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DIESTERS OF BRASSYLIC ACID AS THE PLASTICIZERS FOR POLY (VINYL CHLORIDE)

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INTRODUCTION

The development of plastics' manufacture and continuous progress in the requirement on goods produced of them create the necessity of further studies in that field.

The progress in the scope of raw materials is possible by working out new polymers and plasticizers or by modification of actually existing. Polyvinyl chloride is the most often applied plastic. Softening is one of the possibilities of modifying its properties. The aim of plasticization is to obtain viscously elastic in range of required temperatures of utilization [2].

Among a lot of examined organic compounds the esters of mono-and dicarboxylic acids and mono- and dihydric alcohols has found the widest industrial application as plasticizers. In last few years the esters of azelaic, sebacic and brassylic acids [3] were the subject of interest in aim to enlarge the assortment of plasticizers. There are real possibilites in Poland to manufacture the brassylic acid by ozonolysis of erucic acid and that way, it becoms possible to obtain derivatives of this acid as raw material for plasticizers [1, 4, 5].

EXPERIMENTAL PART

The aim of this work was to obtain various derivatives of brassylic acid and the examination of their usability to polyvinyl chloride plasticization. Brassylic acid obtained by ozonolysis of erucic [14] acid was esterified at various conditions to determine optimum parameters of

that process. Then the essential chemical and physical properties of the synthezied diesters were investigated. As the next step of our work there were investigated the mechanical properties of polyvinyl chloride foils plasticized by brassylates.

SYNTHEZIS OF BRASSYLATES

Seven diesters of brassylic acid were obtained with methyl-, butyl-, isobutyl-, amyl-, isoamyl-, 2-ethylheksyl-, and benzyl- alcohols. These derivatives were obtained by azeotropic esterification with solvent.

The raw material was brassylic acid of 85% purity containing — beside the main constituent — aliphatic acids mono- and dicarboxylic of diffrent (up to C_{13}) lengths of hydrocarbon chain.

DETERMINATION OF THE OPTIMUM ESTERIFICATION'S PARAMETERS

In aim to match the optimum parameters of the process series of esterifications were carried out with application of different amounts of alcohol, solvent, catalyst and reaction time.

In Table 1 there are the results of investigations in which the influence of the amount of applied alcohol on the esterifications' yield have been obserevd. The alcohol was applied in steichiometric quantities and with an excess of 20, 30, 40, 50%. From the industrial point of view it seems quite useful to apply 20% alcohol excess in proportion to steichiometric amount. To determine the influence of quality and quantity of the solvent in the reaction mixture on the esterification's

Table 1

The influence of the quantity of applied alcohol on the yield of brassylic acid esterification

Alcohol	Yield of brassylic acid diester (%)				
	Excess of alcohol (% mol)				
	0	20	30	40	50
Methyl	65.7	85.6	87.9	89.3	89.6
Butyl	70.1	98.2	98.4	99.2	98.9
Isobutyl	71.3	97.5	97.8	98.4	98.7
Amyl	64.9	92.3	90.6	92.0	92.6
Isoamyl	61.3	91.6	89.8	91.2	91.5
2-ethylheksyl	59.8	89.0	87.5	88.0	86.8
Benzyl	62.3	89.6	89.1	88.7	89.5

Constant parameters: catalyst — 3% p-toluenesulphonic acid,
reaction time — 6 hours,
reaction temperature — 80—85°C,
solvent — benzene.

yield a series of processes were undertaken where benzen and toluene were applied. Trails with application of toluene as a solvent were undertaken for two esters only: dibutyl and di-2-ethylheksyl brassylates. But the yields as well as the colour of obtained diesters disqualify him as a solvent in esterification process.

Table 2

The influence of quality and quantity of the solvent on the yield of brassylic acid esterification with butyl, isobutyl, amyl, isoamyl, 2-ethylheksyl and benzyl alcohols

Alcohol	Benzene			Toluene		
	Quantity of solvent (%)	Yield (%)	Colour in iodine scale [12]	Quantity of solvent (%)	Yield (%)	Colour in iodine scale [12]
Butyl	200	89.3	5	200	80.6	12
	300	94.1	5	300	85.1	9
	400	96.8	4	400	85.9	16
	500	97.2	4	500	86.9	12
Isobutyl	200	88.1	2			
	300	90.2	2			
	400	92.3	1			
	500	97.2	1			
Amyl	200	89.2	3			
	300	91.9	2			
	400	92.4	2			
	500	92.8	2			
Isoamyl	200	91.3	1			
	300	88.9	1			
	400	90.2	1			
	500	91.6	1			
2-ethylheksyl	200	85.6	4	200	70.4	7
	300	90.2	3	300	77.3	5
	400	91.6	3	400	76.5	5
	500	92.3	3	500	77.1	5
Benzyl	200	83.5				
	300	89.0				
	400	89.5				
	500	89.8				

Constant parameters: catalyst — 3% p-toluenesolphonic acid,
reaction time — 6 hours,
reaction temperature — 80—85 °C or 95—100 °C,
excess of alcohol — 20% mol.

While the analizing the results in Table 2 it should be ascertained that in each of carried out esterification increasing of the solvent amount positively influences the course of the process. As the optimum quantity of the solvent there was ascertained its 200 wegiht % particiaption in proportion to brassylic acid in case of brassylates: diamyl- and

disoamyl-, but 300 weight % of benzene for the esters of butyl-, isobutyl, 2-ethylheksyl- and benzyl- alcohols.

Methyl-diester was obtained by esterification without a solvent, because during its azeotropic esterification, together with reaction water also the methanol distilled, what negatively influenced the yield.

Table 3

The influence of reaction time on the yield of brassylic acid esterification

Alcohol	Yield of brassylic acid ester (%)				
	Reaction time (hours)				
	3	6	8	10	12
Methyl	88.3	89.5	89.8	91.2	92.1
Butyl	93.9	95.3	95.5	96.8	97.2
Isobutyl	87.2	89.1	88.3	92.3	92.4
Amyl	84.9	93.2	93.0	91.2	85.9
Isoamyl	85.3	91.7	90.8	89.5	88.9
2-ethylheksyl	80.2	89.5	90.2	89.3	85.7
Benzyl	75.6	90.5	91.5	88.4	89.2

Constant parameters: catalyst — 3% p-toluenesulphonic acid,
excess of alcohol — 20% mol,
temperature — 80—85 °C,
solvent — benzen 300% weight in case of butyl, isobutyl, 2-ethylheksyl, benzyl alcohols and 200% weight in case of amyl and isoamyl alcohols.

Table 3 presents the results received during matehing the time of reaction duration. On that basis it was ascertained to establish 6 hours as the optimum to each esterification. The *p*-toluenesulphonic acid in 3 weight % in proportion to brassylic acid was applied as a catalyst in all described above esterifications. It was studied if and in what way the change of quantity and quality of catalyst influences yield of individual process. The results are given in Table 4.

Increasing the amounts of *p*-toluenesulphonic acid to 5 wegiht % causes only in a small degree bether esterification's yield. Because of that 3% weight of *p*-toluenesulphonic acid was found as the optimum quantity of catalyst. Applying the sulphuric acid as the catalyst to all examined esterifications caused distinct worsening the colour of obtained products. Worsening of brassylate's colour is not profitable in case of applying them for plasticizing of polyvinyl chloride. The carried out studies enabled to ascertain the parameters by which the esters of brassylic acid were obtained with highest yield. The parameters are following:

Table 4

The influence of quality and quantity of catalyst on the yield of brassylic acid esterification with methyl, butyl, isobutyl, amyl, isoamyl, 2-ethylheksyl and benzyl alcohols

Alcohol	P-toluenesulphonic acid			Sulphuric acid		
	Quantity of catalyst (%)	Yield (%)	Colour in iodine scale [12]	Quantity of catalyst (%)	Yield (%)	Colour in iodine scale [12]
Methyl	2					
	3	87.6	*	3	78.6	*
	4	89.3				
	5	89.0				
Butyl	2					
	3	96.8	4	3	93.2	7
	4	98.2	3			
	5					
Isobutyl	2	85.8	4			
	3	86.7	3	3	85.9	9
	4	87.3	4			
	5					
Amyl	2	91.7	2	2	93.0	35
	3	92.8	3	3	92.9	58
	4	89.9	4	4	95.7	58
	5	91.0	7	5	89.2	58
Isoamyl	2	89.1	1			
	3	92.0	1			
	4	92.5	1			
	5	92.8	1			
2-ethylheksyl	2	89.8	3	2	92.3	9
	3	90.0	3	3	95.3	16
	4	91.2	3	4	95.8	35
	5	91.8	3	5	90.1	45
Benzyl	2	89.5	*	2	94.3	*
	3	90.5		3	93.4	
	4	91.8		4	93.9	
	5	92.5		5	87.4	

* — solid.

— excess of applied alcohol — 20%,
— catalyst — *p*-toluenesulphonic acid 3% weight in proportion to brassylic acid,
— duration of esterification process — 6 hours,
— solvent — benzene in quantity of 200% weight to 300% weight.

Table 5

Yield of the brassylic acid esterification

Brassylate	Yield (%)
Methyl	89.3
Butyl	97.1
Isobutyl	97.3
Amyl	92.8
Isoamyl	91.4
2-ethylheksyl	90.0
Benzyl	89.9

The yields of obtained individual diesters of brassylic acid (at established parameters) are given in Table 5.

The highest yields were obtained for butyl- and isobutyl- diesters. The chemical properties of obtained brassylates are given in Table 6.

Table 6

Chemical properties of synthesized brassylates

Brassylate	Contents of ester (%)*	Acid value [6]	Ester value [6]	Ester value theor.	Hydroxyl value [7]
Methyl	70.2	1.8	404.1	414	3.8
Butyl	70.7	1.9	312.4	314	3.2
Isobutyl	68.7	1.1	310.5	314	2.9
Amyl	90.1	1.2	287.4	291	5.2
Isoamyl	92.5	1.8	288.1	291	5.0
2-ethylheksyl	93.5	1.5	236.8	239	4.4
Benzyl**	—	2.0	283.5	264	4.5

* The difference up to 100% consisted of esters of shorter hydrocarbon chains dicarboxylic acids.

** The yield was calculated from the ester value because of impossibility to analyse this ester by the GLC method.

Acid values of brassylates do not surpass 2. Ester values differ slightly from the theoretical of corresponding compounds. May be that this is due the fact that the brassylic acid of only 85% purity was used. Applying the technical brassylic acid to the esterification makes more profitable the process of obtaining plasticizers on comercial scale production. Obtaining pure brassylic acid (of about 90% purity) requires additional crystalizations from alcohol and benzene. But the impruities of technical brassylic acid can only in a minimal degree lower the properties of brassylates as plasticizers.

Table 7 presents the more important physical properties of brassylates. The density, dynamic viscosity, flash point, and critical tempera-

Table 7

Comparison of physical properties of brassylic and sebacic acid diesters

Diester	Density [8] (g/cm³)	Viscosity [9] (cP)	Critical temperature of solubilization, °C, [2]	Flash poin, °C [10,11]
Methyl brassylate	1.0463	$12.8_{34°C}$	142	184
Butyl brassylate	0.9254	26.1	150	210
Isobutyl brassylate	0.9200	31.7	155	192
Amyl brassylate	0.9135	71.4	132	205
Isoamyl brassylate	0.9180	41.3	141	154
2-ethyloheksyl brassylate	0.8998	43.5	160	155
Benzyl brassylate	1.0741	$33.1_{45°C}$	162	215
Methyl sebacate	0.9860	3.5	107.7	171
Butyl sebacate	0.9360	$7.9_{25°C}$	126.5	177
2-ethylheksyl sebacate	0.9100	21.0	159.8	200
Benzyl sebacate	1.0550	$13.0_{37,8°C}$	—	239

ture of solubilization (CTS) were determined. Critical temperature of solubilization characterizes the solution abbility of polyvinyl chloride by the plasticizer. The measurement of the CTS consists in heating the suspension of 0.5 g of polyvinyl chloride in 12.5 g of examined diester and rising the temperature to a value at which the solution becomes clear. These physical properties of obtained brassylates were compard to the corresponding properties of sebacates.

Flash points of brassylates and sebacates are similar. The lowest flash points are only in case of isoamyl- and 2-ethylheksyl brassylates, but their values do not disqualify those compounds as plasticizers; because during foil manufacture they do not cause the danger of ignition. Obtaining of polyvinyl chloride foils plasticized by brassylates was the next step of our work. The foils were manufactured using following materials:

1) 70 weight % of polyvinyl chloride,
2) 30% of plasticizer.

The obtained foils were examined at mechanical point of view by determination its 100% modulus, tensil resistance and elongation. The measurements were made according to Polskie Normy (Polish Standarts). The results are inserted in Table 8.

The first item in the table conserns a standart foil to which the isooktyl phtalate was applied as plasticizer. Determinations according to and perpendicular the rolling direction were made in case of every foils. In comparison to the standart foil, the foils being plasticized by brassylates are of good tensil properties.

In Table 9 the mechanical properties of polyvinyl chloride foils pla-

Table 8

Mechanical properties of foils plasticized with brassylates

Diester plasticizer	100% modulus [13] (kG/cm²)		Tensile [13] (kG/cm²)		Elongation [13] (%)	
	1*	2**	1	2	1	2
Isooktyl phtalate	187	192	263	277	268	306
Methyl brassylate	120	128	194	183	347	281
Butyl brassylate	109	114	225	216	257	279
Isobutyl brassylate	122	135	227	244	304	335
Amyl brassylate	135	84	251	202	160	373
Isoamyl brassylate	96	123	180	211	385	415
2-ethylheksyl brassylate	140	139	197	203	347	318
Benzyl brassylate	137	138	189	209	290	350

* According to the direction of rolling.
** Perpendicular to the direction of rolling.

Table 9

Comparison of mechanical properties of foils plasticized by brassylates, adipates, azelates and sebacates

Plasticizer	100% modulus (kG/cm²)	Tensile (kG/cm²)	Elongation (%)
Isobutyl brassylate	126.0	244.5	235
2-ethylheksyl brassylate	139.5	202.6	318
Isobutyl adipate adipinian	76.0	196.0	350
2-ethylheksyl adipate	74.0	183.0	307
2-ethylheksyl azelate azelainian	90.0	176.0	340
2-ethylheksyl sebacate sebacynian	96.0	198.0	355

sticized by 2-ethylheksyl and isobutyl brassylates are compared with the corresponding properties of polyvinyl chloride foils plasticized by diesters adipic, azelaic and sebacic acids. It comes from the comparison that the foils with brassylates are of the better tensile properties.

In general, the examined brassylates apper to be exellent plasticizers comparable with the best commercial products now available such as diesters of adipic, azelaic and sebacic acids.

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ESTRY KWASU BRASYLOWEGO JAKO ZMIĘKCZACZE POLI (CHLORKU WINYLU)

Streszczenie

Na drodze estryfikacji azeotropowej otrzymano siedem estrów kwasu brasylowego: metylowy, butylowy, izobutylowy, amylowy, izoamylowy, 2-etyloheksylowy i benzylowy.

Określono optymalne parametry poszczególnych procesów estryfikacji przez ustalenie ilości i jakości katalizatorów, nadmiaru alkoholu, ilości i jakości stosowanego rozpuszczalnika.

Własności chemiczne otrzymanych estrów określono, oznaczając liczbę kwasową, liczbę estrową i liczbę hydroksylową. Własności fizyczne scharakteryzowano przez pomiar gęstości, lepkości dynamicznej, temperatury zapłonu, barwy oraz krytycznej temperatury rozpuszczania. Następnie otrzymano folie z PCV plastyfikowane uzyskanymi uprzednio estrami kwasu brasylowego i zbadano ich własności mechaniczne.

Otrzymane folie pod względem mechanicznym można porównać z foliami plastyfikowanymi adypinianami, azelainianami i sebacynianami.

Dowodzi to, że otrzymane brasylany można uznać za produkty rozszerzające asortyment dostępnych plastyfikatorów.

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ЭФИРЫ БРАСИЛОВОЙ КИСЛОТЫ КАК СМЯГЧИТЕЛИ ПОЛИ (ВИНИЛХЛОРИДА)

Резюме

Путем азеотропной эстрификации получали семь эфиров брасиловой кислоты: метиловый, бутиловый, изобутиловый, амиловый, изоамиловый, 2-этилогексиловый и бензиловый.

Определяли оптимальные параметры отдельных процессов эстрификации путем определения количества и качества катализатора, излишка алкоголя, качества и количества применяемого растворителя.

Химические свойства полученных эфиров исследовали путем определения кислотного, эфирного и гидроксильного числа. Физические свойства определяли путем измерения густоты, динамической липкости, температуры воспламенения, цвета и критической температуры растворителя. Затем получали поливинилхлоридные фольги пластифицируемые полученными раньше эфирами брасиловой кислоты и исследовали их механические свойства.

Полученные фольги можно в механическом отношении сравнить с фольгами пластифицированными адипинатами, азеланитами и себацинатами.

Вышеприведенные данные свидетольствуют о том, что полученные брасилаты можно рассматривать как продукты расширящие асортимент имеющихся пластификаторов.