



Value-added ground work of polyester film forming co-binder for flexographic solvent based printing inks

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ABSTRACT

A new series of hyperbranched polyester-type polymers were synthesized from a variety of comonomers like adipic acid, 1,2-cyclohexanedicarboxylic anhydride, phthalic anhydride, trimethylolpropane, glycerol, trimellitic anhydride and citric acid using dibutyltin oxide as catalyst according to two steps one pot A_2+B_3 approach by solution polymerization with a fixed monomers ratio. The consequential polymers were brittle, soluble in ethanol, ethyl acetate and methylethylketone. The prepared polymers were utilized as a novel film forming co-binder with nitrocellulose for solvent based printing inks application. The physico-chemical characteristics were confirmed by FT-IR, GPC and acid value as well as hydroxyl value determinations. The mechanical and optical properties of the produced inks printed film were evaluated. The results show that the overall properties of the inks are of promise quality for use as co-binder resins for solvent based printing inks with 50 % partial substitution in formulation.

Introduction

Polyesters are a class of synthetic polymers which are characterized by the presence of repeated ester functional groups along their main chains [1]. They are typically composed mainly of co-reacted monomers with mono, di, or polyhydric alcohol with mono, di or tri-basic acid (or their derivatives) [2]. The family of polyesters comprises a variety of materials with different chemical structures and mechanical properties that are widely used in laminates, industrial construction and installation, molding compounds, coatings, and adhesives [3,4]. Low molecular weight polyesters or co-polyesters are key components for printing ink formulations [5,6]. The role of resins in vehicles is that bring properties such as hold pigment to the substrate, and deliver end use properties, like flexibility, adhesion, or gloss to printing inks [7]. All resins vary in their implementing of these properties. To overcome this limitation, blends of resins are commonly used in ink formulation [8]. Prominent developments in coating applications involve the synthesis of branched polymers [9-11]. Dendrimers and hyperbranched polymers are two-classes of branched architectural polymers; their unique structures might offer exceptional properties which led to novel applications [12-15]. Dendrimers are perfectly mono-disperse macromolecules with 100 %-branched architecture. However, their preparation involves a large number of subsequent steps in order to attain

high molecular weights [16]. Consequently, dendrimers have high production costs and correspondingly high sales prices. For this reason, dendrimers are restricted to very specific applications. On the other side, despite hyperbranched polymers have higher polydispersity and lower degree of branching, in many cases hyperbranched polymers show chemical performances just like dendrimers [17]. A wide range of hyperbranched polymers have been synthesized, amongst hyperbranched polyesters which are one of the most dominating reps [18]. Hyperbranched polyesters particularly that contain hydroxyl and/or carboxylic acid functional groups at linear and terminal structural units can be used to adjust specific properties such as thermal, mechanical and solubility or to prepare core-shell type architectures; add to that modification by submission to post polymerization [19-22]. Many detailed studies on the chemistry and applications of hyperbranched polyester resins are reported [23-28].

The aim of this work is to synthesis and evaluation of hyperbranched polyester polymers which are designed to be used as a novel film forming co-binder for solvent based printing ink formulations. The results of optical and mechanical properties of the obtained printing inks were compared to the inks containing nitrocellulose as mono-binder.

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Materials and Methods

Chemicals

1,2-cyclohexanedicarboxylic anhydride (1,2-CHDC.an), predominantly cis and trimellitic anhydride (Tm.an) (Sigma-Aldrich), trimethylolpropane (TMP) and dibutyltin oxide (Merck KGaA - Germany), adipic acid (AA), citric acid (CA) and phthalic anhydride (Ph.an) (Oxford Lab-India), glycerol (Gly) and cyclohexanone (Loba Chemie-India).

Synthesis of polyesters

The polyesters were synthesized through two steps process of esterification and polymerization including melt condensation followed by polymerization, using monomers composition shown in **Table 1** at fixed molar ratio.

Step1. To a 500 mL three-necked flat bottom flask equipped with a magnetic stirrer, nitrogen gas inlet, thermometer and reflux condenser connected to Dean-Stark tube. 1 mol of dibasic acid/or anhydride, 2 mol of tribasic alcohol and 0.2wt. % (relative to the total weight of reactants) of dibutyltin oxide as a catalyst were charged while a slow stream of nitrogen gas was flushed through the mixture. With continuous stirring the mixture was heated gradually till all of reactants were completely molten, then the temperature of the reaction was raised to 160°C for 5h. **Step2.** Add a solution of 2 mol of tribasic acid/ or anhydride dissolved in 100 mL of cyclohexanone to the flask at once. The reaction mixture was stirred for 2 h at 200°C under reflux, then the solvent was removed under reduced pressure. The resulting polymers were dried in a vacuum oven. The products were solid at room temperature and used without further purification. The process flow of preparing the polyesters is shown in **Fig. 1**.

Table 1: Monomers composition and molar ratio

Group no	Polymer sample code	Chemical composition	Feed ratio
Group I	PEST-5	TMP+ AA+TM.an	2:1:2
	PEST-4	TMP+CHDC.an+TM.an	
	PEST-3	TMP+Ph.an+TM.an	
Group II	PEST-12	Gly+AA+TM.an	2:1:2
	PEST-13	Gly +CHDC.an+TM.an	
	PEST-14	Gly +Ph.an+TM.an	
Group III	PEST-6	TMP+AA+CA	2:1:2
	PEST-7	TMP+CHDC.an+CA	
	PEST-8	TMP+Ph.an+CA	
Group IV	PEST-9	Gly+AA+CA	2:1:2
	PEST-10	Gly +CHDC.an+CA	
	PEST-11	Gly +Ph.an+CA	

Characterization of the prepared polymers

Acid value

Acid value was determined according to ASTM D 1639-90.

Hydroxyl value

Hydroxyl value was determined according to ASTM D 4274-99.

FTIR analysis

FTIR spectra were conducted using Bruker FTIR analyzer; ALPHA-Platinum FT-IR Spectrometer with ATR Platinum–Diamond sampling module from 4000 to 400 cm⁻¹.

Molecular weights determination

The molecular weights were determined using GPC Agilent model 1515 pump system equipped with 1260 infinity refractive index detector and using tetrahydrofuran (THF) as eluent, operating with a flow rate of 1.00 mL/min at 35°C. Column PL-gel 3 Lm Mixed E 300 7.5 mm covering a molecular weight range of 600 – 400,000 mg/g was used and was calibrated using polystyrene standards.

Viscosity of the polyols

The viscosity of the polyols was determined according to ASTM D 4878-03 using the Brookfield digital viscometer model (DV-E).

Solubility in solvents

Solubility parameters were determined according to ASTM D 3132-84. The tested solvents were ethyl acetate, ethanol, isopropanol and methylethylketone.

Printed ink characterization

Ink formulation

The printing inks were formulated as follows; nitrocellulose used as mono-binder in reference sample compared to 50 % replacement of nitrocellulose with polyester as co-binder in tested samples according to the formulation given in **Tables 2&3** respectively. All samples were ground using zircon beads at 100 % of ink mass on a devil shaker for suitable time to obtain a homogeneous matrix.

Printed film thickness

Ink was applied on polypropylene film using hand coater 12. The printed ink film thickness was measured according to ASTM D 1005-95 using KAFER micrometer.

Curling

Curl of the printed ink film was measured according to ASTM D 4825-97.

Adhesion

Adhesion of the printed ink film was measured according to ASTM F 2252-03.

X-rite measurements

(Relative color strength- ΔE^*_{ab} – Transparency)

Printing ink strength, lightness and shade were measured according to ASTM D 2244-02 using EXACT–PANTONE X-rite spectrophotometer.

Gloss

Gloss of the printed ink film was measured according to ASTM D 7163-05 using BIUGED BGD 514 (60°) gloss meter.

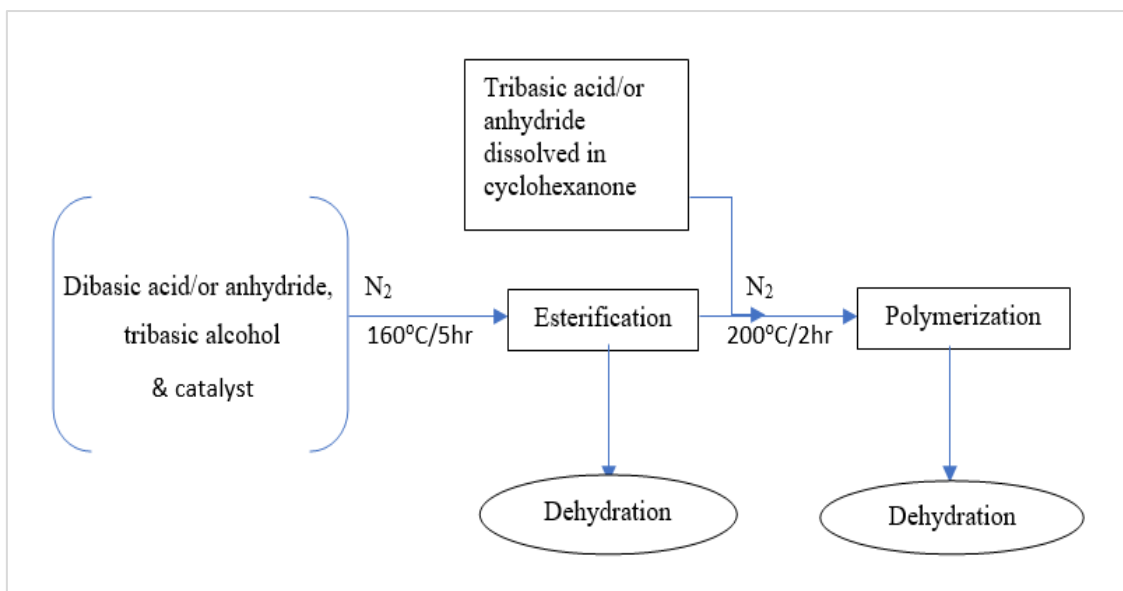


Fig. 1: Process flow of preparing polyester.

Table 2: Reference sample formulation

Component	Weight %
Pigment Cyan	12 gm
Dispersant	1.5 gm
Nitrocellulose resin "As mono-binder"	9 gm
Ethanol	46.1 gm
Ethyl acetate	31.4 gm
Total weight	100 gm

Table 3: 50 % replacement sample formulation

Component	Weight %
Pigment Cyan	12 gm
Dispersant	1.5 gm
Nitrocellulose resin	4.5 gm
Polyester "As co-binder"	4.5 gm
Ethanol	46.1 gm
Ethyl acetate	31.4 gm
Total weight	100 gm

Results and Discussion

Monomers type impact on both synthesis's approach and final properties of the polymer

Hyperbranched polyesters can be prepared through AB_2 polymerization, where AB_2 monomers are intermolecularly polymerized to build up hyperbranched structures, or via $A_2 + B_3$ approach which is recently has there been a growing industrial interest because of AB_2 monomers are rare species in the chemical supply chain [17]. Polyester resins which used in the field of coating applications are commonly consist of both aromatic and aliphatic dibasic acids. The aromatic segment is utilized basically to expand the glass transition temperature (T_g), hardness, and chemical resistance. On the other hand; phenyl ring easily absorbs UV-light limiting the photo-oxidative stability of the polyester [29]. Therefore; cyclohexyl dibasic acids have been suggested as alternatives for

the aromatic dibasic acids, this cycloaliphatic structure would allow intermediate features of the physical properties amongst aromatic and linear aliphatic polyesters with the exception of yellowing resistance that distinguish the linear diacids. Compared to aromatic polyester, T_g of cycloaliphatic polyester is lower, but is higher than linear aliphatic polyester. The flexibility of cycloaliphatic based polyester is also in the midst of aromatic and linear aliphatic polyesters due to their cyclic structure [30].

Preparation and characterization of polyesters

The polyesters were prepared by applying variant of two-stage thermal polycondensation technique (esterification and polycondensation) in a three-necked flat bottom flask. The theoretical chemical structures of the obtained polyester resins are represented in Fig.2a, 2b, 2c and 2d.

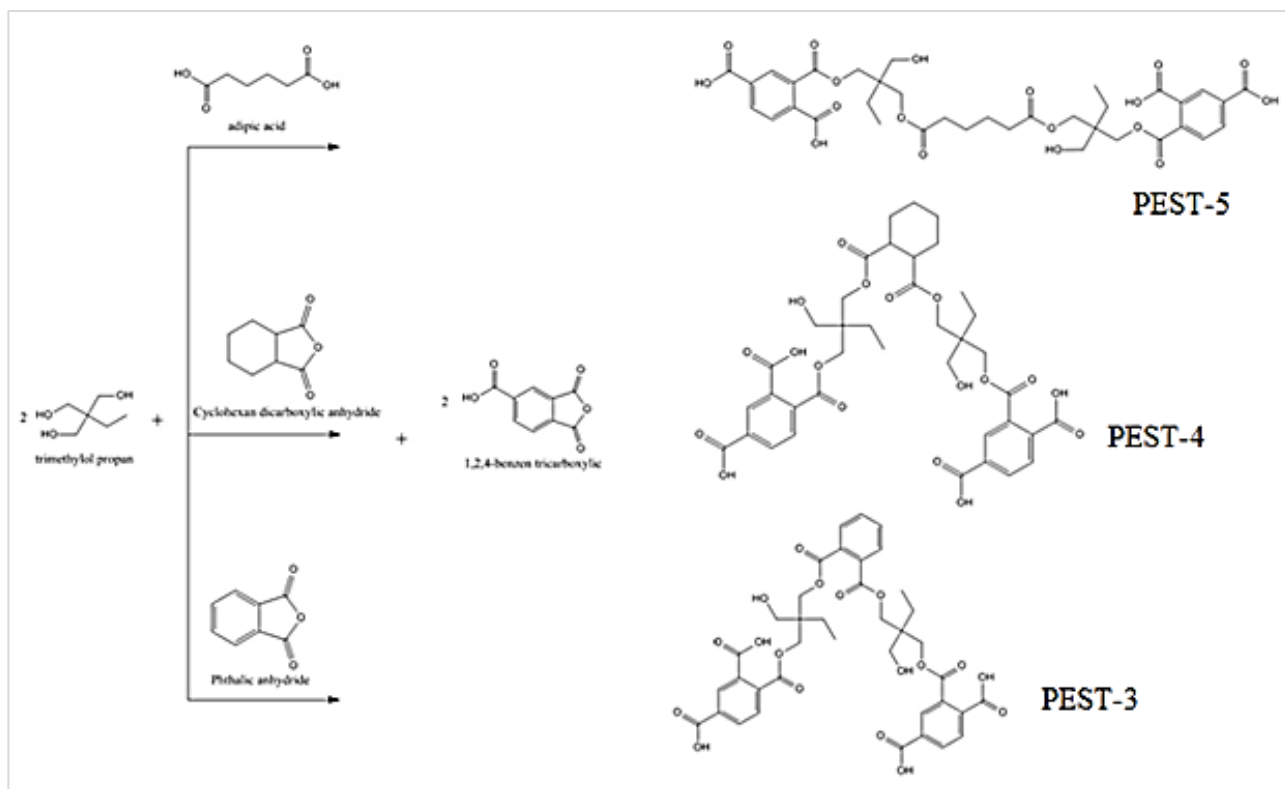


Fig. 2a: Theoretical chemical structures of group (I); PEST-5, PEST-4&PEST-3.

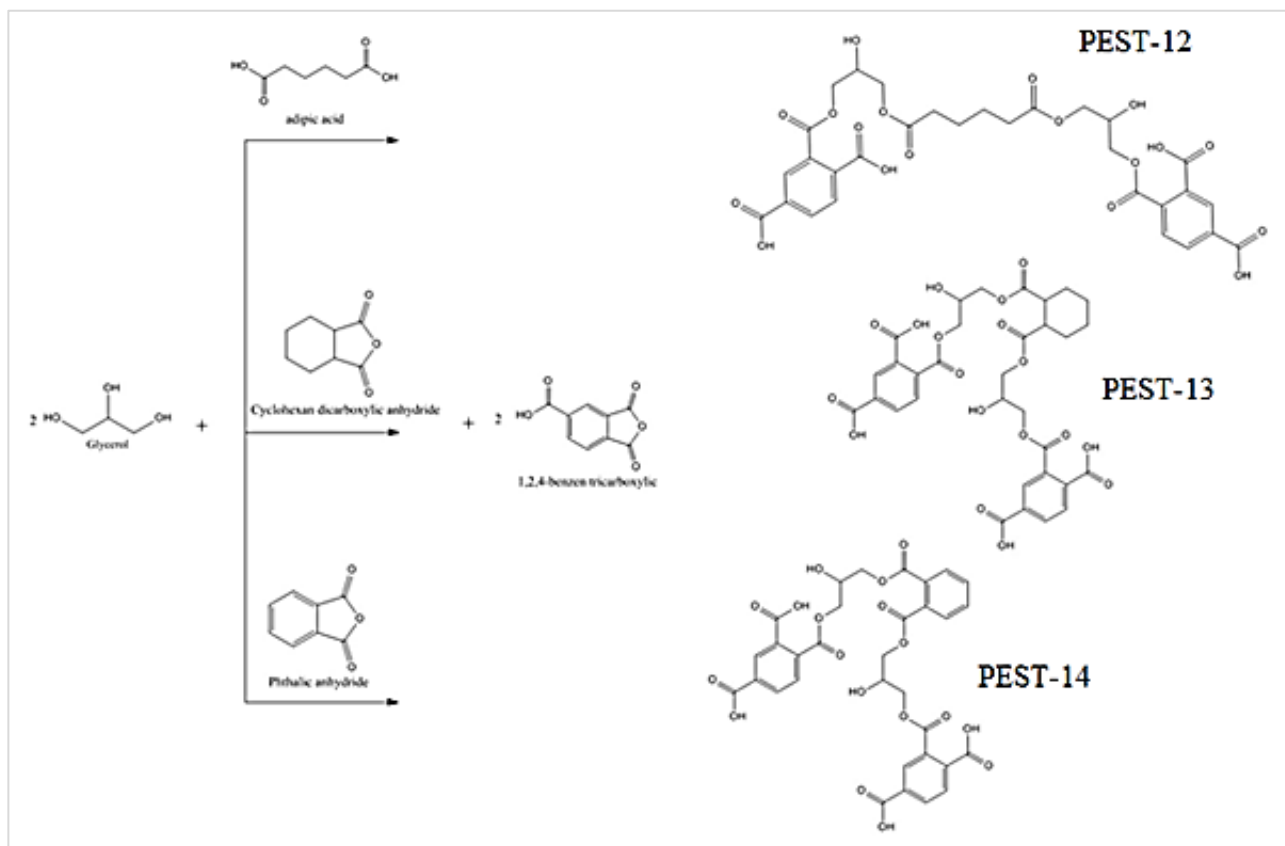


Fig. 2b: Theoretical chemical structures of group (II); PEST-12, PEST-13& PEST-14.

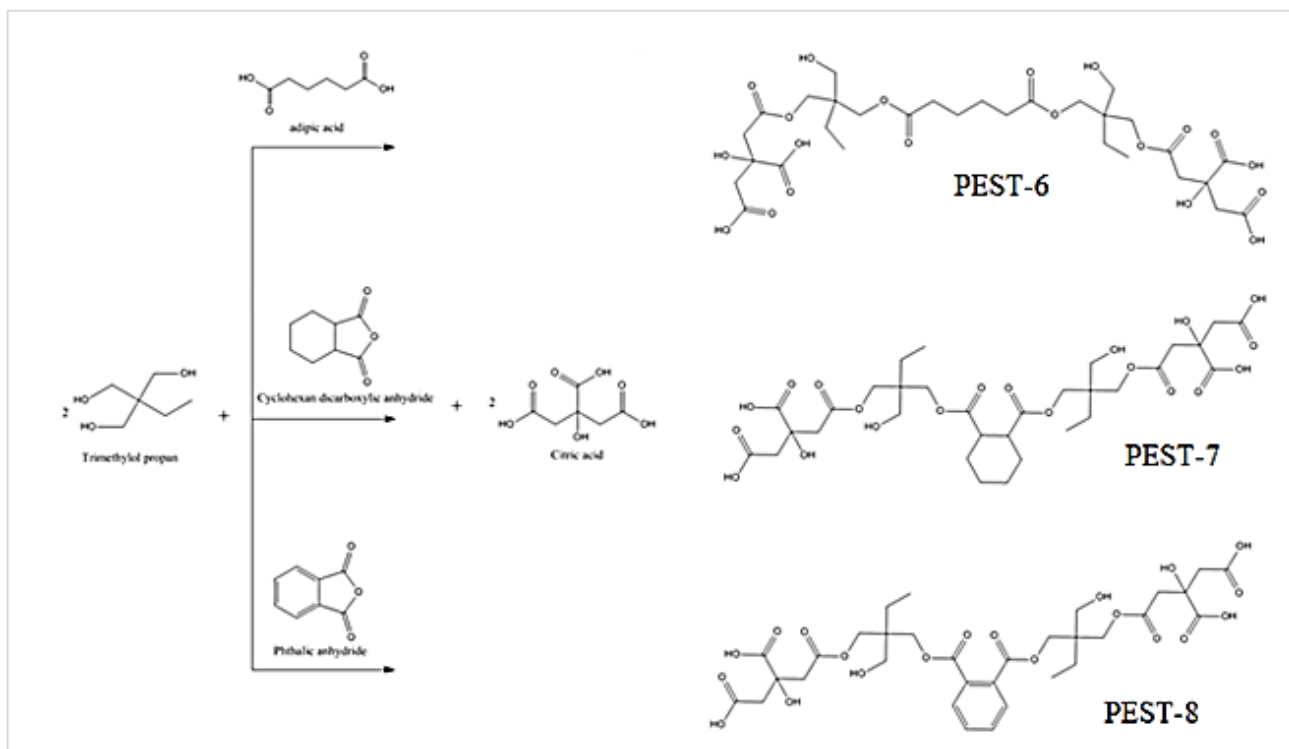


Fig. 2c: Theoretical chemical structures of group (III); PEST-6, PEST-7 & PEST-8.

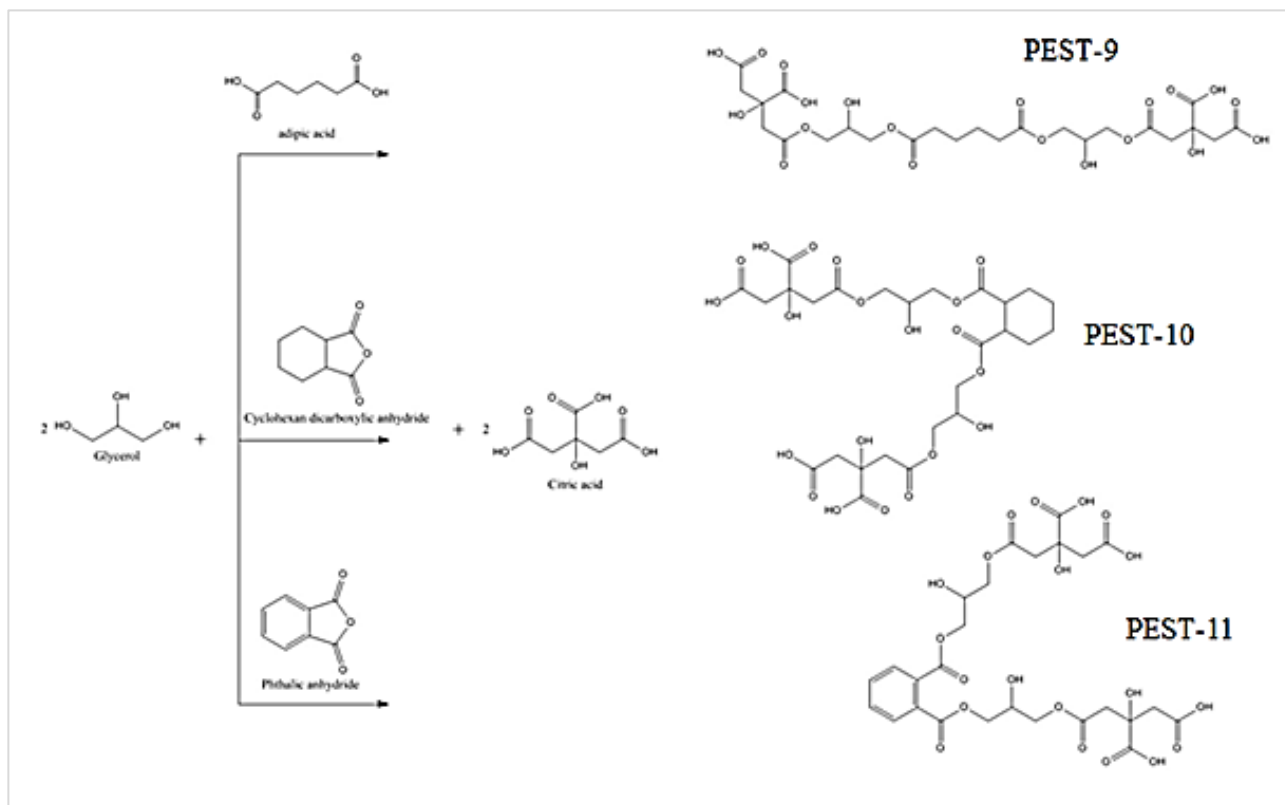


Fig. 2d: Theoretical chemical structures of group (IV); PEST-9, PEST-10& PEST-11.

Fourier Transformed Infrared (FTIR) analysis

The FTIR spectral data of the prepared polyesters are shown in in **Fig.3a, 3b, 3c** and **3d**. The wide band in the (O-H) stretching region is attributed to several contributions of different types of hydroxyl groups. The peak indicates at 3379cm^{-1} , 3445cm^{-1} corresponding to $\text{O}=\text{C}-\text{O}-\text{H}-\text{O}$ and inter/intramolecular $\text{O}-\text{H}\cdots\text{O}-\text{H}$, respectively, which increases the hydrogen bonding strength in the polyester due to regular arrangement of (O-H) functions in three-dimensional space [23].

The peaks centered at 2931 and 2850cm^{-1} correspond to C- H stretching of methylene and methyl groups [31]. The peaks between 1600 and 1800cm^{-1} are due to the ester carbonyl stretching vibrations (C=O), at 1717cm^{-1} due to hydrogen-bonded carbonyl. The peaks at around 1240cm^{-1} , 1173cm^{-1} , 1171cm^{-1} were assigned to (C-O) stretching of ester group. The peaks at about 1050cm^{-1} indicate the -OH banding of primary alcohol and at about 1100cm^{-1} of -OH banding in secondary alcohol.

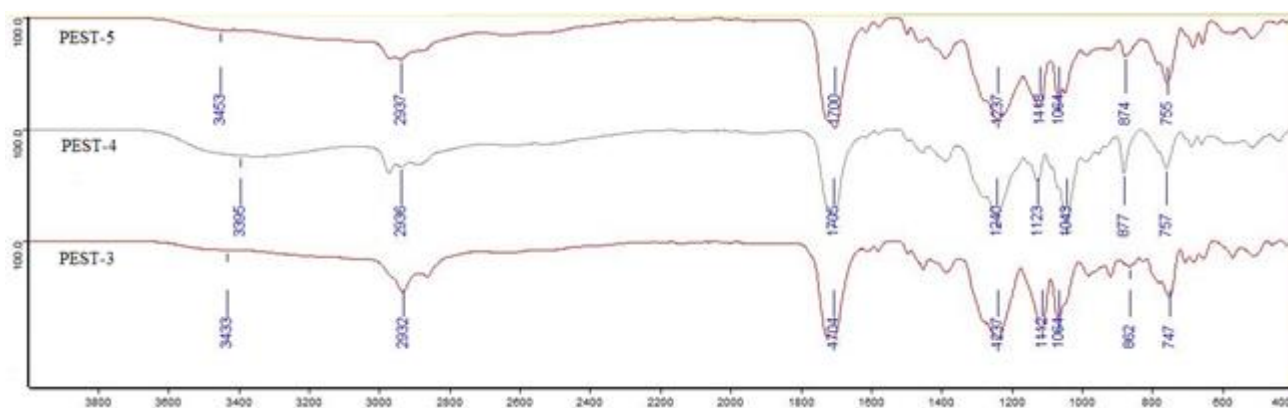


Fig. 3a: FTIR analysis of group (I); PEST-5, PEST-4& PEST-3.

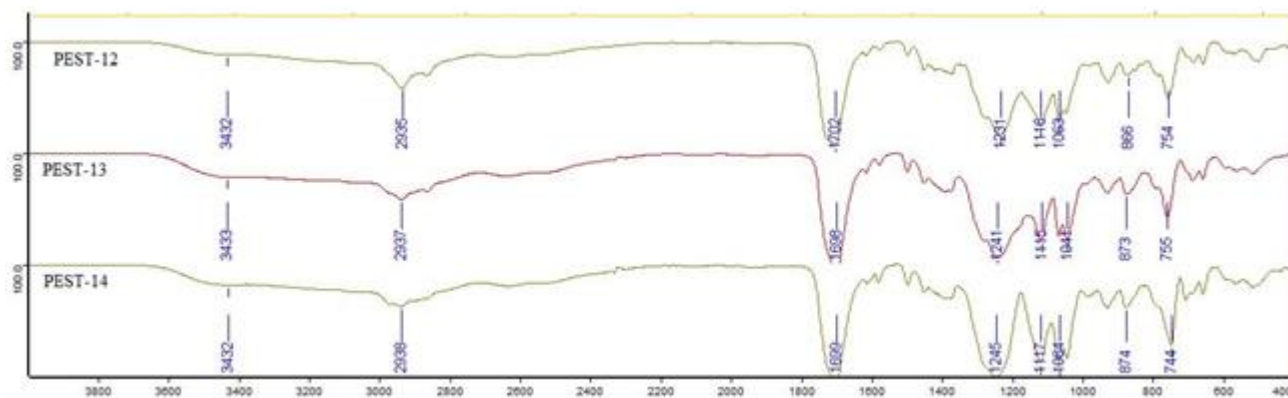


Fig. 3b: FTIR analysis of group (II); PEST-12, PEST-13& PEST-14.

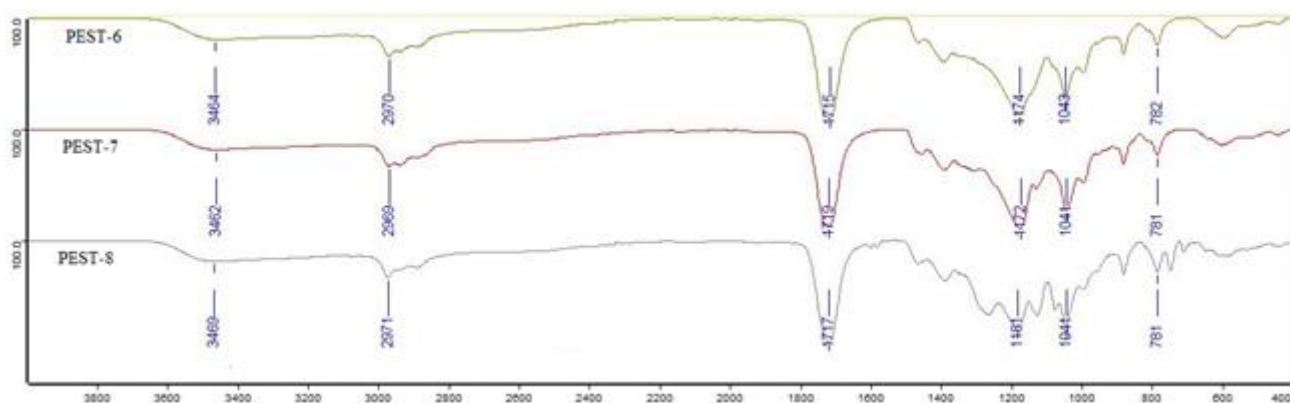


Fig. 3c: FTIR analysis of group (III): PEST-6, PEST-7& PEST-8.

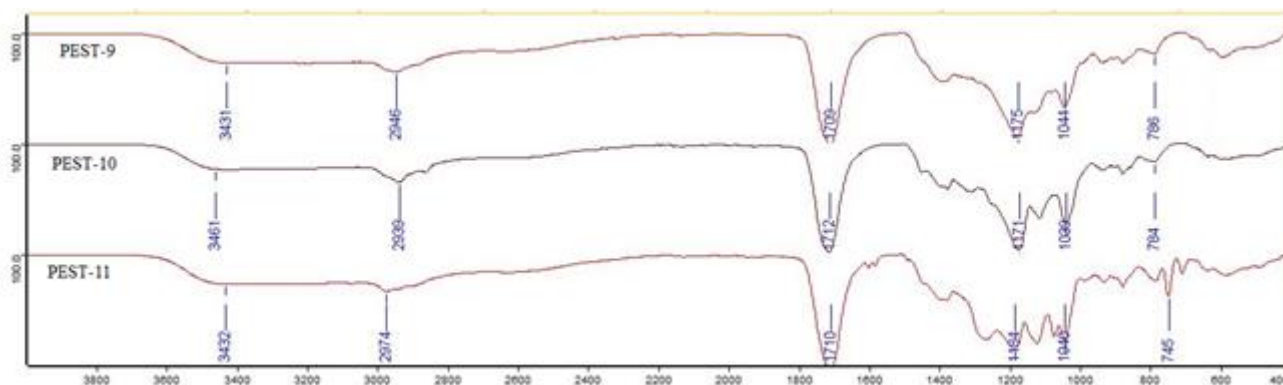


Fig. 3d: FTIR analysis of group (IV): PEST-9, PEST-10& PEST-11.

Gel Permeation Chromatography (GPC) analysis

GPC data of the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) for each polyester oligomer which are listed in **Table 4** indicated that; the designed polyesters are of low molecular weights of 600 - 800 g/mol, **Table 4**.

The GPC values of the molar masses were smaller than those theoretically predicted as a result of using linear polystyrene calibration standards. This is due to the specific branched structure of hyperbranched oligoester that have a smaller hydrodynamic volume compared with a linear polymer of the same molar mass and/or the interaction of a large number of polar functional groups with the column packing, especially in tetrahydrofuran (THF). In addition, the presence of side reactions, such as cyclization, ether formation, decarboxylation and deactivation of carboxylic groups, and self-condensation during melt polycondensation led to a broadening of the molar mass distribution and limits the attainable molar mass [32].

Acid value and hydroxyl values analysis

To further identify the chemical structures; the hydroxyl values (OHV) and the acid values (AV) were also examined by titration, the results of the samples are presented in **Table 5**. All the prepared polyesters exhibited high acid value and relatively low hydroxyl value, which was in agreement with the feed composition. It can be observed that the acid value decreased as reaction progressed. Compared to the later stages of the reaction, the reduction in acid value is faster at the early stages of the reaction.

This pattern of changes in acid value during polyesterification reaction the action explained as due to the decrease in the number of hydroxyl group as the reaction progressed [33] and is also due to the high reaction temperature (200°C), which lead to an increase in the amount of side reactions taking place during the reaction such as thermal decomposition of the ester groups, which yield carboxylic acid end-groups, thus leading to an increase in AV. However, also the hydrolysis of the ester-bonds by traces of water during the bulk polycondensation reaction can-not be excluded [34].

Properties of Polyesters (PEST)

The main characteristic features of the prepared PEST with different co-monomers and the same molar ratio are summarized in **Table 6**.

Viscosity of polymers is an involved function of many interaction variables, such as the molar mass, structure, and conformation of polymer molecules. Compared to traditional polyesters, which are solids or high viscosity liquids at room temperature, the prepared

polyesters (PEST) are very low viscosity liquids at room temperature. As a result, the prepared (PEST) should be very useful for the formulation of high solids coatings. In other words, the higher the level of (PEST), the lower was the volatile organic compounds (VOC) of the coating formulation. With regard to solubility; since polyester would often be used in combination with other resins in coating compositions, when using such blends, it is highly preferable that all the resins are miscible with each other [35].

Printed film properties

All ink formulations were applied on polypropylene film using hand coater. The mechanical and the optical properties of the printed film were determined as summarized in **Table 7**. The mechanical properties represent the physical behaviors of the print on the substrate, mainly curling and adhesion. Curling is the deformation of the printed substrate after printing the ink film, while the adhesion of the printed film is defined as the detachment of the printed ink film from the printed substrate.

It is clear from results that the incorporation of the prepared polyesters (PEST) to ink formulation (50 % replacement ink sample) led to no curling effect and the adhesion properties show no removal of the ink film formed on the polypropylene substrate surface. These mechanical properties could be referred to as due the molecular structure (numerous terminal functional groups) of resins. It is clearly observable that the (PEST) acquired numerous -OH and -COOH sites, which could form hydrogen bonding with substrate and in between the resin molecules that enhanced the adhesion strength of the coating than their linear counterpart [25]. The optical properties were determined as color values $\{\Delta L, \Delta A, \Delta B\}$, (ΔE) and gloss. Where; ΔL is lightness/darkness value, ΔA is red/green value, ΔB is blue/yellow value and (ΔE) is the total color differences. From samples results it was observed that ΔE values were lower than 1, which means that color matching was at a good level of quality and the differences were invisible to the human eye [27]. For the other systems where ΔE as higher than 1 but lower than 4, demonstrating that differences occurred, and these could be observed with the naked eye [28]. Gloss is one of the most important parameters in printing and packaging technology, because gloss affects the print quality by providing a better overall look and greater depth to colors [36].

The gloss values were in the range 98 – 85 gloss units. The data reported in **Table 7** indicated that the prepared polyesters could work as a co-binder resin with nitrocellulose and gave very comparable mechanical and optical properties.

Conclusions

In the present study, a new family of hyperbranched polyesters were prepared by polycondensation reaction using different comonomers in which the molar ratio of the reactants was fixed. The physico-chemical properties of the prepared polyesters (PEST) were characterized and evaluated. The prepared

polymers were evaluated in ink formulation as film forming resin for solvent based printing inks. The results revealed that ink samples with 50 % (PEST) as co-binder have acceptable mechanical and optical characteristics, which confirm the possibility of utilization of the prepared polyesters (PEST) as film forming co-binder in solvent based printing ink formulations.

Table 4: GPC data of the prepared polyesters

Group No	Polymer sample code	Mn (g/mol)	Mw (g/mol)	PDI
Group I	PEST-5	716	1017	1.42
	PEST-4	770	1056	1.37
	PEST-3	754	1041	1.38
Group II	PEST-12	710	1086	1.53
	PEST-13	726	1162	1.59
	PEST-14	666	1119	1.68
Group III	PEST-6	737	1030	1.4
	PEST-7	819	1229	1.5
	PEST-8	801	1235	1.54
Group IV	PEST-9	674	1025	1.52
	PEST-10	680	1081	1.59
	PEST-11	677	1063	1.57

Table 5: Acid values and hydroxyl values of the prepared polyesters

Group no	Polymer sample code	Acid value mg/g (AV)	Hydroxyl value mg/g (OHV)
Group I	PEST-5	257	94
	PEST-4	198	56
	PEST-3	218	87
Group II	PEST-12	299	104
	PEST-13	252	87
	PEST-14	280	90
Group III	PEST-6	266	129
	PEST-7	177	110
	PEST-8	247	128
Group IV	PEST-9	356	189
	PEST-10	293	137
	PEST-11	335	142

Table 6: Characteristic features of the prepared polyesters

Polymer sample code	Viscosity cp (25% solution in ethanol at 25 °C)	Solubility in solvents		
		Ethanol	Ethyl acetate	Methyl ethyl ketone
PEST-5	46.3	soluble	soluble	soluble
PEST-4	35.0	soluble	soluble	soluble
PEST-3	35.5	soluble	soluble	soluble
PEST-12	45.6	soluble	soluble	soluble
PEST-13	30.5	soluble	soluble	soluble
PEST-14	37.4	soluble	soluble	soluble
PEST-6	50.0	soluble	soluble	soluble
PEST-7	41.4	soluble	soluble	soluble
PEST-8	46.2	soluble	soluble	soluble
PEST-9	37.6	soluble	soluble	soluble
PEST-10	32.7	soluble	soluble	soluble
PEST-11	39.5	soluble	soluble	soluble

Table 7: Properties of printing ink

Samples name	Mechanical properties		Optical properties				Gloss Sample
	Curling	Adhesion	ΔE	ΔL	ΔA	ΔB	
Reference	No Curling	No ink removal	Used as a Standard for X-rite				92
PEST-5	No Curling	No ink removal	0.79	0.45	-0.63	0.18	97
PEST-4	No Curling	No ink removal	1.88	1.23	-1.33	0.5	98
PEST-3	No Curling	No ink removal	0.82	0.77	0.25	0.13	91
PEST-12	No Curling	No ink removal	0.59	-0.01	0.65	-0.17	92
PEST-13	No Curling	No ink removal	4.72	1.29	-4.41	1.08	94
PEST-14	No Curling	No ink removal	3.22	1.5	-2.65	0.99	97
PEST-6	No Curling	No ink removal	0.87	0.69	-0.52	0.11	88
PEST-7	No Curling	No ink removal	2.16	-0.29	2.09	-0.48	92
PEST-8	No Curling	No ink removal	1.36	0.32	1.29	-0.27	93
PEST-9	No Curling	No ink removal	1.05	0.55	-0.84	0.27	88
PEST-10	No Curling	No ink removal	1.74	0.71	-1.5	0.36	85
PEST-11	No Curling	No ink removal	2.96	-0.28	2.87	-0.68	95

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