PVC-based materials and are also associated with ensuring the necessary level of characteristics and service life of finished products. The resulting dibutoxy derivatives of acids are oily yellowish liquids; diphenoxy ester is a highly viscous paste-like substance with a low melting point.

The structure of the obtained diesters was confirmed by IR spectra (Figure 1).

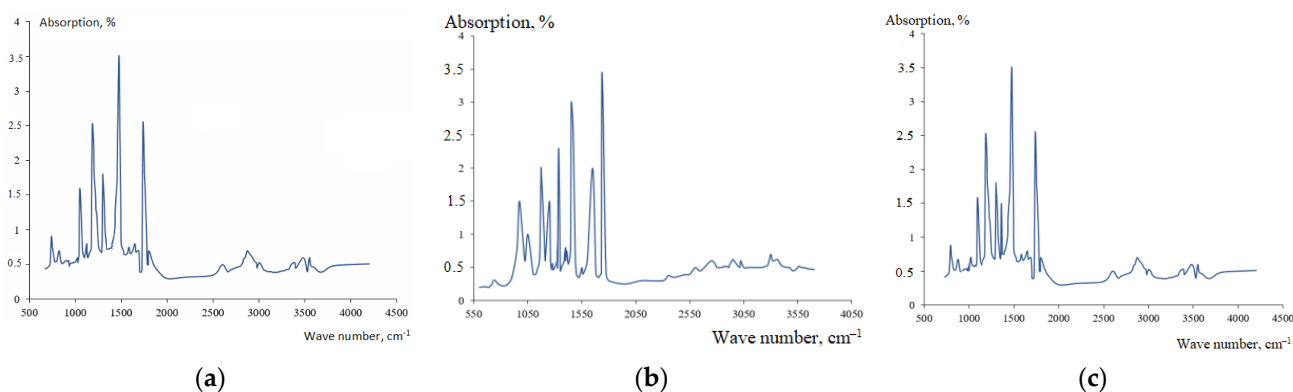


Figure 1. IR spectra of esters. (a) The IR spectrum of dibutoxyethyl adipate; (b) The IR spectrum of diphenoxyethyl adipate; (c) The IR spectrum of dibutoxypropyl adipate.

The spectra lack characteristic absorption bands of the valence vibrations of the carbonyl group in the aliphatic carboxylic acids in the range of $1685\text{--}1687\text{ cm}^{-1}$, as well as in the range of $1740\text{--}1650\text{ cm}^{-1}$, indicating the $\text{C}=\text{O}$ groups in carboxylic acids. Characteristic absorption patterns can be observed in infrared spectroscopy of esters, which help to determine their structural features. One of the key features is the absorption in the region of 1737 cm^{-1} , corresponding to the valence vibrations of the carbonyl group ($\text{C}=\text{O}$).

An absorption of 1173 cm^{-1} is also highlighted, this being associated with fluctuations in the C-O-C ester group. Additionally, two intense peaks at 1330 cm^{-1} and 1050 cm^{-1} can be noted, which reflect asymmetric fluctuations in carbon bonds of CO .

If an aromatic fragment is present in the ester structure, this is confirmed by the absorption for the $\text{C}=\text{C}$ double bond at the level of 1625 cm^{-1} and the C-H group in the range of 1250 cm^{-1} . These spectral characteristics allow for a deeper understanding of the chemical nature and structure of esters.

The esters obtained were investigated for possible use as PVC plasticizers.

Currently, there is no single point of view on the mechanism of polymer plasticization due to the significant influence of various physico-chemical and technological factors on this process: the composition and structure of macromolecules and supramolecular structures; the composition and molecular weight of the polymer; the method of its preparation; the nature, molecular weight and structure of plasticizers; the method and mode of combining components; the nature of their interaction; etc. A well-optimized plasticizer must strike a balance among compatibility, efficiency, non-migration and the durability of the resulting products [30]. The effectiveness of a plasticizer is evaluated based on several key properties: environmental friendliness, odorlessness, compatibility, low volatility, effective plasticization at low temperatures, and minimal sweating or extraction into surrounding media [31].

The main condition for plasticization is the thermodynamic compatibility of the plasticizer with the polymer, i.e., the formation of a true plasticizer solution in the polymer. This makes it possible to vary the concentration of the plasticizer as much as possible. Compatibility depends on the nature of the polymer and plasticizer.

This compatibility is largely influenced by the chemical structure of the plasticizer and the proportion of polar groups it contains. In polyvinyl chloride (PVC), strong polar interactions between the C-Cl groups facilitate segment contact. Ester plasticizers exhibit a

dual structure, combining polar ester groups with non-polar alkyl chains. This structure not only disrupts polar interactions between polymer segments, enhancing their mobility, but also interacts with the polar groups within the polymer matrix, thereby maintaining certain physical and mechanical properties.

Plasticizers can migrate from composite materials through processes like evaporation and diffusion. Notably, an increase in temperature of just 7 °C can double the migration rate of a plasticizer. The migration process occurs from areas of higher concentration to those of lower concentration and is influenced by the polymer's characteristics. A lower interaction between the plasticizer and PVC correlates with reduced compatibility limits and higher migration rates. When the plasticizer concentration is maintained at or below 10%, it becomes fully solvated by the polymer, minimizing molecular separation. Conversely, increasing the plasticizer content raises the number of fragile bonds within the polymer–plasticizer system, thereby enhancing migration tendencies.

Research indicates that when the plasticizer content in PVC compositions ranges from 15% to 35%, there is a nearly linear relationship between migration amounts and plasticizer levels. Understanding compatibility parameters allows for targeted adjustments to both the structure of the plasticizer and the operational characteristics of the final material. This helps mitigate issues such as high volatility and surface migration of impurities, ultimately preserving performance attributes [32,33].

As the production of plasticizers progressed, a number of technical problems were solved to improve the characteristics of polymer formulations, solve technical problems of end use and meet new requirements. Some of the problems included evaporation, the degradation of plasticizers due to volatility or susceptibility to UV radiation, migration of plasticizers into contact media, insufficient lubrication at subzero temperatures and suspected carcinogenic effects on a number of living organisms. The fundamental foundations of these problems are chemical in nature. They are mainly related to thermodynamic, migration and interphase phenomena [34,35].

The calculation of Hansen solubility parameters (HSPs) serves as a means of preliminary theoretical assessment of the plasticizing effect of a substance in relation to PVC [36,37].

According to Hansen, the solubility region of a polymer is expressed by a sphere of radius, R_0 . For PVC, this value is 8.2. The solubility parameter, R_A , between the two materials is calculated using the equation based on the corresponding partial components of the solubility parameter (2):

$$R_A = \sqrt{4 \cdot ([\delta_{d2} - \delta_{d1}])^2 + (\delta_{p2}[-\delta_{p1}])^2 + (\delta_{h2} - \delta_{h1})^2} \quad (2)$$

where R_A is the distance from the center of solubility of the polymer to the coordinates of the solubility parameter of plasticizers; δ_d , δ_p and δ_h are the solubility parameters of the dispersion, polar interaction and interaction due to hydrogen bonds; and indices 1 and 2 relate to the polymer and the plasticizer, respectively.

For high compatibility, it is necessary that R_A be less than R_0 . The R_A/R_0 ratio was called the “red” number (3), reflecting the relative energy difference:

$$RED = R_A/R_0 \quad (3)$$

Table 3 shows the calculated values for the solubility parameters, the total solubility of R_A and the amount of RED for all the obtained diesters.

Table 3. Parameters of solubility: total solubility of R_A and RED numbers for acid diesters.

Compound	δ_d (MJ/m ³) ^{1/2}	δ_p (MJ/m ³) ^{1/2}	δ_h (MJ/m ³) ^{1/2}	δ (MJ/m ³) ^{1/2}	R_A	RED
DBEA	15.29	8.06	4.80	17.94	7.07	0.850
DBPA	15.29	8.30	4.80	17.94	7.07	0.850
DPEA	18.99	9.02	5.49	21.73	1.34	0.296

A *RED* number less than 1.0 indicates a high affinity of the plasticizer and polymer, and with higher numbers, compatibility decreases. The calculated values for individual solubility parameters for dibutoxyethyl adipate and for dibutoxypropyl adipate coincide and are slightly below the limit $\delta_d = 15.4$ for PVC. The minimum value of this indicator was obtained for diphenoxyethyl adipate. However, in general, for all semi-finished compounds, the *RED* number is less than 1, which implies their good compatibility with PVC.

A practical way to assess the compatibility of a compound with PVC is to determine the critical dissolution temperature of the polymer.

When processing plasticized PVC, it is known that good manufacturability is achieved at temperatures exceeding the critical dissolution temperature by 20–80 °C. If the critical temperature of the product is in the range of 90–135 °C, the plasticizer demonstrates excellent compatibility and is suitable for the production of products at normal pressure with heating up to 160 °C. In the case when the critical dissolution temperature of the polymer in the plasticizer is 136–160 °C, its solubility decreases, and it is usually used in a mixture with basic plasticizers. For a comparative assessment of the compatibility of synthesized compounds with the reference plasticizer dioctyl phthalate, parameter *A* was used, which was calculated using a special formula (4):

$$A (\%) = 100 T_{DOP} / T_{cr} \quad (4)$$

where T_{DOP} is the critical temperature of PVC dissolution in DOP and T_{cr} is the critical dissolution temperature of PVC in the compound under study.

The results are presented in Table 4.

Table 4. Parameters of compatibility of diesters with PVC.

Compound	T_{cr} , °C	<i>A</i> , %
DBEA	138	81.0
DBPA	121	99.0
DPEA	134	87.0

The results indicate a strong correlation between the critical dissolution temperature and parameter *A* with the Hansen solubility parameters calculated previously. Among the esters examined, dibutoxypropyl adipate stands out due to its notably low critical dissolution temperature with PVC, suggesting enhanced compatibility with this polymer. This compatibility implies its potential as an effective primary plasticizer, enhancing the performance and processing of PVC materials.

In summary, dibutoxypropyl adipate's properties make it a promising candidate for applications requiring improved flexibility and stability in PVC formulations. At the same time, diphenoxyethyl adipate ($T_{cr} = 134$ °C) can theoretically be used as a combined primary plasticizer for elastic materials and PVC products.

The good solvent capacity of plasticizers does not guarantee the achievement of the complex properties required for PVC plastics. Another key aspect of plasticizers is the glass transition temperature, T_g , of plasticized PVC, which reflects the material's ability to maintain elasticity at lower temperatures. To investigate how synthesized esters influence the properties of PVC, specific compositions were formulated, consisting of 100 parts PVC, 2 parts TBLS, 1.5 parts calcium stearate, 0.25 parts diphenylolpropane and 40 parts plasticizer. For comparison, commonly used plasticizers such as dioctyl phthalate and dioctyl adipate were also evaluated. The impact of the synthesized esters on the segmental mobility and thermal transitions of the plasticized compositions was assessed using Dynamic Mechanical Analysis (DMA) (Figures 2–6, Table 5).

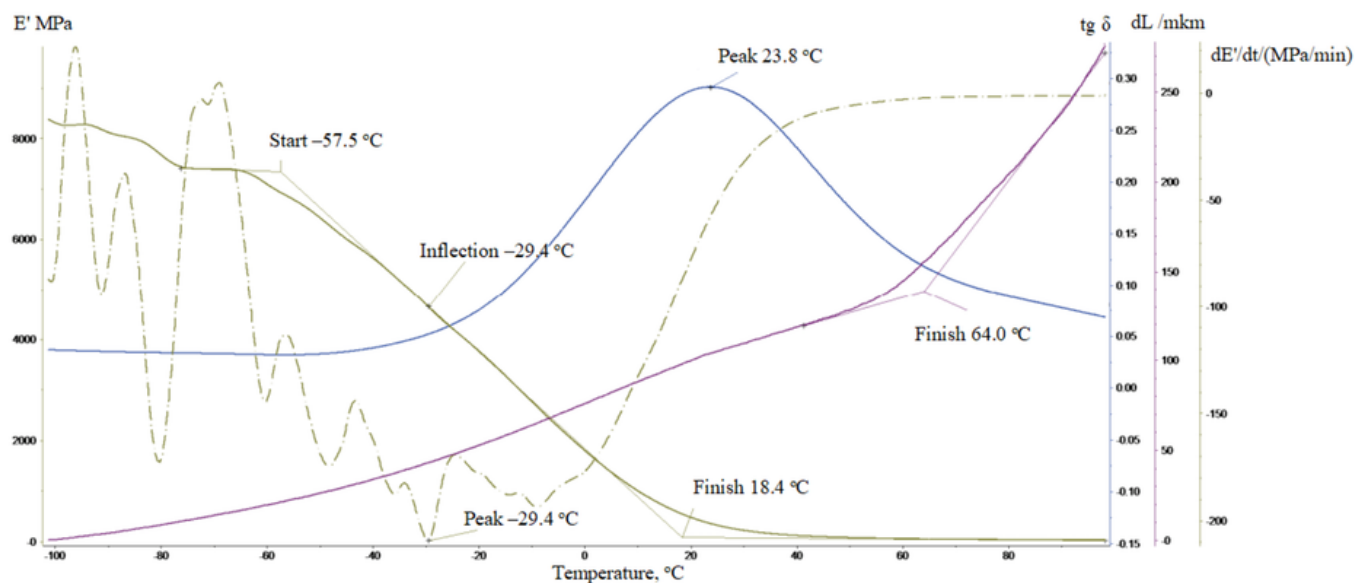


Figure 2. DMA thermogram for PVC, plasticized DBEA.

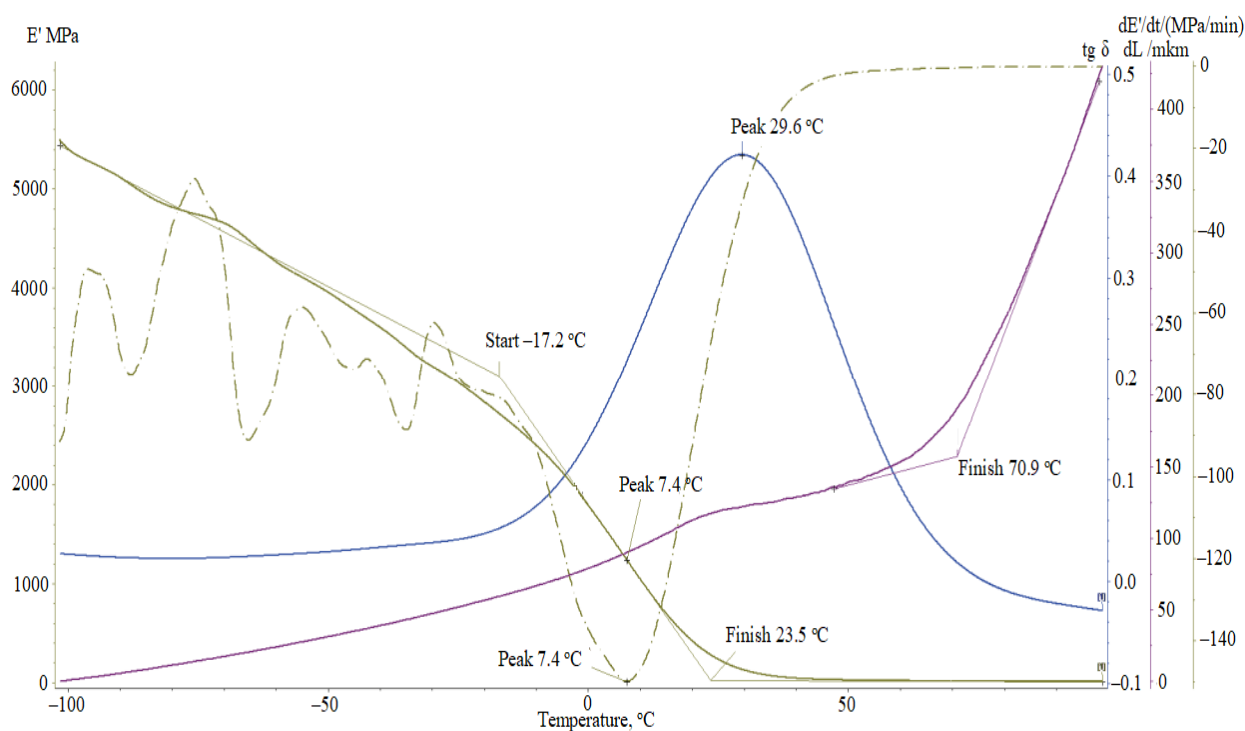


Figure 3. DMA thermogram for PVC, plasticized DPEA.

Table 5. Thermoanalytical characteristics of plasticized PVC compositions obtained by the DMA method.

Plasticizer	E' , MPa	T_s , °C	T_g , °C	T_f , °C	$T_{tg\delta}$ Max, °C	$T_f - T_s$
DOP	5800 (−80 °C)	−29.0	−26.2	23.2	30.0	52.6
DOA	3350 (−80 °C)	−78.4	−65.7	3.2	24.0	81.6
DBEA	7650 (−80 °C)	−57.5	−29.4	18.4	23.8	75.9
DBPA	4450 (−80 °C)	−77.5	−37.6	6.8	17.1	84.3
DPEA	4800 (−80 °C)	−17.2	7.4	23.5	29.6	40.7

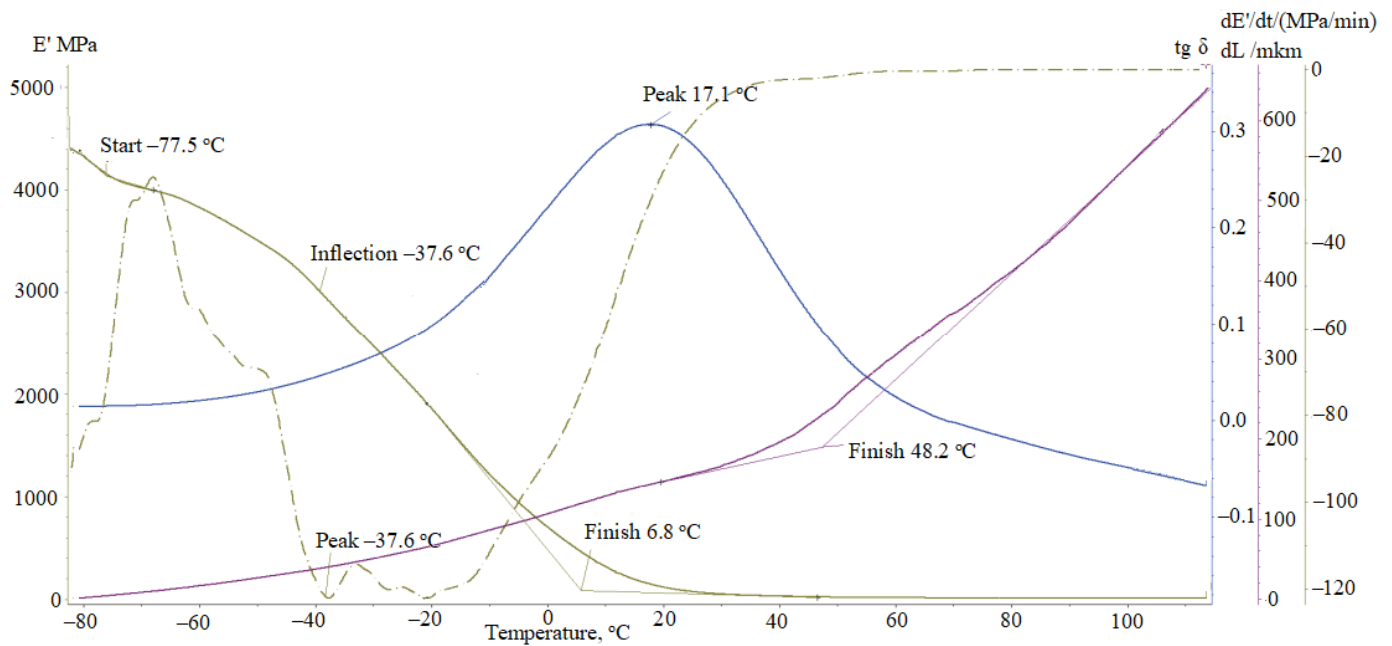


Figure 4. DMA thermogram for PVC, plasticized DBPA.

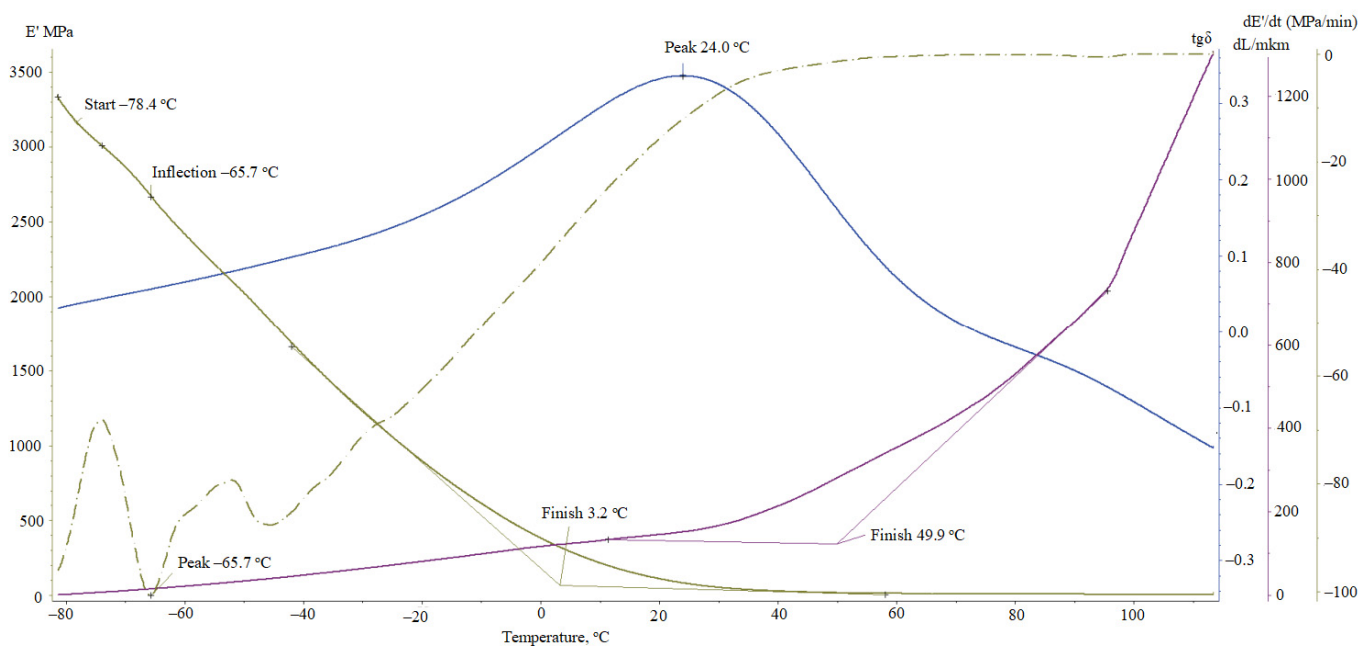


Figure 5. DMA thermogram for PVC, plasticized DOA.

Single transitions of the tangent of the mechanical loss angle, $T_{g\delta}$, can be observed in all the thermograms obtained, which indicates the uniformity of the system and the absence of a second incompatible phase. The structure of the plasticizer has a significant effect on the temperature transitions of PVC plastic (Table 5). The transition of a polymer from a glass-like state to a state of high elasticity is the main relaxation process manifested in the area of major relaxation (α -relaxation). There is a conditional boundary between these two states—the glass transition temperature. At this temperature, there is a sharp decrease in the mobility of segments of polymer molecules [38–40].

In the above table, T_s is the temperature at the beginning of the transition from a glassy state to a highly elastic one, T_g is the glass transition temperature, T_f is the temperature at the end of the transition from a glassy state to a highly elastic one, $T_f - T_s$ is the temperature range corresponding to the α -relaxation region, and E is the modulus of elasticity.

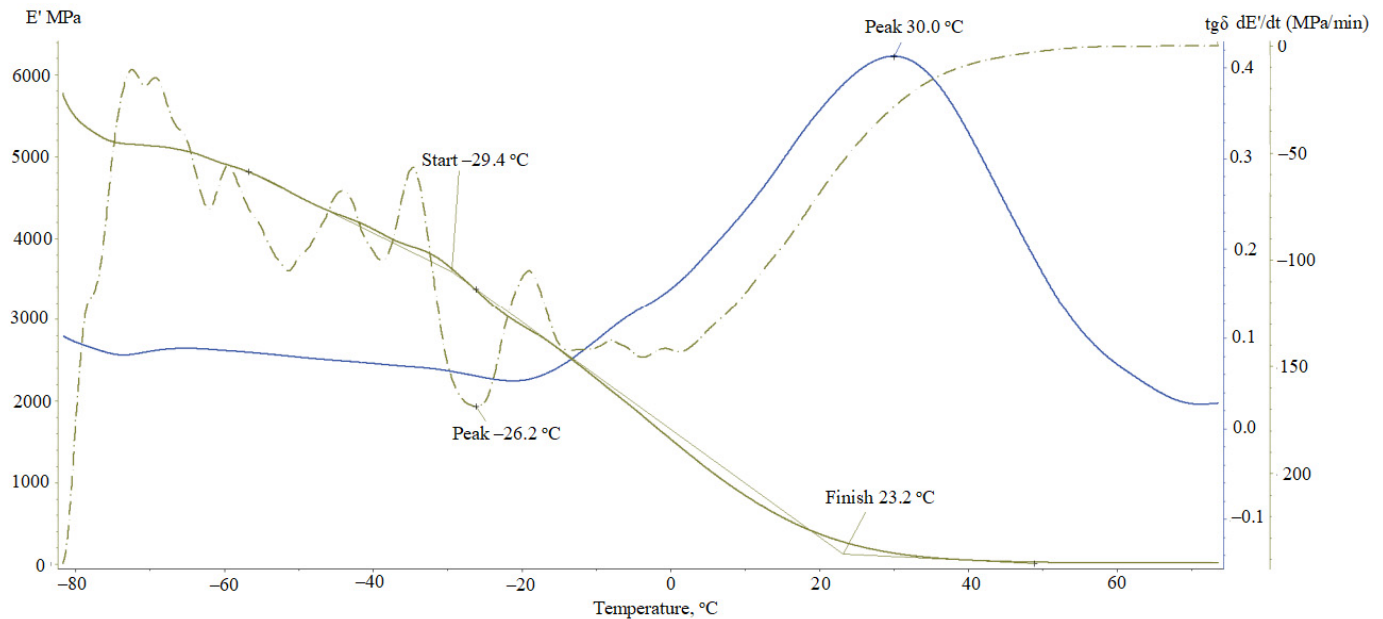


Figure 6. DMA thermogram for PVC, plasticized DOP.

A study of the thermomechanical characteristics of PVC-based plastics has shown that the highest glass transition temperature can be observed in a sample with the addition of DPEA. The transition to a state of high elasticity occurs at a glass transition temperature of 7.4 °C. For PVC plasticized with esters of aliphatic alcohols DBEA and DBPA, the glass transition temperatures are noticeably lower and amount to minus 29.4 °C and minus 37.6 °C, respectively. The obtained indicators exceed the same indicator for plastic with the industrial plasticizer DOP.

Heating of the polymer material causes its softening and reduces the index of the dynamic modulus of elasticity, E' . Such changes in mechanical properties due to temperature are associated with the thermal transition of the polymer from a glassy state to a highly elastic one. The structure of synthesized esters has a direct effect on the modulus of elasticity of plasticized PVC samples at the beginning of dynamomechanical tests: for dibutoxyethyl adipate, the modulus values are higher than for diphenoxyster and branched-structure ester. The order of the index for DPEA is commensurate with the elastic modulus of PVC plastics with a DOP content. The modulus value for DBPA is close to this indicator for DOA, which also has an alcohol group with a branched structure. The temperature ranges of the transition from the glassy state to the highly elastic state (T_f – T_s) for PVC compositions plasticized with DBPA and industrial DOA are quite close: 84.3 °C and 81.6 °C, respectively. The investigated ether even surpasses the industrial DOA in this indicator. For a composition containing DPEA, this transition interval is significantly inferior in magnitude to the esters of aliphatic alcohols and is 40.7 °C, which is slightly lower than for the industrial plasticizer DOP—52.6 °C. In general, the regularity of the influence of the alcohol structure on the elastic modulus is traced: in the case of the presence of an aromatic ring in the alcohol component in the structure of the diester, an increase in the elastic modulus is observed; in the case of a branched structure, there is a decrease in the elastic modulus. The highest value of this indicator corresponds to the aliphatic structure of the normal structure.

The physical properties of polymers are significantly influenced by their chemical structure and the arrangement of polymer chains. A key factor in this is the glass transition temperature, T_g , which can be altered through the incorporation of plasticizers during processing. This process, known as plasticization, results in a reduction in T_g , allowing for enhanced flexibility and mobility within the polymer chains. Plasticizers achieve this by disrupting the secondary bonds that hold the polymer chains together, creating weaker bonds between the polymer and the plasticizer.

From both practical and theoretical perspectives, introducing a plasticizer into a polymer matrix is crucial. Lowering the glass transition temperature expands the temperature range in which the polymer maintains a highly elastic state, improves frost resistance, and reduces viscosity in polymer melts. These changes facilitate processing, particularly for polymers whose T_g or flow temperatures are close to or exceed their decomposition temperatures. The effectiveness of a plasticizer is often evaluated by its ability to depress T_g .

The low-temperature characteristics of plasticizers are vital for applications like sealing plastics, where brittleness can lead to cracking in cold environments. The extent of T_g depression is influenced by the thermodynamic compatibility between the plasticizer and the polymer; greater compatibility allows for higher concentrations of plasticizer to be added, enhancing lubricity and facilitating new applications for polymer materials.

Intermolecular interactions are determined by the volume and structure of the plasticizer molecule, in particular the size of the alkyl chain. For example, dibutoxypropyl adipate exhibits better compatibility with PVC than other studied esters due to its branched ester structure, which enhances solubility and lowers dissolution temperatures within the polymer matrix. A decrease in these characteristics is observed in ether containing aromatic rings in the structure of alcohol. The minimum values of important technological characteristics correspond to an ester based on aliphatic alcohol of normal structure. Polar phenoxy derivative molecules featuring two benzene fragments hinder the segmental mobility of polymer macromolecules, particularly at lower temperatures. As a result, polyvinyl chloride (PVC) containing DPEA exhibits the highest glass transition temperature, reaching 7.4 °C, indicating that the polymer transitions to a glassy state at this temperature. With an increase in the length of the alkyl chain between the ester fragments, the glass transition temperature passes into the region of negative temperatures. The butoxy derivative of the linear structure reduces the glass transition temperature of PVC plastic to a temperature of minus 29.4 °C. This value is slightly lower than that achieved by industrial di(2-ethylhexyl) phthalate (DOP), but it remains comparable to the effectiveness of dioctyl adipate (DOA). It is noteworthy that the introduction of branched alcohols into the ether structure further reduces T_g , reaching a remarkable −37.6 °C for dibutoxypropyl adipate ester (DBPA). This modification enhances the segmental mobility, which significantly affects the temperature transitions of PVC plastic. Plasticizers are crucial for the creation of flexible polymer materials. Their effectiveness can be quantified by their effect on the hardness of PVC measured at a controlled temperature (23 ± 2) °C. The key indicator in this assessment is the “substitution coefficient”, which indicates the amount of plasticizer needed to match the hardness of PVC plastic achieved with DOP. The replacement coefficient can be calculated using a specific formula that takes these variables into account. Thus, structural modifications of plasticizers not only improve the thermal properties of PVC, but also play a significant role in determining its mechanical characteristics (5):

$$\text{The substitution factor} = \text{Amount of plasticizer, wt. h.} / \text{Amount of DOP, wt. h.} \quad (5)$$

To evaluate the effectiveness of the plasticizing properties of synthesized esters, a comprehensive study was conducted focusing on the relationship between plasticizer concentration and the hardness of PVC plasticate across a broad range of dosages. The primary objective was to determine the specific amount of plasticizer necessary for the PVC formulation to achieve a Shore A hardness of 70 conditional units. Additionally, substitution factors for various plasticizers in relation to dioctyl phthalate (DOP) were calculated (Table 6).

Table 6. The effectiveness of the plasticizing effect of synthesized plasticizers.

Plasticizer	Substitution Factor
DBEA	0.91
DBPA	1.02
DPEA	1.19

Based on the findings, it is evident that the structural characteristics of the esters significantly influence their plasticizing effectiveness. The data indicate that phenoxy esters demonstrate a lower plasticizing efficiency compared to their butoxy counterparts. This variation can be attributed to specific substitution factors that affect how these esters interact with polymers, ultimately impacting their mechanical properties and thermal stability. In summary:

- Structural influence: The design and molecular structure of esters play a crucial role in determining their effectiveness as plasticizers.
- Comparative effectiveness: Phenoxy esters are less efficient than butoxy esters, suggesting that the latter may be more suitable for applications requiring enhanced plasticization.

These insights highlight the importance of selecting appropriate ester structures for optimizing plasticizing effects in polymer formulations. Thus, in comparison with DOP, in order to achieve plastic of equal hardness, it is necessary to use 19% more DPEA; the amount of DBPA for a formulation of similar hardness is almost identical.

Butoxy derivatives are characterized by greater effectiveness of plasticizing action in comparison with DOP and ensure the achievement of similar hardness at a lower dosage.

The results obtained are comparable with the data on the plasticizing ability of succinic acid esters presented in [28]. The properties of plasticization have shown the importance of structure. Within the studied range, an increase in the total length of the molecules contributed to an improvement in plasticizing properties, while the addition of alkyl substituents to the middle part of succinic acid esters negatively affected the compatibility of plasticizers. Moreover, with an increase in the size of these substituents, the negative effect increased, which is associated with the ability of these compounds to rotate around the axis connecting the ester groups. According to the authors, a good compromise is digexyl succinate: the T_g index is comparable to that of the plasticizer DEHP.

In another paper [35], the research results confirmed that the length of the side chain plays a more important role than the central structure [41] and that free rotation around alcohol substituents relative to the aliphatic chain of dicarboxylic acid plays an important role in the effectiveness of the plasticizer. The results were obtained by comparing the properties of plasticizers based on succinic and maleic acids with linear side chains in the C_4 – C_8 range. The structure of alcohol in the diester molecule has a huge effect on the plasticizing properties of esters. However, the branched structure of the alcohol group and the presence of an ethyl branch does not increase the mechanical characteristics of PVC compositions with an ester content.

Stuart, A. et al. [42] investigated a number of succinic acid esters and showed that succinates with longer alkoxy chains are as effective or more effective than DOP for plasticizing PVC in terms of percentage by weight.

The incorporation of plasticizers into PVC formulations is crucial for modifying a polymer's structure and enhancing its properties [43]. This targeted alteration results in improved rheological and physico-mechanical characteristics, including strength, frost resistance, brittleness, hardness, melt flow index, toughness and overall manufacturability. Additionally, thermal and electrophysical properties are also positively impacted by these modifications. Research indicates that the manufacturability of PVC compositions is primarily evaluated through the rheology of the melts. A widely accepted method for assessing the recyclability of these polymers is through the measurement of the melt flow index (MFI). This critical indicator helps determine the appropriate temperature range for processing the polymer composition, ensuring optimal conditions for its application. Recent studies have demonstrated that the effectiveness of plasticizers is influenced by their chemical structure and their capacity for conformational changes, as well as their thermodynamic compatibility with the polymer matrix. For instance, different plasticizers exhibit varying degrees of compatibility with PVC, which directly affects their ability to enhance mechanical properties and processing behavior. The choice of plasticizer can significantly alter the fusion and rheological behavior of PVC compounds, impacting their

final physical properties and usability in various applications. The influence of the structure and concentration of the developed dibutoxyethyl adipate, dibutoxypropyl adipate and diphenoxylethyl adipate on the flow temperatures of PVC compositions in comparison with the commercially available plasticizers DOP and DOA was studied (Figure 7).

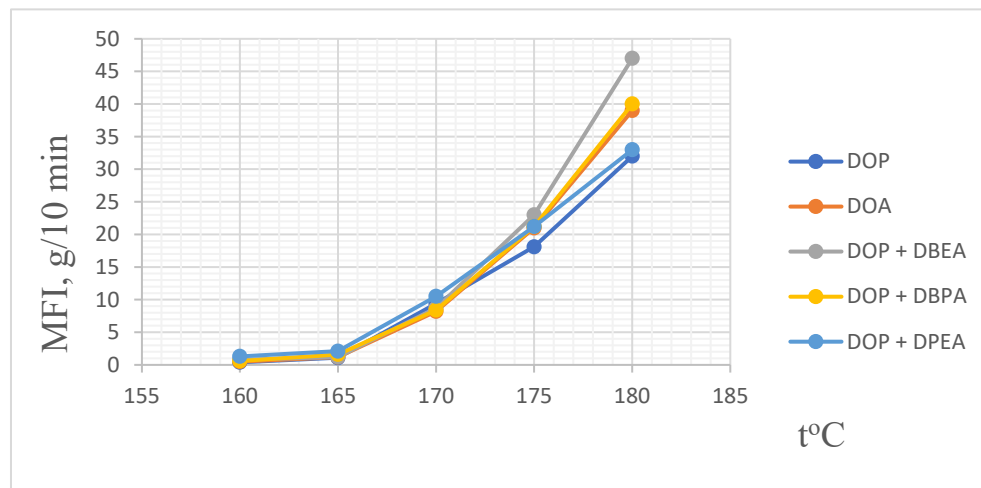


Figure 7. Dependence of the MFI of PVC composition on temperature.

To assess the rheological characteristics of plasticized PVC formulations, the melt flow index (MFI) serves as a critical parameter. This index is commonly utilized to evaluate the recyclability of polymer materials and to inform processing method selection. In this study, we investigated the rheological properties of PVC compositions that included a blend of dioctyl phthalate (DOP) plasticizer and various adipate mixtures. Specifically, a DOP to adipate ratio of 5:1 (by weight) was employed in preparing the PVC composition.

The temperature-dependent behavior of the MFI for these PVC compositions was analyzed under the following formulation (in weight hours): PVC—100; plasticizer—100; TBLS (tertiary butyl lithium sulfate)—1. The composition of the plasticizer was as follows: DOP—83.3; adipate—16.7. The applied load during testing was set at 49 N (Figure 4).

This investigation highlights how different plasticizers, particularly those based on adipic acid, can significantly impact the flow characteristics and processability of PVC composites. Previous studies have shown that the introduction of environmentally friendly plasticizers can enhance the melt flow properties compared to traditional phthalate-based options, indicating a shift towards more sustainable materials in polymer applications.

Experimental studies have demonstrated that increasing temperature significantly enhances the fluidity of PVC melt compositions, independently of their specific formulations, exhibiting a nearly exponential relationship. Notably, the incorporation of DOP with adipates in PVC formulations does not diminish the melt fluidity when compared to similar mixtures containing DOP solely. In fact, mixtures of DOP with esters tend to increase the melt flow index (MFI) of polyvinyl chloride compounds. Among the additives, adipates featuring aliphatic alcohol groups show superior melt fluidity within the examined temperature range. Conversely, compositions utilizing adipate with aromatic alcohol groups display intermediate fluidity values between those of industrial variants like DOA and DOP.

The synthesized derivatives of adipic acid exhibit a pronounced plasticizing effect on PVC, primarily characterized by an enhancement in the fluidity of the PVC melt. This suggests that these adipate derivatives could be advantageous in optimizing processing conditions and improving the performance characteristics of PVC-based materials.

In general, fundamental parameters such as the solubility, compatibility, polarity, molecular weight and functional groups of plasticizers play a crucial role in determining plasticizing properties [44–46]. The structure of the substituent reduces the glass transition

temperature, and the volumetric end fragments separated by a linear chain effectively separate the macromolecular chains of the polymer [47–49].

4. Conclusions

As a result of the synthesis of adipic acid and alkoxyated alcohols of various structures, esters with a yield of more than 87% were obtained. The duration of synthesis is significantly influenced by the structure of the alcohol group in the composition of the adipate, and the maximum duration was observed in the case of the use of aromatic alcohol—phenoxyethanol. The synthesized dibutoxyethyl adipate, dibutoxypropyl adipate and diphenoxyethyl adipate are characterized by the necessary levels of physico-chemical parameters for testing them as promising PVC plasticizers. A preliminary theoretical assessment of the plasticizing effect of diesters in relation to PVC based on the calculation of Hansen solubility parameters showed that the studied compounds have high parametric compatibility with PVC. However, an ether with an aromatic structure stands out markedly in the direction of improving this indicator. The obtained values for the critical temperature of dissolution of PVC in adipates confirm their low migration from PVC plastics, as well as good manufacturability during processing, taking into account the revealed depression of the glass transition temperature. A study of the thermomechanical characteristics of PVC plastics has shown that the expansion of the highly elastic state region for samples containing aliphatic alcohol esters is almost identical to the industrial analogue of DOA and much exceeds the reference plasticizer DOP. In this case, an ether with a branched alcohol structure has the best solvent ability in relation to polyvinyl chloride. In the case of an ether with aromatic alcohol in the composition, the region of the highly elastic state is commensurate with the latter; however, the glass transition temperature of the sample is above zero. Thus, the aliphatic branched structure of the alcohol group of ether significantly improves the effectiveness of its plasticizing action and manufacturability during processing, expanding the temperature range of the highly elastic state, increasing the frost resistance of compositions and reducing the viscosity of polymer melts.

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