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STUDIES ON RELIABILITY OF POLYESTER RESINS IN PLASTICIZING POLY(VINYL CHLORIDE).

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ABSTRACT

Modern technology introduced reinforced plastics in various applications in aerospace fields. The plastic materials in these fields certainly need different additives to improve their physical and mechanical properties. A series of polyesters resins having different structures and molecular weights have been prepared. The molecular weights of the prepared polyesters were determined via end group analysis. These polyesters were blended with dioctyl phthalate (DOP) and the efficiencies of these blends as plasticizers for PVC were evaluated. It was proved that some of the prepared aliphatic polyesters improve the action of the traditional low molecular weight plasticizer. This conclusion was attained by monitoring the mechanical properties (tensile - % of elongation - hardness) throughout a whole year.

Keywords : Polyester, Resin, Plasticizer, Plasticization, Poly(vinyl chloride), PVC, Polyesterification, Ethylene glycol, Diethylene glycol, Triethylene glycol, Butylene glycol, Phthalic anhydride, Adipic acid, Sebacic acid, Succinic acid, Compatibility.

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INTRODUCTION

A Plasticizer has long been defined as a material incorporated into a plastic material to increase its workability and its flexibility. In this broad sense, plasticizers of many kinds were in common use even in prehistoric times. A plasticizer may be incorporated into a resin like PVC in order to impart a new property to the original polymer. In this respect phosphates and chlorinated hydrocarbons are flame retarding plasticizers. Aliphatic dicarboxylic acid esters, adipates, sebacates, and azelates impart good flexibility at low temperatures. Another example is the use of butyl benzyl phthalate (BBP), the industry standard for strain resistance, for vinyl floor covering **[1]** as low temperature flexibility. There is no known plasticizer that can fulfill all the plasticizer requirements. Liquid plasticizers with good general properties and low viscosity are likely show bad aging properties owing to volatility on storage for long periods. This is one of the reasons why the plastics industry is interested in polymeric plasticizers. It is necessary that the molecular weight of polymeric plasticizers must range within definite limits, that is between 1000 and 30000, but molecular weights from 1000 to about 8000 afford the best performance **[1]**. According to Jones **[2]**, the efficiency of a plasticizing material decreases with increasing molecular weight. Therefore, it is often necessary to combine high molecular weight plasticizers with low molecular weight ones to combine their characteristics.

There are very many potential starting materials available for the preparation of polyesters **[3-7]**. One or more varieties of glycols or acids can be used in this respect. The choice of raw materials is governed by many rules concerned with the relation between compatibility of the prepared polyester with the resin to be plasticized when these polyesters are used as plasticizers.

The present investigation aims to prepare a series of polyesters by fusion method via polycondensation reaction at elevated temperatures between glycols and dibasic acids or anhydrides and study their efficiency as plasticizers for PVC.

EXPERIMENTAL

***Materials*:** polyhydric alcohols, ethylene glycol (EG), diethylene glycol (DG), triethylene glycol (TG) and 1,3 butylene glycol (BG) and dibasic acids, succinic acid (SU), adipic acid (AD) and sebacic acid (SE) as well as phthalic anhydride (PHA) were reagent grade and used without further purification. All Chemicals were obtained from Aldrich.

***Preparation of polyesters*:** The polyester resins were prepared by reacting the appropriate amounts of saturated dibasic acid or acid anhydride and glycols according to the ratios tabulated in Table 1. The average number of ether linkage of the glycol systems and the total carbon atoms in the repeating units are tabulated in the last two columns in Table 1. Once the various glycols and acids or anhydrides were weighed and charged into a kettle, they were constantly agitated and heated until a desired acid value has been reached. In the initial phase of the reaction, the drop in the acid value was rapid and the increase in the viscosity was quite slow. Towards the late stages of the reaction, the reverse was true. Twenty two polyester resins were prepared by the method described in ref. **[3]**. The polyester resins were analyzed for acid and hydroxyl values **[8]**, for the sake of calculating the molecular weights via end group analysis.

Preparation of Plasticized PVC Sheets: Ba-Zn stabilizer for PVC, known as IRGASTAB BZ 556, obtained from CIBA-GIEGY was used for heat stabilizing the PVC during the preparation of the test sheets. The utilized quantity of Ba-Zn stabilizer was 2.5 wt.-% with respect to the weight of the PVC resin. The selection of this concentration was based on the early investigations **[9-11]**.

In the present investigation the *Dry blending* method was applied for the polyesters having moderate viscosity. In this method, the appropriate amount of plasticizer is totally absorbed into the desired grade of PVC resin by stirring for a few minutes at 50°C - 80°C to yield a dry powder barely distinguishable in outward appearance from the original resin **[12]**.

Here the plasticizer blends (viscous polyester + dioctyl phthalate, DOP) and heat stabilizer were mixed with PVC powder directly by stirring without a need of being firstly dissolved in a solvent. The temperature of the blend was raised to 60° C while stirring for 30 min.

On the other hand, the solid polyesters were incorporated into the sheets using the technique described by Taverdet and Vergnaud **[13]**. In this respect, the solid polyester was blended with DOP and the heat stabilizer. The mixture was dissolved in the least quantity of acetone solvent and added to the PVC powder to yield paste. The paste was then stirred vigorously and allowed to stand for several hours before molding to evaporate the solvent.

The quantities of the PVC resin and the plasticizers utilized for preparing the test sheets were: 80 wt.-% (40 g) PVC powder (K 61), 10 wt.-% (5 g) Polyester and 10 wt.-% (5 g) DOP.

After incorporation of the plasticizer and the heat stabilizer to the PVC powder, the plasticized PVC sheets were prepared by the aid of a hot melt press. A stainless steel frame having the dimensions of 20 x 20 x 0.1 cm was used for preparing the sheets utilized in the tensile measurements while another frame having a thickness of 0.4 cm was used for shaping the sheets utilized for measuring the hardness.

It has been proposed **[14,15]** that at low temperature (165^{O}C - 170^{O}C) the time required for completing the pressing process is about 12 min. Using such a long time in the pressing process at the above mentioned temperature range leads to a reduction in the efficiency of the added stabilizer. Accordingly, a total pressing time of 5 min at temperature 180^{O}C and pressure ranging between 8-10 tons was used during the present investigation.

According to the selected conditions, different plasticized test sheets were prepared by applying an initial pressing stage for 2 min. at the above specified pressure. The pressure was then released for few seconds to get rid off the air bubbles. The molten mixture was exposed to the same pressure again for another 3 min. The pressed molten sample was then cooled under the same pressure in order to obtain non deformed flat sheet of uniform thickness.

Tensile Properties of PVC Sheets: Measurements of tensile strength of the prepared sheets in the form of standard dumbbell-shaped test specimens under defined conditions of temperature, humidity and testing machine speed, stress-strain diagrams were measured using a Zwick mechanical testing machine. A great care was exercised to ensure that all samples are prepared in exactly the same way and slippage while testing was prevented insofar as possible. Each sample was measured at least five times and the reported value, for each specimen, was taken as the average of these five measurements.

Hardness: In the present study the hardness (Shore D) was measured using a Zwick hardness tester (3102) according to ASTM D 2240-75. The thickness of the specimens was 4 mm. For better reproducibility, a constant load was used to press the indentor against the specimens. The hardness value was taken as an average of ten readings from different locations.

RESULTS AND DISCUSSION

Present investigation deals with the study of the plasticization potency of different polyester / DOP blends. In this respect, the prepared polyesters were blended with DOP in an equivalent proportions (50 : 50 wt.- %). To emphasis the effectiveness of these blends as plasticizers, it is desired to compare the mechanical properties of the PVC sheets plasticized by these blends with that plasticized with DOP alone. It is of interest to mention that the prepared polyesters were designed with great care in such a way to be compatible with PVC.

The measured acid and hydroxyl values of the synthesized twenty two polyester resins are listed in Table (2), These values were used for calculating the molecular weights via end group analysis. The obtained $<M_n>$ values as well as the physical states of the investigated polyesters and the prediction of their compatibility with PVC are also listed in Table (2).

Compatibility of polyesters with PVC: There is remarkably little published information concerning the relationship between the dependence of compatibility of polyester plasticizer with PVC on the structure of these polyesters. In general, the compatibility depends on both melting point and degree of polar character of polyester. In this respect, introduction of an oxygen atom into the straight chain diols, as in diethylene and triethylene glycols, causes a pronounced drop in the melting points of the derived polyesters. This is attributed to an increase in the flexibility of the chain, which presumably leads to an increase in the magnitude of the entropy, thus reducing the melting point. On other hand, the introduction of oxygen atoms into the polyester chain leads to an increase in the polarity of the polyester. Both parameters cause an increase in the compatibility of the polyester with PVC **[16]**. On the other hand, incorporating benzene or cyclohexane ring in the polyester chain through 1,4-positions raises the melting temperature of the produced polyesters as compared with the acyclic analogies **[16]**.

An important objective, therefore, was to prepare liquid polyesters and some polyesters containing benzene rings which form a part of the chain through 1,2-positions to find out their compatibility with PVC.

The compatibility predictions of the prepared polyesters with PVC are listed in Table (2). These predictions are based on the structural parameters (Table 1) of the studied polyesters. Unfortunately, Table (2) shows that the all polyesters including phthalic anhydride are solid polyesters except P12 at which TG and BG are used as glycol system. Incorporation of these higher glycols results in an increase of the number of ether linkage in the repeating units and hence yields liquid polyester at ambient temperature (i.e. polyester with low melting point). The incompatibility predictions of the polyesters P7 - P11 with PVC, as shown in Table (2), are based on their high melting points (solid polyesters at ambient temperature). While the incompatibility of P12 is predicted as a result of the low value of the average number of carbon atoms (7) in the repeating units.

The overall polarity of a polyester plasticizer is an important factor governing its compatibility with PVC. As the number of carbon atoms in the diol and dicarboxylic acid components is reduced the polarity of the resulting polyester increases, and vice versa. The polarity is also increased by introducing ether-oxygen atoms into the chain of one or more of the reactants. The required balance between the total number of carbon atoms and the number of ester groups apparently exists when the number of carbon atoms is not less than 10, and not greater than about 20 **[16]**; but these limits are not known with certainty. No really systematic investigation of these relationships appears to have been published.

Based on the above mentioned relationships, one may arrive to the speculation that P5 is incompatible while P6 and P19 possess limited compatibility. The compatibility predictions will be confirmed in the following section by testing the mechanical properties (tensile and hardness shore D) of the plasticized PVC sheets.

Tensile properties: In the present work, not only the initial part of the stress-strain curves were used to obtain generalized data on the properties of the plasticized PVC sheets but also its ultimate stress and the relative elongation at rupture. The obtained values, for PVC sheets plasticized with polyesters under investigation blended with DOP (50 : 50 wt.- %), are listed in Table (3). These values represent the data measured after seven days and after one year.

It is well known **[1]** that the hardness and tensile modulus of a PVC compound increase measurably during the period immediately following processing. A recent study carried out by Guerrero **[17]** has shown that even when the moduli of the thermally dried casted PVC sheets, are measured just 15 min after casting process, there was an evident anti-plasticization effect. Accordingly, in the present investigation, the plastisized PVC test samples were stored at room temperature for seven days before these tests were measured.

In the group of plasticizers P1-P4, the average number of carbon atoms of the repeating units lies between 10 and 20. Accordingly, the controlling parameters are the number of ether linkage and the molecular weight of the polyester. The average number of ether linkage of P1, P2, P3 and P4 are 0.0, 1.0, 2.0 and 0.0, respectively. Table (3) shows that the highest elongation and lowest tensile strength are assigned for P3 in both measurements i.e., after one week and one year. This reveals that P3 is the most compatible within this group. Upon comparing the elongation data, after one year, of plasticized PVC with P1/DOP-P4/DOP blends and DOP as sole plasticizer, it is observed that the percentage of reduction in elongation in the latter case is 34.2% while the highest percentage of reduction when DOP was blended with the polyesters P1-P4 is 25.6%.

With respect to P5, the tensile strength and percentage of elongation after one week, as shown in Table (3), are 10.8 kg cm^{-2} and 161, respectively. The former value slightly increased to 11.2 kg cm^{-2} and the latter one slightly decreased to 140 after one year. These petty changes in conjunction with the original low value of elongation and high value of tensile strength indicate that

P5 is a moderately compatible plasticizer and not incompatible as predicted theoretically.

Apart from P7-P11 and P19, all other polyesters are liquids possessing different degrees of plasticization efficiency. Within the group of polyesters P13 - P15, the highest polarity is assigned for P14 (see Table (1), average number of ether linkage is 1). The incorporation of TG in P14 instead of DG and BG in P13 and P15, respectively, increases also the total number of carbon atoms of the reactants. As a result of these two parameters it was presumed a good compatibility of this polyester. The tensile strength and the elongation data after one week reveal that P14 acts as good plasticizer. The data of the tensile test after one year indicate that the highest compatibility within this group is assigned for P15. This may be attributed to the high value of molecular weight (3252) and low acid value (7.2) compared with molecular weights of 2429 and 2671 for P13 and P14, respectively and acid values of 18 and 16.7, respectively. Certainly, there is a lack of systematic investigations on the influence of the acid value on the plasticization efficiency. The present finding may offer a great body of evidence on the effect of the acid value of the plasticizer on PVC properties. However, the present finding runs in harmony with the assumption **[18]** that the increase in the acid value of the plasticizer reduces its stability.

Table (3) shows that PVC sheets plasticized with polyesters P7 - P11 afford poor mechanical properties after one week. The data of tensile strength and % of elongation reveal that the polyesters P7 - P11 are not compatible with PVC. This finding agrees with the theoretical prediction of compatibility as shown in Table (2). Accordingly, these sheets were not considered for evaluation after one year.

Hardness: In the present work, the hardness shore D is used to categorize the efficiency and compatibility of the prepared polyesters as plasticizers for PVC. The obtained values, for PVC sheets plasticized with polyesters under investigation blended with DOP (50 : 50 wt.- %), are listed in Table (4). These values represent the data measured after ten days and followed throughout the year.

The hardness data, in general, indicate that the lower the value of hardness the better the plasticization efficiency of the plasticizer. On the other hand, the little increase in the hardness value with time is associated with a better compatibility due to the polymer - polymer miscibility **[19-21]** which reflects on the extent of exudation of the polyester plasticizer.

With respect to the plasticization efficiency, the data of the hardness [Table (4)] reveal that the most potent samples are P3, P4, P15, P16, P20 and P21. These polyesters afford initial values $\leq$ 63. Table (1) shows that the average number of carbon atoms / reactants used for preparing these polyesters is bigger than 9. The influence of the number of ether linkage on the plasticization efficiency is obviously noticed in case of P2, P14, P17 and P18. These polyesters provide initial values of hardness ranging between 65 and 66. These low values of hardness reflect the efficiency of these polyesters in plasticizing PVC. This efficiency may be attributed to the effect of combination of a total number of carbon atoms exceeding 10 and an appropriate degree of polarity afforded by the ether linkage incorporated in the chains of these polyesters (see Table 1 & 4).

Apart from the group of polyesters based on phthalic anhydride (P7-P12) other polyesters (P1, P5, P19 and P22) furnish moderate plasticization efficiencies (hardness = 70 : 72).

An attempt to elucidate the compatibility of the polyesters under investigation with PVC was performed by comparing the values of hardness after one year with the initial values. Careful inspection of the data tabulated in Table (4) reveals that the lowest increase in hardness i.e., the lowest exudation of the plasticizer is for P18. However, the data lead to the speculation that P2, P14, P17 and P18 are the best polyester plasticizers among the prepared samples. This speculation is based on the initial and final hardness values from which the extent of exudation can be estimated. Based on the percentage of the increase of hardness, the extent of exudation can be arranged according to the sequence P14 > P2 > P17 > P18. Accordingly, it can be said that P18 is the best plasticizer among the studied ones. This finding runs in harmony with the data obtained by measuring the tensile properties after one year. The initial values hardness and the corresponding values after one year for the PVC sheets plasticized with P18-DOP blend and DOP reveal that the increase in hardness is about 14% for the former plasticizer system while it is about 23% for the latter one.

CONCLUSION

The data reveal that the incorporation of polyester plasticizers may improve the plasticization potency of DOP by extending its workability time due to the reduction of the volatility of the plasticizer mixture.

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Table 1 **Constituents and structural parameters (<-O-> and TCN) of the prepered polyesters**

code	Glycol (mole)				Dicarboxylic acid (mole)				<-O->*	TCN^{+}
	EG	DG	TG	BG	SU	AD	SE	PHA		
P1	1.10	--	--	--	--	0.50	0.50	--	0.0	10
P2	--	1.10	--	--	--	0.50	0.50	--	1.0	12
P3	--	--	1.10	--	--	0.50	0.50	--	2.0	14
P4	--	--	--	1.10	--	0.50	0.50	--	0.0	12
P5	1.10	--	--	--	0.50	0.50	--	--	0.0	7
P6	1.10	--	--	--	0.50	--	0.50	--	0.0	9
P7	0.55	0.55	--	--	--	--	--	1.00	0.5	5
P8	0.55	--	0.55	--	--	--	--	1.00	1.0	6
P9	0.55	--	--	0.55	--	--	--	1.00	0.0	5
P10	--	0.55	0.55	--	--	--	--	1.00	1.5	7
P11	--	0.55	--	0.55	--	--	--	1.00	0.5	6
P12	--	--	0.55	0.55	--	--	--	1.00	1.0	7
P13	0.55	0.55	--	--	--	1.00	--	--	0.5	9
P14	0.55	--	0.55	--	--	1.00	--	--	1.0	10
P15	0.55	--	--	0.55	--	1.00	--	--	0.0	9
P16	--	0.55	0.55	--	--	1.00	--	--	1.5	11
P17	--	0.55	--	0.55	--	1.00	--	--	0.5	10
P18	--	--	0.55	0.55	--	1.00	--	--	1.0	11
P19	1.10	--	--	--	--	--	0.50	0.50	0.0	8
P20	--	1.10	--	--	--	--	0.50	0.50	1.0	10
P21	--	--	1.10	--	--	--	0.50	0.50	2.0	12
P22	--	--	--	1.10	--	--	0.50	0.50	0.0	10

*** Average number of ether linkage in the glycol system**

+ Total number of carbon atoms in the reactants

Table 2 Acid values, hydroxyl numbers, molecular weights,physical states of the prepared polyesters and theoretical prediction of their compatibility with PVC.

code	Acid value	Hydroxyl number	$<M_n>$ x 10^{-3}	State at 25°C	predicted compatibility
P1	18.4	27.2	2.461	waxy	compatible
P2	20.4	23.2	2.573	liquid	compatible
P3	11.5	20.8	3.474	liquid	compatible
P4	27.4	29.8	1.962	liquid	compatible
P5	12.3	37.6	2.249	liquid	incompatible
P6	13.4	29.1	2.640	waxy	limited compatibility
P7	17.9	26.1	2.550	solid	incompatible
P8	23.0	25.7	2.304	solid	incompatible
P9	24.9	28.4	2.105	solid	incompatible
P10	28.3	39.0	1.667	solid	incompatible
P11	19.7	26.3	2.439	solid	incompatible
P12	28.7	29.7	1.921	liquid	incompatible
P13	18.0	28.2	2.429	liquid	compatible
P14	16.7	25.3	2.671	liquid	compatible
P15	7.2	27.3	3.252	liquid	compatible
P16	16.4	23.6	2.805	liquid	compatible
P17	16.0	25.7	2.691	liquid	compatible
P18	20.4	27.2	2.357	liquid	compatible
P19	12.8	25.4	2.937	solid	limited compatibility
P20	22.3	24.1	2.418	liquid	compatible
P21	21.3	20.5	2.684	liquid	compatible
P22	9.3	23.9	3.380	liquid	compatible

Table 3 **Tensile strength (TS) and % elongation (E) of plasticized PVC sheets with various polyesters / DOP blends.**

code	After one week		After one year	
	TS (kgcm^{-2})	E %	TS (kgcm^{-2})	E %
P1 / DOP	9.0	209	10.3	160
P2 / DOP	8.7	221	10.6	165
P3 / DOP	7.6	242	9.7	180
P4 / DOP	8.9	225	9.8	177
P5 / DOP	10.8	161	11.2	140
P6 / DOP	9.3	184	10.6	168
P7 / DOP	16.4	18	---	---
P8 / DOP	12.7	105	---	---
P9 / DOP	---	---	---	---
P10 / DOP	12.0	120	---	---
P11 / DOP	13.1	90	---	---
P12 / DOP	12.4	110	---	---
P13 / DOP	9.9	175	11.4	120
P14 / DOP	8.4	232	9.8	178
P15 / DOP	8.4	230	9.1	192
P16 / DOP	7.8	236	9.3	180
P17 / DOP	8.2	215	9.0	186
P18 / DOP	8.0	220	8.8	195
P19 / DOP	11.0	144	---	---
P20 / DOP	8.8	190	9.4	150
P21 / DOP	8.4	198	9.6	150
P22 / DOP	9.3	158	10.5	130
DOP	7.9	244	8.9	182

Table 4 Hardness (shore D) for PVC sheets containing different polyesters blended with DOP (50/50 wt %) as a function of time.

code	Hardness (shore D) after different times in days					
	10	80	150	215	250	387
P1 / DOP	70	70	74	76	76	76
P2 / DOP	65	67	67	75	75	75
P3 / DOP	61	62	67	70	73	75
P4 / DOP	60	67	67	71	74	76
P5 / DOP	72	74	75	77	77	78
P6 / DOP	65	69	70	70	76	77
P7 / DOP	80	81	81	82	84	84
P8 / DOP	78	78	80	82	82	83
P9 / DOP	79	79	81	83	84	85
P10 / DOP	71	78	79	81	82	82
P11 / DOP	76	77	79	83	83	84
P12 / DOP	75	75	75	80	82	84
P13 / DOP	71	71	73	78	79	81
P14 / DOP	65	68	71	74	76	76
P15 / DOP	62	68	71	75	76	76
P16 / DOP	60	62	65	68	76	76
P17 / DOP	66	68	69	75	76	76
P18 / DOP	65	66	67	70	70	74
P19 / DOP	70	72	72	79	81	82
P20 / DOP	63	65	69	76	76	77
P21 / DOP	63	70	70	75	76	78
P22 / DOP	72	75	76	82	82	83
DOP	57	57	59	60	67	70