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Mechanical and Thermal Properties of PVC , PS and PMMA with New Resinounce Plasticizers

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Abstract

A new plasticizers prepared and characterized as ester of 1,3-bis[4-(3,5-dimethyl ol-4-hydroxy phenyl-isopropylidene)-2,6-dimethylol phenoxy]propane-2-ol(I) as described. The esters prepared were butyrate, caproate and benzoate.The new plasticizers were characterized by elementary analysis ,spectroscopic techniques and molecular weight determination. The physical ,rheological and thermal stability characteristic are also included.
The efficiency of plasticization were examined with polyvinylchloride(PVC), polystyrene(PS) and polymethyl methacrylate(PMMA). This plasticizers shows a great effect in increasing the melt flow index of the polymers and decreasing the total input in the melting process.

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Introduction

Polyvinylchloride(PVC), Polystyrene(PS)and Polymethyl methacrylate(PMMA) widely produced plastics, after ethylene and polypropylene due to their valuable properties ,high chemical resistance and low cost. It is observed the heating of PVC above 70^{0}C ,the properties of the polymer changed. At processing temperature used in practice (130-200 ^{0}C) degradation may take place(1-6).

It has been found that a certain materials call stabilizers retarded the degradation The degradation reaction and proceeded the polymer at low temperature. The stabilizers should be a low molecular weight and highly comparable and completely miscible with the material. To aid melt flow of the polymer during the processes a certain plasticizers are added.

In previous work we have synthesized and studied new plasticizers having resinous structure (1),these plasticizers shows outstanding efficiency with PVC(2) ,PS(3) and PMMA(4,5).In this paper new type of resinous intermediate(I) was synthesized in one pot reaction system(6),then transferred to several esters. Some results concerning their efficiency as a plasticizers are presented. The detailed of rheological and mechanical properties of the plasticized polymer published elsewhere(7-10).

Experimental

(a) The inter mediate compound (I) was prepared in our labroteries.
(b) Polymer samples :

The commercial PVC Sicron 548 FM with K-value = 70 and commercial plasticizer dioctylphthalate (DOP).The commercial PMMA sheet [η*]* =263cm^3/g was used in this studied, the polymer were purified by reprecipitation to remove any commercial additives. The commercial polystyrene with [The commercial polystyrene with [η] = 9.5 cm3/g, was used in this study after being repreciptated.
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(c) The other chemicals were used supplied by fluka. The solvents were purified by standard methods(11).

Measurements

Infrared spectra were recorded on Pye-Unicam SP3-100 .
H^1 NMR spectra were recorded on a 90MHz ,Bruker spectrospin;TMS was used as internal standard. The compounds were measured as saturated solutions in $CDCl_3$, duration tests were also carried out using D_2O.

Microanalysis were carried out at the Alfred Bernhart micro analytical laboratories.

Synthesis

The esters were synthesized by treating compound(I) with the suitable acid chloride in the presence of pyridine under dry conditions adopting the usual esterification procedure (10). The esters prepared in this study butyrate, caproate and benzoate. The esters were purified , dried then characterized .

Characterization

The intermediate compound(I) and the plasticizers were characterized by elemental analysis ,and spectroscopy (infrared and NMR),the analysis results are shown in table (1).

The number of hydroxyl groups in compound (I) was determined by colorimetery14),since the alcoholic hydroxyl groups from colored complex with ceric ammonium nitrate ,this technique was proved to be efficient for quantitative analysis of alcoholic hydroxylic groups(15). On the other hand the number of hydroxyl groups was also determined by colorimetery i.e. 9±0.5, and 9. ±0.1 respectively.

The number of ester groups in the plasticizers was determined by NMR and back titration technique(16),the results obtained show that all the hydroxyl groups(alcoholic and phenolic) in the plasticizers were esterified i.e. eleven ester groups per molecule was found.

Thermal analysis

Thermal stability of the plasticizers was studied using MOM derivatograph thermoanalyser which measures TG,DTG,DTA and temperature spontaneously. Two procedures used ,(a) isothermal analysis, by heating the sample at constant temperatures following the procedure of G.A.Adam etal (12),(b)by heating the sample at constant heating rate 10^0/min.and measuring the weight loss as a function of temperature ,typical thermo grams are shown in figure(1).All the measurements were carried out against stander α-Al_2O_3 in the presence of air. The thermal stability of the plasticized polymers was also studied, typical thermograms are shown in figure(2).

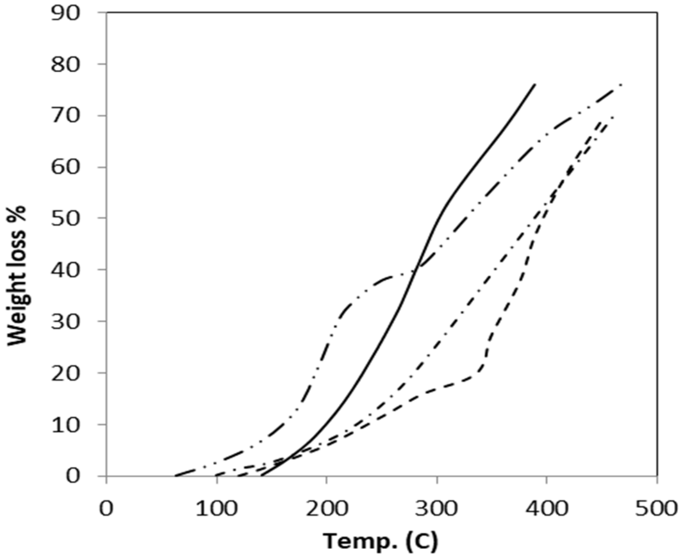

Fig 1. Typical thermogravimetric curves for the , butyrate (–··–), caproate (-·-), benzoate (----) and DOP (——) plasticisers.

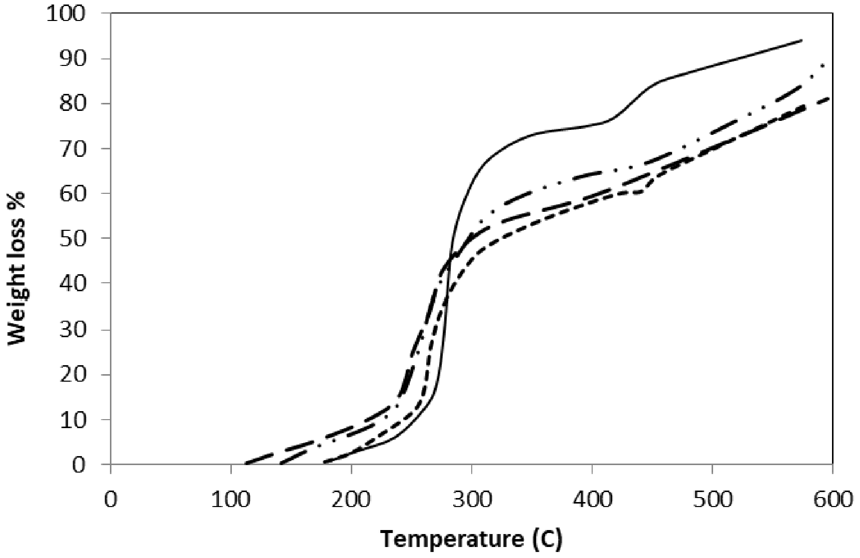

Fig 2. The thermal stability of plasticised PVC with butyrate (-··) , Caproate (—··—) , benzoate (----), and DOP (——) plasticisers.

Rheological properties

The effect of new plasticizers on the melt flow rate index(MFI)of PVC,PS and PMMA was examined using the melt flow index tester model 3/8 (Davenport Co.). The plasticized polymer sample containing different percentage of plasticizers were prepared by dissolving the polymer and the plasticizer in solvent , then thin films were cast from the homogenous solutions , dried at room temperature overnight then dried under vacuum at 80^0C for 24 hours, the solvents used were THF for PVC and acetone for PS and PMMA. Some plasticized PVC samples were prepared by mixing the PVC powder with the plasticizer solution in acetone, the solvent was evaporated from the swollen polymer powder. A homogenous plasticized PVC were obtained by both procedures.

The MFI of the plasticized samples was measured applying ASTM D-1238 ,several types of MFI measurements were carried out :

(a) The MFI of the plasticized polymer samples was measured at various applied loads and various temperatures, typical results are shown in figure (3,4 and 5).for PVC, PS and PMMA respectively.

(b)The effect of the plasticizers concentration on the MFI of the plasticized Polymers was studied at different temperatures and under several applied loads, the results obtained are shown in figure (6,7 and 8) for the three polymers.

(c)A comparative study was carried out using commercial plasticizer dioctylphthalate(DOP).

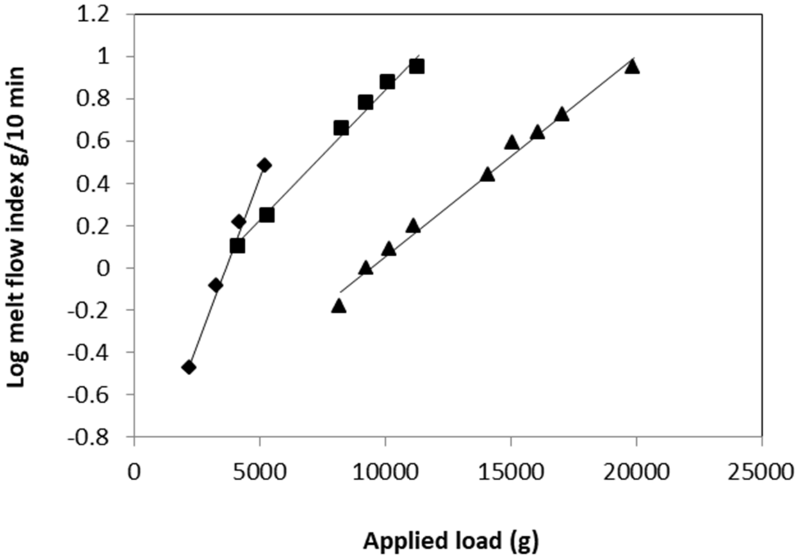

Fig 4. The effect of various plasticizers on the melt flow index of plasticized polystyrene at constant temperature (150 °C) and plasticizer concentration (10%). Butyrate ▲ , caproate ■, benzoate ●.

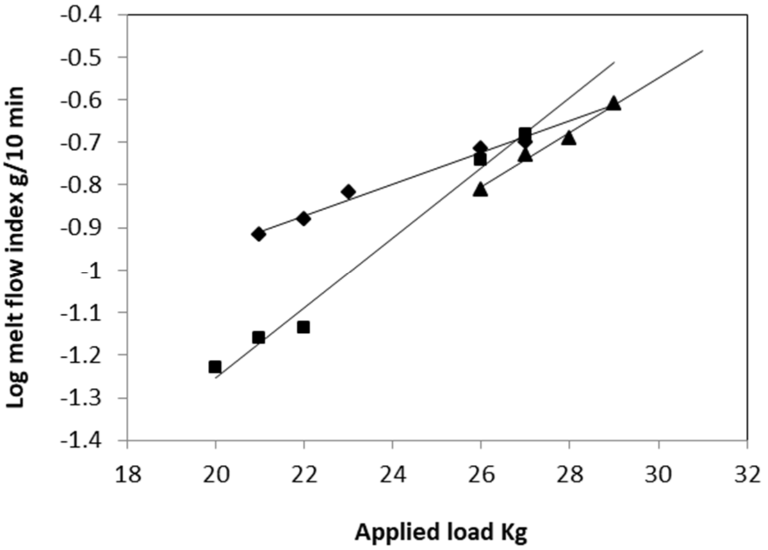

Fig 5. The effect of various plasticizers on the melt flow index of plasticized PMMA at constant temperature (170 °C) and plasticizer concentration (10%). Butyrate ▲ , caproate ■, benzoate ● .

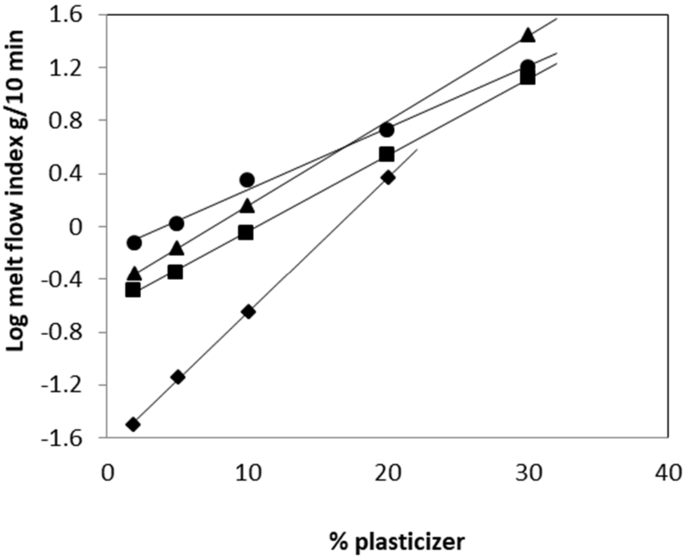

Fig 6. The effect of plasticizer concentration on the melt flow index at constant applied load (8 Kg) and at constant temperature (200 °C) for plasticized PVC with Butyrate ▲, caproate ■, benzoate ● and DOP ♦ plasticizers.

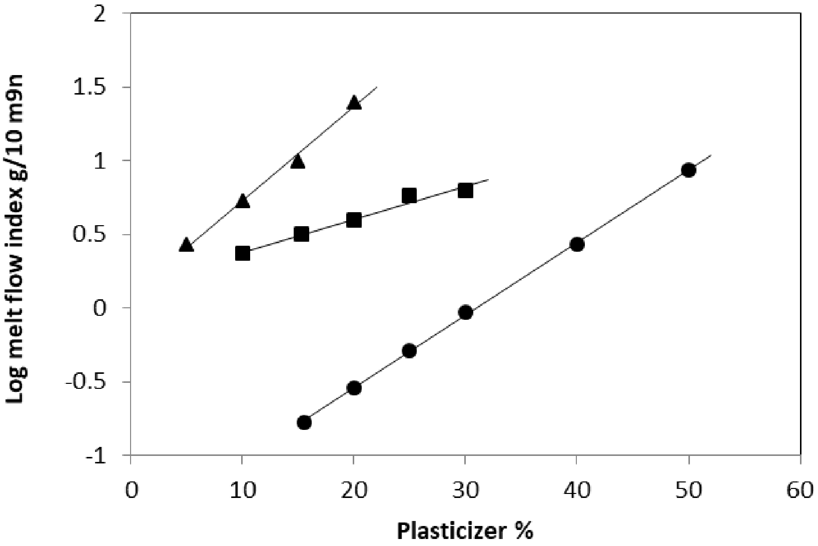

Fig 7. The effect of plasticizer concentration on the melt flow index at constant applied load (8 Kg) and at constant temperature (110 °C) for plasticized polystyrene with Butyrate ▲, caproate ■ and benzoate ● plasticizers.

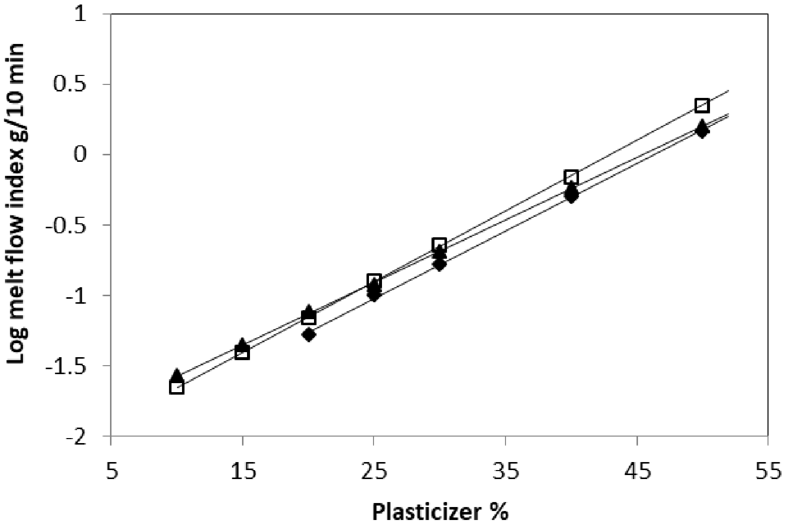

Fig 8. The effect of plasticizer concentration on the melt flow index at constant applied load (6 Kg) and at constant temperature (170 °C) for plasticized PMMA with Butyrate ▲, caproate □ and benzoate ● plasticizers.

Result and discussion:

The new intermediate compound (I) sets to very hard crosslinked resin catalyticaly at room temperature and thermally at temperature range (80 – 150 ^{0}C). The set resin shows good thermal stability ,non-soluble in organic solvents, chemical resistance with fine shiny laminating surfaces(6) .

The new plasticizers have interesting properties ,e.g.high boiling point ,low volatility,…etc.The plasticizers show good thermal stability as shown in figure (1).From the thermal analysis thermograms several thermal stability characteristics were determined as shown in table (3) ,e.g. decomposition temperature as determined from thermogravimetery (TG), difrential thermogravimmetry (DTG), and the 50% weight loss temperature. From the instantaneous slopes of the isothermal curves at different temperatures the energy of activation was calculated from the decomposition process over the initial 15% weight loss, applying Arrehneus equation(17).

Linear relationships were obtained between the applied load and Log.(MFI),(figures 3,4 and 5) from studying the effect of the plasticizers on MFI at different temperatures ,the total energy input in the melting Process was estimated using the general formula$^{(18)}$:

$$\mathbf{Log\ (MFI) = \frac{E}{2.303RT}}$$

The results obtained are shown in table (2) ,the plasticizers show great efficiency in increasing the MFI of the plasticized PVC , PS and PMMA ,the MFI increases with increasing the plasticizer concentration (see figures 6 , 7 & 8), on the other hand the plasticizers have great effect in decreasing the total energy input ,typical results are shown in figure (9) and table(2).

The effect of butyrate and caproate plasticizers on the MFI of plasticized PMMA was very small at 170^{0}C ,while at higher temperatures the polymer disintegrated.

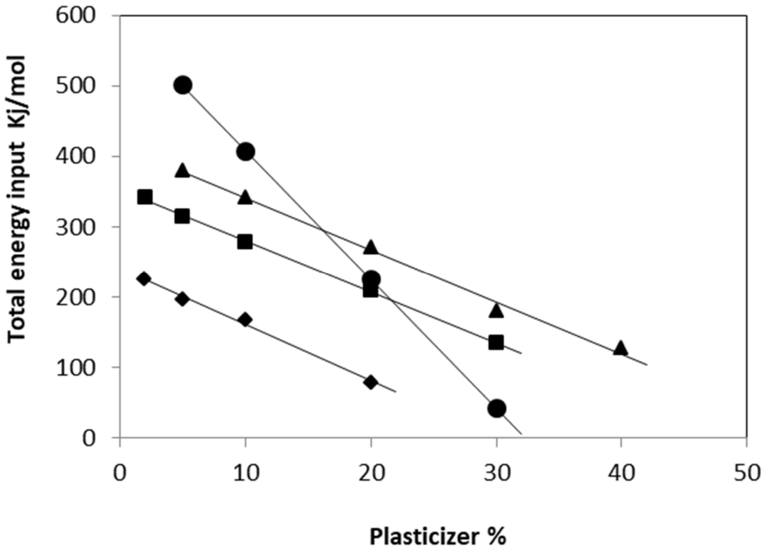

Fig 9. The effect of plasticizer concentration on the total energy inputat constant applied load (8 Kg) and at temperature range (190 – 200 °C) for plasticized PVC with Butyrate ▲ , caproate ■ , benzoate ● and DOP ♦ plasticizers.

Table(1): The elemental analysis results for the new resinous intermediate (I) and the new plasticizers .

Sample	**%Calculated**		**%Determined**	
	%C	**%H**	**%C**	**%H**
Butyrate Plast.	67.02	7.75	66.68	7.30
Caproate Plast.	70.16	8.85	68.81	8.21
Benzoate Plast.	74.68	5.06	73.42	5.13

Table(2): Some physical and rheological properties of the plasticizers.

The Plasticizer	B.P.^{0} C	Solubility Parameter	Total enery* input KJ/Mole		
			PS	PMMA	PVC
Butyric plast.	226	10.27	118	223	405
Caproic plast.	242	9.99	110	134	340
Benzoic plast.	294	10.42	104	99	170

*Determined from MFI measurements for 10% plasticized polymers at temperature ranged: 120-150 , 170-180 , 190-200 ^{0}C for PS , PMMA and PVC respectively.

Table (3) : Some thermal stability characteristics of the plasticizers

Plasticizers	Decomposition temp. (^{0}C) DTG	50%loss	TG	Activation energy (^E KJ/mole)	Temp. range^{0}C
Butyrate	365	375	255	37.63	325-340
Caproate	385	395	310	49.26	290-310
Benzoate	410	435	275	50.58	300-340

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