Plasticizers and Lubricants of Adipic Ester Type with Complex Structure

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The paper deals with the synthesis and characterization as polymer processing aids, i.e. as plasticizers and/ or lubricants, of some mixed (unsymmetrical) diesters of adipic acid by using aliphatic alcohols of variable length, such as C4, C6, C2-6, izo C10 and izo C13, along with complex aliphatic-aromatic alcohols, like 2-phenoxyethanol, 2-[(o-sec-butyl)phenoxy]ethanol and 2-[(p-nonyl)phenoxy]ethanol, respectively. The diesters derivatives obtained this way showed plasticizing and/or lubricating properties. The variation of such properties was studied by varying the polar / unpolar ratio within each structure of the considered product. Interesting correlations were recorded and the theoretical premises were fully proved.

Keywords: unsymmetrical adipic diesters, plasticizers, lubricants, phenoxy-ethanols

The present paper is a part of an extended programme, started many years ago, through which a large variety of derivatives of esteric type with a complex structure were realized. These synthesized products were examined and evaluated as polymer processing aids, especially as plasticizers and/or as lubricants for polyvinyl chloride processing and as tribological lubricants, respectively [1-9].

Based on the asymmetry and polyfunctionality principles, there were synthesized asymmetric esters by taking into account different acidic structures such as trimellitic, pyromellitic, citric, phosphoric, o-phtalic, adipic and sebacic. The considered principles motivate the anticipated objective of obtaining such compounds which might prove a real versatility, that is to be in a position to show a consistent adaptability capacity as regards the final applicability direction. That means that they might possess adequate properties either as plasticizers, or as lubricants used in the field of polymer processing, or as fluid with specific tribological properties. The polyfunctionality principle expressed mainly by a suitable equilibrium between different functions (esteric, etheric, aliphatic, aromatic ones) of polar or non-polar nature, allows to obtain products which could take part in one or in another classes mentioned above.

The asymmetry principle has also a major importance in order to obtain valid products from an industrial application and/or technological point of view. Even if, one might admit, a product shows remarkable properties in one or in another of the specified directions, but it presents, for instance, some unsuitable physical characteristics, such as an excessive high melting point which signifies that it will present fluidity features that could not be preserved at below 0⁰C too, it will auto-exclude itself from a presumptive utilization by considering its reduced handling capacity.

By realizing unsymmetrical products which posses different functional elements that are able to disturb a hypothetical supramolecular assembling, it will be possible to acquire a proper fluidity even in the negative temperature domain.

These characteristics or one may say "qualities", represent a decisive argument for permitting the use of some derivatives in the tribological field.

These desiderata were carried out by realising ester derivatives using, on the one hand, aliphatic alcohols with the chain length increasing from C3, C4 up to C13 and, on the other hand, taking into account as another alcoholic component some complex hydroxyl derivatives of an aromatic-aliphatic nature. In order to create another perturbation centre of the symmetry of the whole molecule considered, alchilic pendant chains of variable length and on different positions on the aromatic nucleus were admitted.

In this way a molecular ensemble particularly complex becoming able to meet the performance requirements claimed by the different applicability directions was created.

The literature of the last years records a similar interest, assuming, for sure, appropriate approaching ways of these objectives.

Thus, the synthesis of a cold resistant plasticizer of an adipic mixed ester type based on n-octyl and n-decyl alcohols is reported [10]. The mixed ester was realized through a direct esterification process between adipic acid and n-octyl and n-decyl alcohols. The influence of the synthesis parameters on the yield was mainly studied, that is the effect of the reaction temperature, time, level of the catalyst amount and the ratio between the raw materials. The optimum conditions determined were: reaction temperature 210⁰C, reaction time 45 minutes, mass ratio of the mixture of n-octanol and n-decanol to adipic acid was 3.88, using 1.2g catalyst based on 20.2g adipic acid; the mixed adipic ester yield was 95.5%.

The synthesis and evaluation of the performance of a mixed glycidyl ethyl hexyl phthalate considered as a novel plasticizer for polyvinyl chloride films was reported in another elaborated study [11]. It was emphasized that in order to improve the processability and prevent the thermal degradation of PVC, various plasticizers and heat stabilizers have to be compounded. Phtalic plasticizers and metal soap stabilizers are usually used with epoxides as co-stabilizers. Epoxidized soybean oil (abbreviation ESO) is one of the most commonly used epoxides because of its

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typical combined roles as a plasticizer and heat stabilizer in PVC compounds. ESO, however, sometimes causes surface contamination of PVC compounds because saturated fatty acids such as stearic and palmitic acids in soybean oil easily bleed into surface. In addition, some ingredients in ESO with hydroxide groups and unreacted double bonds during epoxidation, also tend to increase the bleeding of ESO. This is due to their low compatibility with PVC resins. In this study a novel plasticizer of PVC resins like glycidyl ethyl hexyl phthalate was synthesized and its performance was evaluated with the purpose to overcome the deficiencies mentioned above. This plasticizer was designed to act as normal phtalic plasticizers and also to act as a heat stabilizer like ESO. Through the addition of epoxy groups in phtalic compounds, the resistance to bleeding was improved, and the plasticizing and heat-stabilizing effects in PVC compounds were preserved. The mechanical properties, thermal stability and bleeding properties of the films were investigated [11].

In the same synthesis direction of esters with a mixed structure (that is: asymmetric) the realization of some citric esters by using alcohol mixtures was reported. In this way a new type of additives, which belong to the class of plasticizers that are adequate for a large variety of polymers, was obtained. The alcohol mixture is defined as Nacol type fatty alcohols. LINPLAST 46 HCT showed compatibility with PVC [12].

An interesting concept regarding the plasticizer domain, is reported by a japonese patent. In this work the mentioned plasticizers are manufactured from polyhydric alcohol (I)-alkylene oxide (II) adducts with I/II molar ratio 1/3-1/15, and monocarboxylic acids. The example provided claims the use of an ester of octanoic acid with an glycerin-ethylene oxide 1:8 adduct, ester used to plasticize a methyl methacrylate-butyl methacrylate copolymer. Thus, 100 parts of the mentioned copolymer was kneaded with 100 parts plasticizer to give a paste, which was cast on a glass sheet to give a sheet showing no bleeding before and after storage at 50⁰C and relative humidity 95% for 14 days, shape recovery 91% after stretching 50% in the longitudinal direction, and good impact absorbing property [13].

The plasticization of some special polymers, like poly(lactic acid) (abbreviation PLA), by the help of oligomeric malonate ester amides, constitutes the subject of a paper which reports the decreasing of the glass transition temperature of films resulted by compounding PLA polymer with the mentioned plasticizers [14]. Two oligomeric malonate ester-amides and an oligomeric malonate ester were synthesized. The synthesis was performed by reacting di-ethyl-bis hydroxymethyl malonate (abbreviation DBM) with adipoyl dichloride and one of two diamines, i.e. triethylene glycol diamine (TA) and polyoxypropylene glycol diamine (PA), or triethylene glycol (TEG), giving three plasticizing agents denoted as DBMATA, DBMAPA and DBMMAT, respectively. The synthesized products were characterized by size exclusion chromatography and Fourier transform IR spectroscopy, and blended with PLA at a concentration of 15 wt%. Dynamic mechanical analysis, differential scanning calorimetry and tensile testing were used to investigate the physical properties of films from the resulting blends. All three plasticizers decreased the glass transition temperature of PLA, and the largest decrement was observed for PLA/DBMATA. Films of DBMATA and DBMAT showed enhanced flexibility in strain at break as compared to neat PLA. Subsequently, it was found that thermal annealing of the plasticized materials (4h at 100⁰C)

encouraged cold crystallization, inducing phase separation in the blends and caused them to regain the brittleness of neat PLA. On the other hand, by aging (6 weeks) the blends at ambient conditions, cold crystallization could be avoided and the flexibility of the films maintained [14].

In a Chinese patent the realization of plasticizers that have excellent compatibility with polyvinylbutyral resins is reported. Thus, aliphatic dicarboxylic acid bis(alkoxy dietylene glycol) esters with the general formula: $R(OCH_2CH_2)_2OOC-(CH_2)_n-COO-(CH_2CH_2O)_2R$, where R = C1-10 alchyl and n = 4-6, were obtained. Such compounds show low volatility and can be used as plasticizers [15].

Japanese researchers report the realization of some ester type plasticizers with a complex structure which show a low level of volatility, possess biodegradability character and present also a decreased bleeding out. By using such plasticizers in order to plasticize polyester compositions, the films obtained under these conditions show a good transparency. The plasticizers with acetylation ratio $\geq$ 50% comprise acetic esters of polyhydric alcohol-alkylene oxid adducts. Thus, a composition containing polylactic acid (Lacea H 440) and 20 phr plasticizer prepared by reacting 1.1 mol glycerol with 11 mol ethylene oxide, then with 1.6 mol acetic anhydride, was extruded into 1 mm thick sheet, showing tensile strength 13.2 MPa, tensile modulus 14.9 MPa (JUS K 7113) and a weight loss 0.3% after storing at 50⁰C for a week [16].

The literature review of the very last period of time permits to withdraw some very interesting conclusions. Though many remarks are recorded referring to the most used plasticizer in the field of PVC processing, which is di-2 ethyl hexyl phthalate (DOP), especially in connection with its assigned cancerous activity (very difficult to prove, however), and it is currently suggested to replace it by vegetable-oil based plasticizers, at least in the field of food packaging and food-contact materials [17], many studies which deal with the synthesis of DOP under optimum conditions and by using catalyst systems more and more performing are reported [18]. The suggested catalyst was $TiSiW_{12}O_{40}-Al_4(SiW_{12}O_{40})_3 / TiO_2-Al_2O_3$. This catalyst showed many advantages, for example it decrease the corrosion of equipment and the pollution in the environment, and has higher esterification activity and selectivity. The treatment of products is simplified and the catalyst may be used repeatedly. The reaction conditions recommended were the following: molar ratio of alcohol to anhydride 2.25:1; the amount of catalyst 1.78% related to the alcohol and acid anhydride mass; the reaction temperature 150⁰C and the reaction time 2.5 h [18].

Another team of Chinese researchers suggested the use of a nano solid superacid SO_4^{-2} / Fe_2O_3 catalyst for the synthesis of di-2ethyl hexyl phthalate [19]. The nano solid superacid SO_4^{-2} / Fe_2O_3 was prepared under specific conditions, and its catalytic activity for the synthesis of DOP was studied and was compared to the catalytic activity of normal SO_4^{-2} / Fe_2O_3, SO_4^{-2} / TiO_2, SO_4^{-2} / ZrO_2 and H_2SO_4. At the same time, the factors affecting the esterification process, such as the manner of the catalyst synthesis, the dosage of the catalyst and the esterifying time, were studied and the optimum synthetic conditions were obtained. The appropriate conditions were as follows: weight of the catalyst was 2.8g (weight of phtalic anhydride was equivalent to 1.0 mol), molar ratio of 2-ethyl hexanol to phtalic anhydride was 2.5:1, reaction time was 2.0h, reaction temperature was 150⁰C. The yield of the ester was over 99.1%. The catalyst could be used many times without any treatment and without any pollution action on the environment. Comparing with normal catalysts, the nano

solid superacid catalyst had obvious advantages [19].

In the same way it is reported the synthesis of di-2 ethyl hexyl sebacate by using a solid superacid catalyst of SO_4^{-2} / TiO_2-Al_2O_3 type. Under optimum conditions, the product yield reached 98.5% using the mentioned catalyst [20].

Exxon firma suggests the use of nonyl alcohols less branched in order to synthesize adequate plasticizers. Thus, less branched C9 alcohols are used to provide plasticizer trimellitate esters particularly suitable for high temperature applications such as wire and cable insulations. These less branched plasticizers are more economical compared to current commercial products [21].

The synthesis of diisopentyl maleate plasticizer was performed by using an aminosulfonic acid catalyst, through the esterification of maleic anhydride with isopentanol. Under optimum conditions the product yield reached 93.7% [22].

Since di-isononyl phthalate (DINP) became the competing rival of di-2 ethyl hexyl phthalate (DOP), based on more or less solid reasons, many studies are reported in which a quantitative determination of DINP in PVC plastics is attempted. The proposed method, i.e. the partial least square method, was applied under specific circumstances. The linearity of the studied sample curves is very good, with the correlation coefficient of 0.9999. This method is simple, reliable, rapid, free of the influence of the substrates and suitable for the quality control of line production [23].

The realization of biodegradable plasticizers constitutes an actual problem of large interest, this domain being constantly explored. Consistent reviews are reported [24], in some instances being suggested more or less ingenuous solutions, like the one which claims the possibility to obtain biodegradability properties by mixing 10-25% plasticizers with 60-85% starch [25].

The world-wide concern referring to the disposal of different waste material in the surrounding, the effect of chemistry on nature, is expressed in numerous studies, for instance the influence of lubricants on global environment is reviewed [26].

In the research frame exposed in the preamble of this paper are inscribed, as we have already mentioned, different approaching alternatives such as the synthesis of some adipates based on 3-(4'-methylcyclohexyl) butanol. It was stated, exactly within the spirit of our researches, that the di [3-(4'-methylcyclohexyl) butyl] adipate presents a low pour point and can be used as either lubricant or plasticizer for thermoplastics [27].

Japanese scientists report the realization of a synthetic ester lubricating base oil for refrigeration devices obtained by esterification of a mixed alcohol and a mixed carboxylic acid, in which the ester has a hydroxyl value of ≤ 5.0 mg KOH / g an acid value of ≤ 0.05 mg KOH / g and a kinematic viscosity of 30-1500 mm²/s at 40⁰C. The mixed alcohol is composed of 65-99.95 mol % pentaerythritol and 0.05-35 mol % dipentaerythritol; the mixed carboxylic acid is composed of 25-55 mol % of a C5-C8 monocarboxylic acid 45-75 mol % isononanoic acid (especially 85.50-99.95 mol % 3,5,5 trimethyl hexanoic acid). The lubricating composed is suitable for a refrigeration unit using a chlorine–free hydrofluorocarbon [28].

The possibility to obtain a refrigerator lubricating base oil, in the same direction of investigation, is reported. The base oil comprises mainly synthetic esters prepared by reacting pentaerythritol having carbonyl value of ≤ 50 μmol/g with saturated C4-C18 fatty acid to obtain the ester product having Na content ≤ 100 ppm and ash content

$\leq 0.02\%$ wt%. The pentaerythritol ester base oil is superior in lower degree of coloration, high thermal resistance and lubricity [29].

Grease base oil is realized also by some Japanese researchers. Thus, the base oil contains ester of trivalent alcohol with fatty acid or trimethylol propane with fatty acid and has a viscosity of ≤ 9000 mPa.s at -40⁰C, a pouring point of $\leq -40⁰C$, a volatilization volume of $\leq 35\%$ wt % after heating at 180⁰C for 500 h, and a viscosity index of ≥ 130. The product has excellent lubricity, especially at low temperatures [30].

As regards our specific frame of investigation one can mention the researches performed by some other scientists, such as by Gryglewicz et.al [31-33], which have reported the results of studies accomplished on the synthesis and biosynthesis of adipic and sebacic esters with biodegradability character and considered as base oils.

As a result of our attempting approach in order to analyze the results published in the last period of time by the specialty literature, we have succeeded to define more properly our specific way of investigation. We have reported a series of results obtained under these circumstances, the latest referring to the sebacic esters [34].

In the same way we have started the present study with the aim to realize asymmetric (or unsymmetrical) adipic diesters by using alcohols with a complex structure of an aliphatic-aromatic type, namely 2-phenoxyethanol, 2-[(o-sec butyl)phenoxy]ethanol and 2-[(p-nonyl) phenoxy] ethanol, respectively, in conjunction with aliphatic alcohols with short and long chain, such as n-butanol, n-hexanol, 2-ethyl-hexanol, isodecanol and isotridecanol.
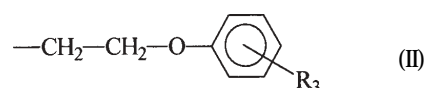
The adipic diesters built under these circumstances are defined by the general formula (I):

$$R_1OOC\text{-}(CH_2)_4\text{-}COOR_2 \qquad (I)$$

where:

R_1 = n-butyl, n-hexyl, 2-etyl hexyl, isodecyl and isotridecyl radical

R_2 = radical with the following structure defined by the general formula (II):

$$\text{—}CH_2\text{—}CH_2\text{—}O\text{—} \hexagon\text{-}R_3 \qquad (II)$$

where R_3 = H, o-sec-butyl and/or p-nonyl.

By taking into account the complex alcohols with an aromatic-aliphatic structure, three groups of asymmetric adipic diesters have been synthesized.

Through the analysis of the structures promoted by the general formula (I) it is possible to observe an evident complexity characteristic of compounds, in which the polyfunctionality and asymmetry are obvious. Thus, besides the existence of esteric groups, which respond mainly to the promotion of the compatibility characteristics with the base polymer, can be also remarked the presence of some etheric bridges of an alkyl-aryl type which intensifies the same character. The polarizable aromatic cycle may increase, to a certain extent, this feature. The aliphatic pendant chains on the aromatic ring may produce more perturbance of the molecule symmetry, becoming a supplemental asymmetry factor, beside that one induced by the lack of symmetry of the considered adipic ester. This fact results from the use of an alcohol with a progressive increasing chain length as a co-esterification partner.

Under these circumstances, there are provided sufficient variables in order to allow to obtain a large interval of values both as for the intrinsic physico-chemical characteristics of the derivatives themselves, and as referring to the specific properties of a processing polymer aid and/or of a tribological lubricant.

Depending on the ratio of the polar to the non-polar functions, one may record either plasticizer qualities or lubricant ones, features which can be turned to good account especially in the polyvinyl chloride processing, which still represents the most important example in the field.

In the case of derivatives which contain a large quantity of alkylic-chain, one may render profitable the specific properties of fluids which can be used in the tribological domain. The results of these researches were published both in the country [35] and abroad [36].

Experimental part

The alcohols used for the realization of the asymmetric adipic esters present a complex structure of an aliphatic-aromatic nature, and they were synthesized by using a special ethoxylation alternative, namely through the reaction of 1,3 dioxolan-2-one (ethylene carbonate) with the adequate phenols, according to our procedures patented and published previously [37].

The principal physico-chemical values recorded for these complex alcohols are the following:

2-phenoxy-ethanol; molecular formula $C_8H_{10}O_2$; molecular mass, M = 138; density, d = 1,109 g/cm^3; refractive index, n_D^{20} = 1,5370.

2-[(o-sec-butyl)phenoxy]ethanol, molecular formula $C_{12}H_{18}O_2$; molecular mass, M = 194; density, d = 1,0164 g/cm^3; refractive index, n_D^{20} = 1,5175.

2-[(p-nonyl)phenoxy]ethanol, molecular formula $C_{17}H_{28}O_2$; molecular mass, M = 264; density, d = 0,978 g/cm^3; refractive index, n_D^{20} = 1,5113.

The aliphatic alcohols used: n-butanol, n-hexanol and 2-ethyl-hexanol were pure samples and they were provided by Merck; and isodecanol and isotridecanol by BASF (Germany), respectively.

The synthesis of the unsymmetrical adipic diesters was performed in a solution esterification process, using p-toluensulfonic acid as catalyst, the water being extracted azeotropically by means of a solvent (usually toluene), according to our similar (standard) procedures formely described [38], and in conformity with an elaborated stoichiometry, on the basis of a precisely established method for this particular case [39].

The synthesized and purified adipic diesters were characterized by chemical and physical indices specific to this class, while the tipical properties which define the polymer processing aids were determined in accordance with the standardized testing techniques in the field. Thus, the dynamic viscosity was measured by means of a Rheotest device, RV type (VEB Prüfgeräte-Werk, Medingen / Dresden), the critical solving temperature (the TCS criteria, or KLT, Kritische Lösung Temperatur, nachThinius) was determined by the use of a Boetius microscope equipped with a heating plate, on a suspension PVC, Kw = 67. The gelifying power was recorded with the help of a Brabender plastograph, PL/3S type, using the standard receipt, that is PVC (suspension) Kw = 67 (100 : 3) p; plasticizer (50 : 3) p; stabilizing agent basic: lead stearate (0,6 : 3) p; rotation speed 50 rot/min; 50 cm^3 vat; measuring domain (1 : 5) . 5; temperature 160^{0}C.

In order to realize the sheet out of which the test-pieces (samples) were punched for the determination of the

performance and efficience properties, the standard receipt was used, namely: PVC (suspension), Kw = 67, 100 p; plasticizer, 50 p, stabilizing agent: Ba-Cd stearate, 2 p; the mixture was processed (rolled-laminated) on a mini-roll during 5 min, at 160^{0}C, friction coefficient 1 : 1,2. The samples for the tensile strength test were realized by using a punching die according to SR EN ISO 2898-2:2003. The samples for the determination of the performance level were round with a 5 cm diameter.

The lubrication number was calculated on the basis of the Bötner-Rosenthal relationship (equation):

$$C_L = 1000 \ \frac{E}{T \cdot m_D}$$

where:

C_L = lubrication number,

E = total quantity of ingredients expressed as procentage of the PVC quantity,

T = temperature of the vat, ^{0}C.

m_D = the minimal couple, Kg.m,

The values of the minimal couple were extracted from the Brabender plastogram recorded on the same device, with the difference that for this essay an adequate receipt was used, that is: PVC (suspension) Kw = 67, 100 p; tribasic lead sulphate (stabilizer without any lubricating effect), 2 p; lubricant 1 p; the amount of the receipt was reduced at the level of 30 p PVC, using the vat of 30 cm^3, the domain 5; rotation 30 rot/min, and at a temperature of 160^{0}C.

The flash (flammability) point was measured according to ASTM D 92 and the pour (flow) point according to ASTM D 97.

Note. In order to facilitate the reading of tables and make easier the identification of products and reading of tables, a coding system was used involving an abbreviation principle for the respective diesters. Thus, 2-phenoxy-ethanol is identifiable as FE (phenol-ethoxylated); 2-[(o-sec butyl)phenoxy]ethanol as OSECBUT; 2-[(p-nonyl)phenoxy]ethanol as p-N. Similarly, n-butanol is described as BUT, n-hexanol as HEX, 2-ethylhexanol as 2EH, isodecanol as IZO 10 and isotridecanol as IZO 13. Accordingly, the following unsymmetrical adipic diesters were obtained: (A) BUT-p-N, HEX-p-N, 2EH-p-N, IZO 10-p-N and IZO 13-p-N; (B) BUT- OSECBUT, HEX- OSECBUT, 2EH -OSECBUT, IZO 10-OSECBUT and IZO 13-OSECBUT; (C) IZO 10-FE and IZO 13-FE.

Results and discussion

The main chemical and physical indices of these unsymmetrical adipic diesters are presented in table 1. The analysis of the data inscribed in this table permits to withdraw the following considerations:

- the molecular mass presents values ranged within an interval of 378 and 574 mass units. The values recorded show that these realized compounds are placed into a middle category between the classical (standard) plasticizers with a relatively small molecule, such as di-2 ethyl-hexyl adipate (DOA) or di-2 ethyl-hexyl phthalate (DOP), and polymer plasticizers, which consist especially of polyesters with a larger molecular mass;

- density constitutes another parameter which expresses the variability of the realized structures, a remarkable correlation being ascertained. Thus, within the frame of each group a decrease of the values was recorded as the chain length of the considered aliphatic alcohol increases. The comparison of the groups with one another, also reflects the influence of the structure upon the density values. One may observe the fact that the derivatives built on the basis of the alcohol with an aliphatic-aromatic structure but without an alkyl pendant group on the aryl

Table 1

Table 1
VALUES OF THE MAIN PHYSICAL AND CHEMICAL CONSTANTS

Characteristic / Adipate code	Molecular formula	Molecular mass M	Density g/cm^3 d	Refractive index n_D^{20}	Dynamic viscosity mPa.s
BUT-p-N	$C_{27}H_{44}O_5$	448	0.9963	1.4872	89.13
HEX-p-N	$C_{29}H_{48}O_5$	476	0.9866	1.4833	77.17
2EH-p-N	$C_{31}H_{52}O_5$	504	0.9728	1.4831	95.72
izo 10-p-N	$C_{33}H_{56}O_5$	532	0.9715	1.4830	113.67
izo 13-p-N	$C_{36}H_{62}O_5$	574	0.9596	1.4824	113.92
BUT-OSECBUT	$C_{22}H_{34}O_5$	378	1.0282	1.4884	34.64
HEX-OSECBUT	$C_{24}H_{38}O_5$	406	1.0075	1.4810	27.18
2EH-OSECBUT	$C_{26}H_{42}O_5$	434	0.9927	1.4803	41.64
izo 10-OSECBUT	$C_{28}H_{46}O_5$	462	0.9818	1.4790	36.34
izo 13-OSECBUT	$C_{31}H_{52}O_5$	504	0.9696	1.4782	46.74
izo 10-FE[*]	$C_{24}H_{38}O_5$	406	1.0002	1.4773	-
izo 13-FE[*]	$C_{27}H_{44}O_5$	448	0.9726	1.4760	-

* Slow crystalization tendency in time

nucleus, present the highest density values; these values decrease as a substituent with a progressive length is introduced on the aromatic ring. The remarkable succession of this parameter certifies, on the one hand, the validity of the theoretical structures suggested, and, on the other hand, emphasizes the high level of purity of the products;

- the refractive index follows in all respects a similar variation. At this point one can notice that this parameter is able to present different values, i.e. it is in a position to discern or to differentiate the products even in the situation of a variation of 2-3 carbon atoms, by having in view that we deal with complex molecules and relatively large ones, which contain between 24 and 36 carbon atoms;

- the values of the dynamic viscosity are generally small for all the terms of these groups. It is difficult to establish a distribution rule of the values in the case of this parameter. It is obvious that the multitude of functions induces this character but one may say that especially those of aliphatic and aromatic type, manifest the most pregnant influences with a reciprocal reverse effect;

Note. The viscosity index values, which is an important parameter in terms of defining the attributes of a tribological fluid, are placed around a value of 100, a remarkable level of performance, such results were reported in our previous paper regarding the lubricity properties within the frame of tribological features of these unsymmetrical adipic diesters [36].

In order to proceed to define the processing polymer aids properties, either as a plasticizer or as a lubricant, the calculation of the values of the solubility Hildebrand parameter δ, is desirable. Even if this criterion is not instituted as a measure (index) of compatibility, it offers, however, an indication in this sense, being considered a predictor parameter.

The values of this parameter calculated on the basis of small constants and on the main physico-chemical

characteristics, are presented in table 2, according to the calculation method provided by the literature [43]. For a better understanding the aspects revealed by this parameter, the δ values of PVC and of the most representative primary and secondary classical plasticizers, that is for DOA and DOP, are also mentioned. The analysis of the data inscribed in this table, permits to observe a very close value level to that of the standard samples. Many values are even better than that of DOP, and all are better than the DOA value. From this point of view one may admit that the anticipated compatibility level would be plainly superior to DOA and close to DOP. Within the framework of each group, the δ values decrease as the length of the aliphatic alcohol used increases. This aspect means a reduction of the compatibility which is fully explicable by the fact that the polarity level implicitly diminishes.

The effective level of compatibility was estimated by measuring the critical solving temperature, the TCS criterion, and by defining the gelification capacity which was evaluated from the maximum couple values of the Brabender plastogram and also by the shape of the registered curve itself.

The values of these measurements are presented in table 3. From the data inscribed in this table, as regards the TCS criterion, results a secondary plasticizer character for the quasi-all tested terms, with the exception of the izo 10-FE example which presents a primary plasticizer TCS value. However, the maximum couple values indicate a superior compatibility level which is similar to that of primary plasticizers at least for the terms without an alkyl-pendant chain (series FE) and also for those diesters built on the basis of OSECBUT, that is an isobutyl rest which means a relatively short aliphatic chain,. The shapes of the effective curves recorded by the Brabender plastograph are in a position to establish with no doubt the plasticizing character, either as primary or as secondary. On the basis

Table 2

HILDEBRAND δ SOLUBILITY PARAMETER VALUES, CALCULATED ON
THE BASIS PHYSICO-CHEMICAL CHARACTEISTICS AND SMALL
CONSTANTS

Characteristic Adipate code	Hildebrand δ solubility parameter, $[cal/cm^3]^{1/2}$
PVC	9.660
DOF	8.830
DOA	8.472
BUT-p-N	8.977
HEX-p-N	8.918
2EH-p-N	8.772
izo 10-p-N	8.785
izo 13-p-N	8.709
BUT-OSECBUT	9.106
HEX-OSECBUT	8.968
2EH-OSECBUT	8.819
izo 10-OSECBUT	8.759
izo 13-OSECBUT	8.697
izo 10-FE	8.8934
izo 13-FE	8.7034

of these registered plastograms one may observe that all terms of series p-N and the last term of OSECBUT series belong to the secondary plasticizer class with shapes quasi-similar to that of DOA, while the rest of terms, that is series OSECBUT and FE, present curves similar to that considered for a primary classical plasticizer, that is DOP.

The second defining attribute which is taken into consideration in order to establish the qualities of a polymer processing aid is represented by the efficiency criterion.

The data that express this criterion are registered in table 4, that is the Shore hardness and the results derived from the tensile strength test. One must mention the fact that in this table only the values of the terms which have permitted to extract a sheet from the mixing mill are presented; the terms izo 13-p-N and izo 13-OSECBUT, which possess a large quantity of alkylic chain, did not permit this fact, indirectly proving a reduced compatibility level but implicitly suggesting aptitudes for the lubricants domain.

One can observe that the tensile strength (at break) presents very good values indeed, much better than those of the standard samples considered, while the elongation at break are almost equal with those of DOA and DOP. The 100% modulus values are in some cases very good and equivalent with those of DOA (excellent in this sense), in another cases the values are much poorer.

The Shore hardness values are comparable with those of DOP for the groups (series) with a reduced amount of alkylic pendant chain on the aromatic nucleus (series OSECBUT and FE), while the terms of the group p-N present a higher level of hardness, which means an adverse efficiency.
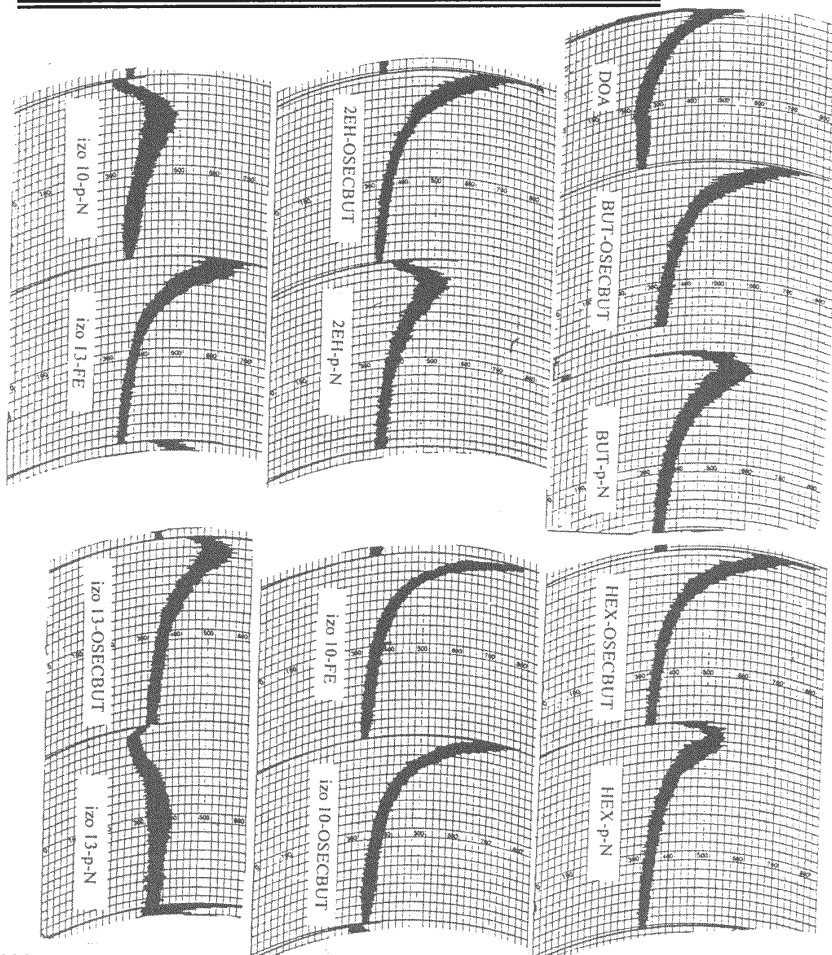

Fig. 1. Brabender plastograms for gelification
power determination

Table 3
COMPATIBILITY CRITERION

Characteristic / Adipate code	TCS, ^{0}C	Maximum couple from the Brabender plastogram, N.m
DOA	134-135	26.49
DOF	117-118	37.27
BUT-p-N	147-149	26.00
HEX-p-N	147	26.00
2EH-p-N	156-159	23.54
izo 10-p-N	155-158	22.56
izo 13-p-N	163-165	17.66
BUT-OSECBUT	136-138	34.58
HEX-OSECBUT	133-135	35.32
2EH-OSECBUT	141-142	34.33
izo 10-OSECBUT	140-141	35.80
izo 13-OSECBUT	145-148	25.50
izo 10-FE	126-128	37.77
izo 13-FE	140-141	31.39

Permanence defining constitutes the third fundamental attempting approach in order to settle the plasticizer qualities. The due values of this criterion are recorded in table 5.

The migration resistance, that is the resistance leaving the system by exposing the sample in contact with a solid surface, is estimated. The resistance against the extraction with oil and water was also examined. All products tested under these circumstances proved a very good migration resistance, the values recorded being situated within the limits presented by the majority of the most used common plasticizers. Water and oil extraction resistance is also very good, at the same level being situated water absorption tendency.

These tests prove a strong anchoring of these unsymmetrical adipic diesters in the polymer, a fact which induces implicitly a superior level of performance.

Having in view the interpretation of the structural aspects mentioned in the preamble of this paper, one may consider the fact that there are enough structural elements within these diester models, especially of aliphatic nature, which are a position to allow the development of lubricant qualities useful in the field of polymer processing.

Therefore we proceeded to check the lubricity capacity expressed by the lubricant number, which was calculated by using the couple values deduced from the Brabender plastograms recorded under previously expressed conditions.

Figure 2 presents the respective diagrams, while in table 6 the values of the lubricant number are listed in accordance with the mentioned relationships. From the values registered one may remark that a relatively little variation exists as regards to the lubricity effect expressed by the lubricant number. This fact may be explained by the large dimensions of the considered molecule, and also by the great content of aliphatic function, respectively, other structural elements not being able to express a semnificative influence. The lubricant number values determined in this way allow to include the tested compounds within the internal lubricants category ($c_L < 20$).

From the same table we can withdraw another two attributes especially important in the sense of defining the valuable qualities of these compounds, expressed by the effective end use directions, either as lubricants for polymer

Table 4
EFFICIENCY CRITERION

Characteristic / Adipate code	Shore A hardness [^{0}Sh]		100% modulus [kgf/cm^2]	Tensile strength, σ [kgf/cm^2]	Elongation at break, %
	3″	10″			
DOF	83	80	65.74	149.27	317
DOA	68.6	65.33	82	192	333
BUT-p-N	86.66	85.33	157.9	230.15	277
HEX-p-N	87.66	87	122.05	193.62	332
2EH-p-N	89.66	89	267.85	426.07	324
izo 10-p-N	90	89	72.85	111.75	477
BUT-OSECBUT	78	75.66	103.6	221.25	324
HEX-OSECBUT	80.33	79	69.91	143.75	310
2EH-OSECBUT	82.33	80.66	100.62	193.70	300
izo 10-OSECBUT	83	81.33	58.57	105.14	513
izo 10-FE	80.33	78.66	51.56	102.50	525
izo 13-FE	85.66	84.33	61.47	111.03	517

Characteristic / Adipate code	Resistance to Migration (against rubber), %, - 24h / 70°C	Resistance to Water, 24h / 20°C		Resistance to Oil extraction, %, - 168h / 20°C
		Absorption, %, +	Extraction %, -	
DOF	0.9486 - 1.9691	0.3374	0.0309	- 0.044
DOA	2.6571 – 4.2252	1.5588	3.4222	4.143
BUT-p-N	2.0774 - 2.1565	0.4045	0.4303	- 0.263
HEX-p-N	1.9866 - 2.2877	0.8222	0.3900	0.277
2EH-p-N	1.2987 – 1.2626	0.5822	0.3214	0.385
izo 10-p-N	3.3094	2.8047	0.8215	-0.1460
BUT-OSECBUT	1.4885 – 2.7943	0.8900	0.4065	0.926
HEX-OSECBUT	2.2519 – 2.9560	0.5628	0.2943	0.906
2EH-OSECBUT	1.3269 – 2.3710	0.3541	0.195	0.471
izo 10-OSECBUT	1.5472	2.5668	0.4810	-0.3989
izo 10-FE	3.3660	1.5479	0.3189	0.1321
izo 13-FE	2.7672	0.7638	0.2516	0.5628

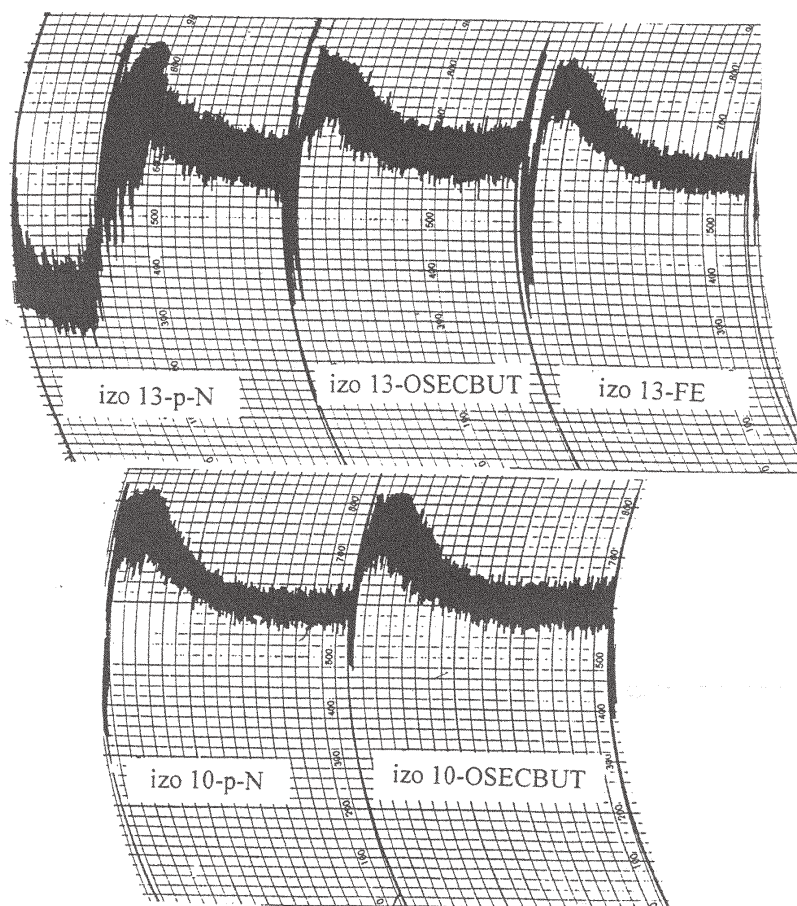**Table 5**
PERMANENCE CRITERION

Fig. 2. Brabender plastogram for lubricant number determination

Table 6

LUBRICATION NUMBER, AT 160°C

Characteristic / Adipate code	Minimum couple from Brabender plastogram, kg.m	Lubrication number, C_L	Pour (flow) point, ^0C	Flash point, ^0C
izo 10-p-N	2.31	8.11	<-42	225
izo 13-p-N	1.4	13.39	<-42	238
izo 10-OSECBUT	2.35	7.97	<-42	212
izo 13-OSECBUT	1.8	10.41	<-42	224
izo 10-FE	1.95	9.61	-	202
izo 13-FE	1.6	11.71	-	202

processing or as tribological lubricants.

Firstly, one may remark the very low values of the pour (flow) points which are below -42°C (in fact a level due to the minimum cooling capacity of the testing devices), aspect that constitutes a particularly valuable feature. One cannot record a significant variation of these values as a function of the considered structure.

Secondly, the flash point presents, generally, values above 200°C, a slight increase with the increase of the molecular mass being recorded. This parameter is also able to certify an optimum level which is in a position to recommend the use of these products in different applicable directions.

Conclusions

On the basis of the **polyfunctionality** and **asymmetry** principles, series of unsymmetrical adipic diesters were realized by taking into account special alcohols with a complex aliphatic-aromatic structure, namely 2-phenoxy-ethanol, 2-[(o-sec-butyl)phenoxy]ethanol, 2-[(p-nonyl)phenoxy]ethanol, respectively, along with aliphatic alcohols with an increasing chain length, that is n-butanol, n-hexanol, 2-ethyl-hexanol, isodecanol and isotridecanol.

By relying on these principles and depending on the realized structures, one may study both the progressive increase effect of the alkyl chain brought in by the aliphatic alcohol and the influence of the aliphatic-aromatic alcohol nature on the whole characteristics of this class of compounds, considered able to be used as polymer processing aids.

On the basis of polar to nonpolar fraction ratio, it became possible to record either typical plasticizer properties, primary or secondary ones, or lubricant features, both attributes being entitled to suggest the use of these derivatives especially for polyvinylchloride processing.

In the case of estimating the possibility to turn to good account the plasticizing properties, the recorded values level of the compatibility, efficiency and permanence criteria, lie within the specific performance interval.

The usefulness of this class of compounds in the tribological lubricant domain, was certified by specific analyses for this field of investigation, while the results of these attempting approaches were presented in different international congresses and were also published in specific journals.

This class of unsymmetrical adipic diesters represents a priority, not being previously reported in the literature, and the intrinsic structure, the synthesis conditions and also the purification and characterization methods, were protected by patents. Through a global valuation of all aspects of this attempt, the theoretical premises which grounded the elaborated research program were fully validated, and a doubtless applicability perspective of this class of compounds could be anticipated.

References

1.MIRCI, L.E., BORAN, S., Mat. Plast., **42**, nr. 2,2005, p. 124
2.MIRCI, L.E., BORAN, S., Mat. Plast., **42**, nr. 1, 2005, p. 47
3.MIRCI, L.E., BORAN, S., Brevete române°ti RO 116 961, RO 118 951, RO 120 634, RO 121 112
4.MIRCI, L.E. BORAN, S., C.B.I. A/00654-2004, C.B.I. A/00558-2006
5.MIRCI, L.E., BORAN, S., 8th Pacific Polymer Conference, 24-27 Nov. 2003, Bangkok, Tailands, Abstr. P 131, CD ROM, 4 pg.
6.MIRCI, L.E., BORAN, S., LUCA, P., BOIANGIU, V., 14th Intern. Coll. Tribology, Technische Akad. Esslingen, Ostfildern, Germania, 2004, January 13-15, vol I, p 511
7.MIRCI, L.E., BORAN, S., LUCA, P., BOIANGIU, V., World Tribology Congress III, Washington D.C., USA, 2005, Progr. p. 30, CD ROM, 4 pg.
8.MIRCI, L.E., BORAN, S., LUCA, P., BOIANGIU, V., J. Synth. Lubrication, 2005, 22, nr. 2, p 161
9.MIRCI, L.E., BORAN, S., LUCA, P., BOIANGIU, V., J. Synth. Lubrication, 2007, 24, nr. 1, p 51
10.WANG, SHUGING; GAO, CHONG; XIA DAISULIAO, Jiagong Yingyong, 2004, 16(4), p 34
11.KIM, SANG-WOO; KIM, JEONG-GON; CHOI, JUNG-JK, JEON, IL-RYUN; SEO, KWAN-HO, Journal of Applied Polymer Science, 2005, 96, nr. 4, p1347
12.ALBER FRANK, et al., I P Com. Journal, 2004, 13 Iulie, 4, nr. 8, p.15
13.SUZUKI, OSAMU; YAOITA, YOSHIYUKI; SHIRAISHI, HIDEHIKO, Jpn Kokai Tokkyo Koho JP 2005, 154623 (16 Iunie 2005/27 Nov. 2003).
14.LJUNGBERG, NADIA; COLOMBINI DIDIER, WESSLER BENGT, Journal of Applied Polymer Science, 2005, 96, nr. 4, p 992
15.CAI, JINJUN; LIN, LIXING; YANG, MINGZHI, C N 1,500.771 (2 iunie 2004; 19 Noi. 2002)
16.SASHIDA,KAZUYUKI; KAMIYA, SOICHIRO, Jpn. Kokai Tokkyo Koho JP 2005, 232403 (2 Sept 2005/23 Febr. 2004)
17.KRISTOFFERSEN, BENNO LYNGE, Dansk Kemi, 2005, 86(3), p.22
18.ZHANG, JING; WANG, JING; WANG, FANG; WANG, CHUAN-SHENG; KONG, XIANG-WEN Shenyang Huagong Xueyuan Xueyuan Xuebao, 2003, 17(4), p 245.
19.MENG, XIAN-CHANG; WANG, MENG-GE, LIU, BAO-SHENG, Huaxue

Yu Nianhe, 2004, 26, nr. 6, p 334.

20.CHEN, QUN, Yingyong Huagong, 2004, 33, nr. 5, p 42.

21.GODWIN, ALLEN D., STANAT JON E., SAPLIS, RICHARD, U.S. US 6.969.736 (29 nov. 2005 / 27 mai 2004).

22.YU, SHAN-XIN; RUI-NING, Huaxue Yu Nianhe, 2004, 26, nr. 5, p.256

23.WANG, CHENG-YUN; GONG, LI-WEN, Suliao Keji, 2004, nr. 4, p.27

24.TAKEDA, SHOJI, Konbatekku 2004, 32, nr. 9, p 69.

25.ZHU,SHUNSHENG, Faming Zhuanli Shenging Gongkai Shuomingshu, CN 1.550.515 (1 dec. 2004 / 10 martie 2003).

26.KATAOKA, SEIJI, Sosei To Kako, 2005, 46 (528), p 4.

27.LAPPE, PETER; BALZAREK, CHRISTOPH, Eur. Pat. Appl. EP 1.516.865 (23 martie 2005 / 20 sept. 2003).

28.YAMADA, MUNEHIRO; SHIZUKA, NOBUHIKO; MEMITA, MICHIMASA; MIYASHITA, HIROKO, Eur. Pat. Appl. EP 1.533.363 (25 mai 2005 / 21 nov. 2003)

29.NEGISHI, MASATAKA; HASHIMOTO, JIRO; SAKAMOTO ZOSHINOBU, Jpn Kokai Tokkyo Koho JP 2005, 170.997 (30 iunie 2005 / 9 dec. 2003).

30.KIMURA, HIROSHI; TONG, DA-MING; IMAI HIROSHI HASHIMOTO, JIRO; NEGISHI, MASATAKA; SAKAMOTO, ZOSHINOBU, Jpn Kokai Tokkyo Koho JP 2005, 213.377 (11 august 2005 / 29 ian. 2004).

31.KOLWZAN B., GRYGLEWICZ S., J. Synth. Lubrication, 2003, 20, nr. 2, p 99

32.GRYGLEWICZ S., KOLWZAN B., J. SYNTH. LUBRICATION, 2004, 20, nr. 4, p 281

33.GRYGLEWICZ S., OKO F.A., Industrial &Engineering Chemistry Research, 2005, 44, nr. 6, p 1640

34.MIRCI, L.E., BORAN, S., Mat. Plast., 42, nr. 2, 2005, p 124

35.MIRCI, L.E., BORAN, S., A XXIX-a Conferinţă Naţională de Chimie, 4-6 oct. 2006, OLTCHIM, Rm. Vâlcea, Progr. p 20, Rezumate CS III- p. 15

36.MIRCI L.E., BORAN S., LUCA P., BOIANGIU V., 15th Intern. Coll. Tribology, Technische Akademie Esslingen, Ostfildern, Germania, 17-19 ian. 2006, Synopses Synthetic Base Oils, p 236; CD ROM 8 pg.

37.MIRCI L.E., Brevete româneºti, RO 100130, cf. CA, 118 (1993), 24102r; RO 100131, cf. CA, 118 (1993), 59411t; RO 103075, cf. CA, 122 (1995), 12499v; RO 105571, cf. CA B1, 129 (1998), 15975c

38.MIRCI L.E., Brevete româneºti, RO 109644, cf. CA B1, 133 (2000), 5396h; RO 111760, cf. CA B1, 133 (2000), 31362p; RO 112611, cf. CA B1, 133 (2000), 90272g; RO 113851, cf. CA B1, 134 (2001), 254001s; RO 116961

39.MIRCI, L.E. ºI BORAN, S., C.B.I. A/00558, 12.07.2006

40.BÖTNER E.F. ºI ROSENTHAL C., Kunststoffe, 1972, 62, nr. 10, p 685

41.MIRCI L.E., BORAN S., MÃTIEª M.,Mat. Plast., 38, nr. 1, 2001, p 52

42.MÃTIEª M., GHEORGHE C. ºI PÃTRU M., Mat. Plast. 1990, 27, nr. 3, p 127

43.SEARS J. K. ºI DARBY J. R., The Technology of Plasticizers, John Wiley & Sons, New York, 1982, p 1166

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ELASTOMERI DE SPECIALITATE

Editura Politehnica Timisoara, 2003,
ISBN 973-625-040-7, 419 pag.

Prin lucrarea "Elastomeri de specialitate" s-a intenţionat realizarea unei sinteze privind cauciucurile speciale, categorie importantã de materiale polimerice, domeniu aflat într-o dinamicã ascendentã cu multiple ºi foarte diverse aplicaţii.

Cartea este alcatuitã din 12 capitole în care sunt prezentate o serie de elastomeri cunoscuţi în literatura ca "elastomeri de specialitate". Fiecare capitol cuprinde date referitoare la unul din tipurile de elastomeri de specialitate trataţi. Intre aceºtia se menţioneazã: polietilena cloruratã ºi clorosulfonatã, cauciucul policloroprenic, cauciucurile fluorurate, cauciucul siliconic, cauciucurile epoxidice, cauciucurile tiocolice, poliuretanice, cauciucul etilenã-acetat de vinil, elastomeri acrilici, cauciucul polinorbornenic, cauciucul poliocten-americ ºi elastomerii polifosfazenici.

Sistematizarea datelor referitoare la fiecare clasã de elastomeri de specialitate urmeazã o succcesiune logicã: prezentarea produsului, precursorii necesari sintezei, variante tehno-logice, aspecte chimico-structurale ºi caracterizarea polimerilor, procedee de prelucrare, utilizãri. Este de remarcat faptul cã pentru fiecare clasã de elastomeri sunt scoase în evidenţã condiţiile specifice de prelucrare ºi materialele auxiliare necesare pentru designul unor proprietãţi prestabilite. Materialul prezentat în aceastã lucrare este însoţit de grafice ºi tabele care permit o înţelegere mai bunã a particularitãţilor elastomerilor de specialitate în cele mai diferite condiţii (solicitãri mecanice, termice, rezistenţa chimicã, proprietãţi reologice, biocompatibilitate etc.).

Cartea intitulatã "Elastomeri de specialitate" este importantã prin volumul impresionant de informaţii pe care îl oferã ºi se adreseazã în primul rând studenţilor din anii terminali de studii de la facultãţile de chimie industrialã precum ºi specialiºtilor care îºi desfãºoarã activitatea în fabrici de prelucrare a elastomeilor.

In acelaºi timp aceastã lucrare poate constitui un ghid util pentru cei interesaţi de cunoºtinţe pertinente despre elastomeri de specialitate pentru aplicaţii foarte diverse.

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