ESTERIFICATION AND POLYESTERIFICATION REACTIONS WITH INDUSTRIAL APPLICATIONS. POLYESTERS OBTAINED FROM MIXTURE OF DICARBOXILIC ACIDS AND DIOLS

Dorina MODRA, Cosmina ANDRAŞESCU, Ramona OPROIU, Remus NUŢIU

UNIVERSITY OF WEST TIMIŞOARA
1900 Timişoara, Str. Pestalozzi, România
E-mail: rnutiu@saratoga.ro

Abstract

This paper is continuing the research of authors in domain of polyesterification reactions with industrial applications. It was pursued the obtaining of new polyesteric oils using mixtures of adipic acid and phtalic acid and two different diols.

$$n\ HOOC\text{-}R\text{-}COOH + n\ HO\text{-}R'\text{-}OH \rightleftharpoons HO\text{-}(CO\text{-}R\text{-}CO\text{-}O\text{-}R'\text{-}O)_n\text{-}H + (n\text{-}1)\ H_2O$$

The polyesterification reaction was realized without catalyst, at 220-225^oC temperature, in presence of one chain switch. The obtained oils were physical-chemical characterized. The color of these oils was situated between 4 and 12 mg I_2/100 ml solution of KI; the densities between 1.080 and 1.160 g/cm^3, at 20^oC and the dynamic viscosities were situated between 2000 and 147400 cP. In this way it's offer the possibility to obtain the esteric oils with a large viscosity domain.

Keywords: *polyesterification reaction, dicarboxilic acids, diols*

INTRODUCTION

Polyesterification reaction is important as scientific as technologic point of view. Flory and co-workers developed the theory of polyesterification reaction first. [1,2]. About this type of reaction was realized a lot of other study for the kinetic and for the mechanism [3-7].

Polyesterification reaction is between a dicarboxilic acid and a diol, with water elimination and formation of polycondensation product:

$$n\ HOOC\text{-}R\text{-}COOH + n\ HO\text{-}R'\text{-}OH \rightleftharpoons HO(\text{-}CO\text{-}R\text{-}CO\text{-}O\text{-}R'\text{-}O\text{-})_nH + (n\text{-}1)\ H_2O$$

The polyesterification can take place in the presence of an external catalyst. In the absence of this, the diacid monomer acts as its own catalyst for the reaction.

The polyesterification reaction can take place in the presence or in the absence of switches of chains, too.

Through this paper, it's continuing our research in domain of polyesterification reactions with industrial application [8]. We used as monomers mixtures of adipic (AA) and phtalic (FA) acid, respectively mixtures of two diols: 1,2–propylene glycol (PG), monoethylene-glycol (MEG) or 1,3-butane-diol (1,3 BD) with neopenthyl-glycol (NPG). This type of polyesterification proposes to obtain better plasticizers.

EXPERIMENTAL

The installation used in polyesterification it was a classical installation, described in previos paper [8]. The reactants used in polyesterification reaction are mixture of two dicarboxilic acids (adipic acid and phtalic acid) and two diols (monoethylene-glycol, 1,2–propylene-glycol, 1,3-butane-diol and neopenthyl-glycol) in different molar ratio. As switch of chain we used 2-ethyl-hexanol and decanol. The characteristics of these raw materials were discussed in previos paper [8].

In stead of phtalic acid we used phtalic anhydride, an industrial product, purity 98.4%, melting point 131-132^{o}C, density at 20^{o}C 1.530 g/cm^{3}.

The polyesterification reaction was realized in melting, at temperature until 220-225^{o}C, in nitrogen atmosphere. At the beginning the reaction was guided at normal pressure and ultimately in vacuum. The water is stripped off continuous, during the process. When the acid number reached the expected value, it was realized the devolatilization of polyesters. By this way it's stripped out the excess of diols, too.

In Table 1 are containing the molar ratios of reactants and the conditions of polyesterification of acids and diols mixtures.

Tabel 1. *The molar ratios of the reactants and of switch of chain and the conditions of polyesterification reaction*

No	Molar ratio		Temp. of work [^{o}C]	Time of reaction [h]
	Raw materials	Switch of chain		
1	AA : AF : PG : MEG 1 : 0.32 : 0.768 : 0.678	2-Ethyl-hexanol 0.1	225	21
2	AA : AF : PG : MEG 1 : 0.33 : 0.611 : 0.611	2-Ethyl-hexanol 1.047	230	22
3	AA : AF : PG : MEG 1 : 0.33 : 0.58 : 0.58	2-Ethyl-hexanol 0.786	220	24
4	AA : AF : NPG : 1,3 BD 1 : 0.71 : 1.23 : 1.33	Decanol 0.08	220	24
5	AA : AF : NPG : 1,3 BD 0.68 : 0.405 : 0.972 : 0.70	Decanol 0.51	225	28
6	AA : AF : NPG : 1,3 BD 1 : 0.71 : 1.63 : 1.77	Decanol 0.01	220	24

The physic-chemical determinations of compounds and the methods used were described in previous paper [8].

RESULTS AND DISCUSSIONS

Continuous determining the acid number respectively the dynamic viscosity of reaction mass pursued the polyesterification process.

Figure 1 represents the variation of the acid number versus time. We observe a diminution of acid number more pronounced in the lots where we worked with excess of diol. In this case, after 25 hours the acid number presents a reduced value (less than 3 mg KOH/g). In lots with excess of dicarboxilic acids, the diminution of acid number is slower in time. In final, the value was between 10-23 mg KOH/g.

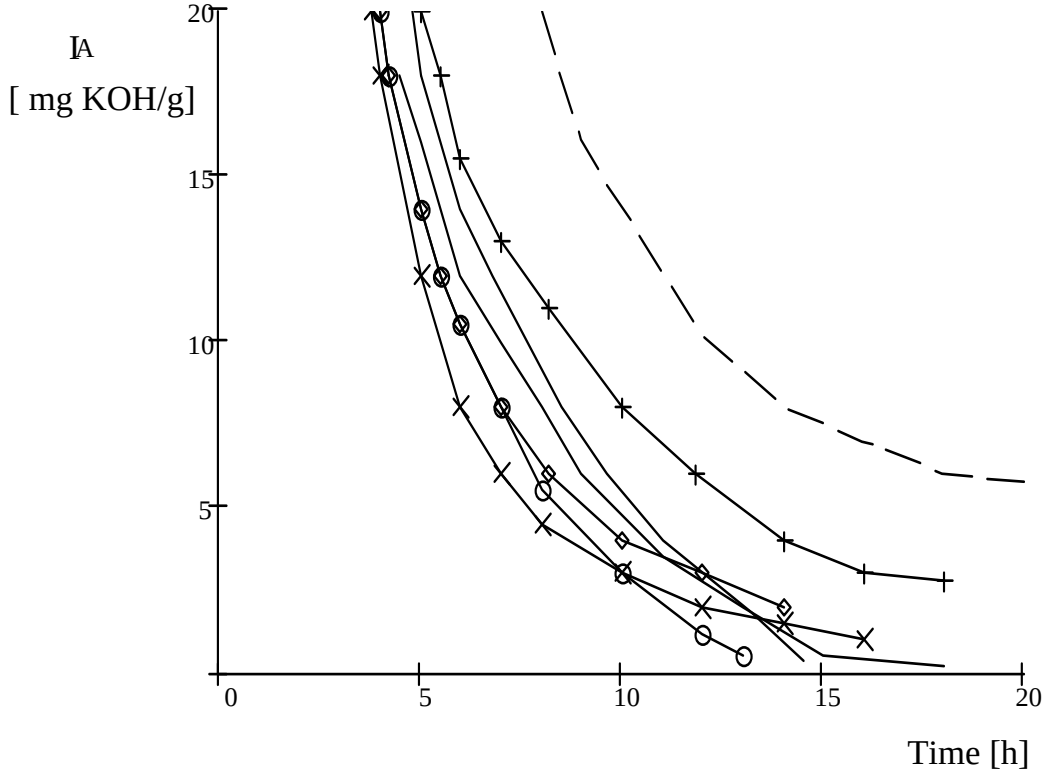

Fig. 1 *Acid number versus time*

The diminution of acid number to the small value (2-3 mg KOH/g) is require long times of reaction. We observe this in figure 2 where is considering the lots with excess of diols.

Figure 3 represent the variation of dynamic viscosity (in cP) versus time. The viscosity increases more pronounced in the lots 1 and 2 where the quantities of chain switch are small (less than 0.1 molar). In the lots, which much quantity of chain switch, the increase of viscosity is slower, and the final value of viscosity is less than 2000 cP.

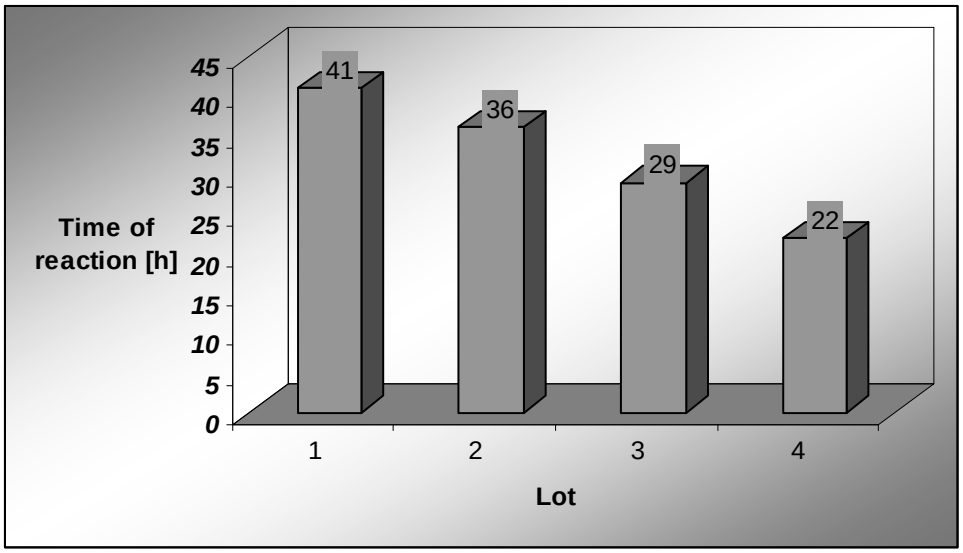

Fig. 2 *Time of reaction in hours necessary for an polyesterification at 225-230^{o}C until the acid number touch the value 2 mg KOH/g*

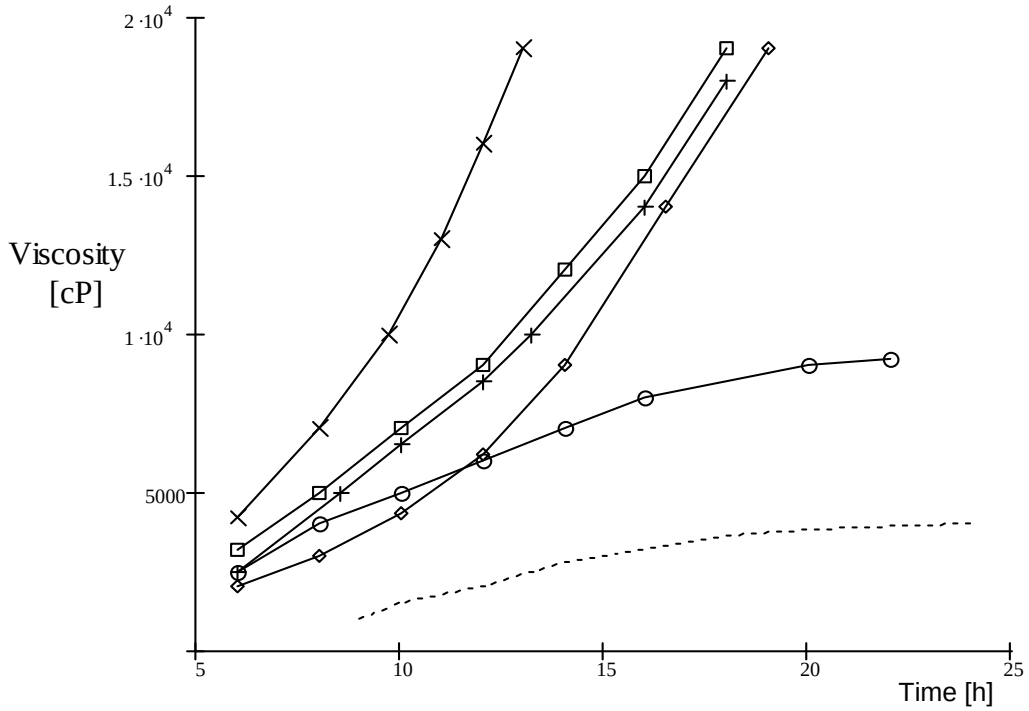

Fig. 3 *The variation of dynamic viscosity (cP) versus time of reaction (h)*

In Table 2 are containing the physic-chemical properties of obtaining polyesters. There are viscous oils, with color on iodine scale between 4-12 mg iodine/100 ml solution KI.

Table 2 *The physic-chemical properties of obtaining polyesters according with table 1*

No	The characteristic	The polyesters charges					
		1	2	3	4	5	6
1	Color, iodine scale [mg I_2/100 ml sol KI]	12	4	8	8	4	8
2	Acid number [mg KOH/g]	23	0.5	18	10.6	3.8	3.02
3	Hydroxyl number [mg KOH/g]	31	20.95	28	22	6	7
4	Refraction index, at 20^{o}C	1.488	1.472	1.473	1.478	1.487	1.487
5	Viscosity at 20^{o}C [cP]	147422	678	1800	7400	1387	2000
6	Density at 20^{o}C [g/cm^3]	1.11	1.10	1.15	1.08	1.16	1.15
7	Flash point [^{o}C]	210	220	230	235	230	230

The color of polyesters is influenced by the quality of raw materials. While the polyesterification process, the air has an oxidative influence to the oils, determining their coloring.

For avoiding this fact, the reaction was realized in presence of nitrogen atmosphere.

The refraction indexes of studied polyesters are between value 1.470 -1.488 at 20^{o}C and the density between 1.080-1.160 g/cm^3.

The dynamic viscosity, determinate at 20^{o}C, is varying in large limits, between 680-148000 cP (mPa·s).

The flash points of this esteric oils is higher than flash points of esters of dicarboxilic acids used as plasticizers. There are between 210-235^{o}C.

CONCLUSIONS

The polyesterification reaction of mixture of adipic and phtalic acid and two different diols was realized in melting, at 220-230^{o}C, with chain switch and without catalyst. The obtained polyesters were characterized from physico-chemical point of view.

The dynamic viscosity values of this, in large limits, show the multiples possibility for obtaining and capitalizing this polyesters.

In our next paper we intent to present the evaluation studies of the esteric oils as plasticizers for plastic masses.

BIBLIOGRAPHY

1. P.J. FLORY, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953
2. P.J. FLORY, Chem. Rev.,39, 137 (1946)
3. A.E. MUNSTAFA, M.A. SHAABAN, Acta Polym., 41 (9), 504 (1990)
4. S.D. HAMANN, D.H. SOLOMON, J.D. SWIFT, J. MACROMOL. Sci. Chem., A2, 153 (1968)
5. J.L. MCCARTHY, B.J.R. SCHOLTENS, J. Appl. Polym. Sci., 42, 2223 (1991)
6. J. OTTON, S. RATTON, J. POLYM. Sci. Part A: Polym. Chem., 29, 377 (1991)
7. J. OTTON, S. RATTON, J. POLYM. Sci. Part A: Polym. Chem., 26, 2183 (1988)
8. D. MODRA, L. PITULICE, R. NUTIU, Annals of Univ. West Timisoara, Ser. Chem., 12, 2003 (in print)
9. D. MODRA, C. ANDRASESCU, R. OPROIU, R. NUTIU, Revista de Chimie, Bucuresti, 2003 (in print)