COMPARISON OF CHEMICAL NANO STRUCTURE, RHEOLOGICAL AND MECHANICAL PROPERTIES OF LONG OIL ALKYD RESIN SYNTHESIZED USING POLYBASIC ACIDS CATALYST

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ABSTRACT
In this research, chemical nano structures, rheological and mechanical properties of long oil alkyd resin which was synthesized using different polybasic acid catalysts have been studied. These catalyst were phosphoric acid, 1,2,4-benzene tricarboxylic acid and succinic acid. The new compounds were compared with reference formula of long oil alkyd resin. For this idea, same formula of clear air drying varnishes were prepared based on different long oil resins which have been synthesized using different catalysts and reference long oil alkyd resin. FTIR spectroscopy was employed to investigate the nano chemical structures of the resins and varnishes. The rheological properties of varnishes, i.e., viscosity, drying time, glossary and film thickness and the mechanical properties, i.e., hardness, adhesives test, bending test and impact tests of films have been investigated. The results revealed that nano chemical structure of alkyd resins and theirs varnishes is totally the same. Also the rheological and mechanical properties of varnish which was prepared with succinic acid catalyst was better than that which was prepared with 1,2,4-benzene tricarboxylic acid. Moreover, the prepared vanishes were better than accustomed varnishes.

Keywords: long oil alkyd resin, polybasic acid catalyst, unsaturated modified polyester, 1,2,4-benzene tricarboxylic acid, characterization of alkyd resin properties

INTRODUCTION

Alkyd resins especially long oil alkyd resins are the cheapest resins that have been applied for decorative painting. Two process parameters to produce any product that are very important are economical and high quality of products (Mazandarani *et al*. 1992). For a long time, alkyd resins are known to be important in coating and paint industries due to their low cost. They are derived from relatively inexpensive raw materials and they are highly soluble in less expensive and harmful solvents. Alkyd resins are widely applied in industrial and semi industrial sectors as cheap surface covering for metal corrosion protection as well as for decorative purposes (Kumar *et al*. 2010).

Alkyd resins are prepared by condensation polymerization reaction between three kinds of compounds including poly-hydrate alcohols such as glycerol, penta erythritol, polybasic acids such as phthalic anhydride, maleic anhydride and fatty acids or triglyceride oils either by fusion or by solvent processes. Metallic soaps or salts (usually octoates) are driers and used for air drying alkyd resins. These compounds contain either alkaline earth metals or heavy metals which are applied to catalyze the oxidative cross-link reactions between unsaturated part of fatty acid or oil of resin and oxygen. Driers are branched to two categories: primary (surface) and secondary (deep) driers. Primary driers promote rapid surface drying of wet film of coatings and secondary driers promote oxygen uptake, peroxide formation and decomposition at ambient temperature. Complex oxidative or free radical chemistry also involved that leads to the formation of polymer chain to another polymer chain cross-links (Oyman *et al*. 2005).

The water solubility is not an important mechanical property of polymers, therefore is not necessary to determined. Due to non-ionic high molecular weight compounds containing high level of hydrophobic groups of polymers, they are expected to show very low solubility in water (NSW, AUSTRALIA, 2001). Some mechanical properties of resin such as glossary, hardness and drying time are very important especially for alkyd resins which are used in printing industrial as ink (Kang *et al*. 2000).

Although changing in formulation of long oil alkyd resin through replacing maleic anhydride with phetalic anhydride not only made the stereo structure of the alkyd molecule bigger but also reduced the condensation time of esterification reaction. Therefore the viscosity of resin increased within the same time interval (Vaso *et al*. 2010). Cobalt octoate catalyzed oxidation of fatty acids or vegetable oils modify long oil alkyd resins to increase resin elasticity. Oxygen and oils are connected together as Z,Z (cis-cis) or E,E (trans-trans) epoxide cycle. Other products of oxidation reaction between oxygen and fatty acids or oil include endo-peroxides, epoxides, aldehydes, ketones, carboxylic acids and alcohols. Hardness and glossary of air drying alkyd resin varnishes completely depend on these compounds (Odian *et al*. 1991 and Mazandarani *et al*. 1992).

American Society for Tests and Materials (ASTM), DIN standard and Japanese standard consist of common standard tests and experimental methods, which can be used and the results matched based on their references. All tests and methods to determine rheological and mechanical properties of air drying vanishes and resins which have been done in this study were based on ASTM standards (ASTM 2005). In this study, we investigated the utilization of catalyst in synthesizing long oil alkyd resin to increase product quality.

MATERIALS AND METHODS

In this work, industrial materials were utilized in order for the obtained results to be applied for industrial manufacturing. On the other hand, industrial materials are economical as compared to experimental materials. The materials were: Soya fatty acid from Paxan Company of Iran, titer point 24 °C and Iodine number 124 mg KOH/g fatty acid, Phetalic anhydride from IG. Petrochemical Company of India, melting point 134 °C and acid number 390 mg KOH/g fatty acid, Maleic anhydride from USP Technology Group of Taiwan, melting point 53 °C and acid number 520 mg KOH/g fatty acid, Glycerin from EVYAP Company from Turkey, purity percent 99%, Pentaerythretol from Koninda Canada, melting point 248 °C, White sprit solvent from Petrochemical Company of Iran, boiling point150 °C, Toluene from Petrochemical Company of Iran, boiling point 110 °C have used.

In this study, a long oil alkyd resin formula was proposed as a reference base (Re) and three different long oil alkyd resins which were synthesized with same formulation of Re resin using different catalysts (phosphoric acid , 1,2,4-benzene tricarboxylic acid and succinic acid) with same steochiometry relation as polybasic acid catalysts have been chosen (Table 1). The reason for choosing Re formula as a reference base formulation of long oil alkyd resin is because it is widely used industrial paint and coating in Iran.

Table 1: Long oil alkyd resin formulations which have applied for air drying long oil alkyd varnishes (%)

Resins	Material								
	Soya Fatty acid	**Phetalic Anhydride**	**Malic Anhydride**	**Pentaerethrol**	**Glycerin**	**Toluene**	**Phosphoric acid**	**1,2,4- Benzene tricarboxylic acid**	**Succinic acid**
Re	46.16	28.99	0.86	8.05	13.47	2.47	----	----	----
N1	46.16	28.99	0.86	8.05	13.47	2.27	0.2	----	----
N2	46.16	28.99	0.86	8.05	13.47	2.34	----	0.13	----
N3	46.16	28.99	0.86	8.05	13.47	2.26	----	----	0.21

Air drying varnishes of long oil alkyd resins Re, N1, N2 and N3 were prepared based on formulation shown in Table 2. The viscosity of resins is an important parameter for wet film thickness of varnishes and also effect dry film thickness of varnishes. Thus viscosity of varnishes which have been prepared according Table 2 formulations have to regulated with White Sprite solvent.

Table 2: Air drying long oil alkyd varnishes formulation (%)

Name of Materials	**Name of varnishes**			
	Ref.	Sam. 1	Sam. 2	Sam. 3
Long oil alkyd resin Re	**100**	**-----**	**-----**	**-----**
Long oil alkyd resin N1	**-----**	**100**	**-----**	**-----**
Long oil alkyd resin N2	**-----**	**-----**	**100**	**-----**
Long oil alkyd resin N3	**-----**	**-----**	**-----**	**100**
Cobalt Octoate (10%)	**0.5**	**0.5**	**0.5**	**0.5**
Calcium Octoate (5%)	**1**	**1**	**1**	**1**
Zirconium Octoate (33%)	**1.5**	**1.5**	**1.5**	**1.5**

Characterization of all four long oil alkyd resins which were used for preparation of varnishes and for all varnishes was carried out using FTIR spectroscopy. FTIR analysis was employed to investigate the chemical structures of resins and varnishes before and after application. Rheological properties of varnishes and resins including viscosity, drying time, glossary measurement, and thickness of film for characterization of products have been employed. Viscosity of resins and varnishes were measured by Brookfield viscometer model ST-DIGIT R and Ford cup 4 and 6 BYK. Wet and dry thickness of film of varnishes was determined by BYK and Elcometer Company. Mechanical properties of varnishes including glossary, hardness, bending test, impact test, adhesives test, and water resistant of films have been investigated to characterize varnish products. Braive glossometer has been used for glossary, hardness meter model 3034 M 1 of Braive Company and Mandrel, Impact, scratch tester from BYK Company was used to measure bending, impact and adhesives tests of varnishes films.

RESULTS AND DISCUSSION

The FTIR spectra of long oil alkyd resins which identified chemical nano structures of resins show in Figure 1. FTIR method is a powerful method for quantitative and qualitative investigation on nano structure of materials. Actually, qualitative application of FTIR method is more useful for identification of products; especially identification of functional groups of organic compounds. FTIR method is the best tools for reach and investigation of chemical nano structures of alkyd resins. Translation of FTIR spectra of long oil alkyd resins and their varnishes may help us to identify and characterize rheological and mechanical properties of resins and varnishes.

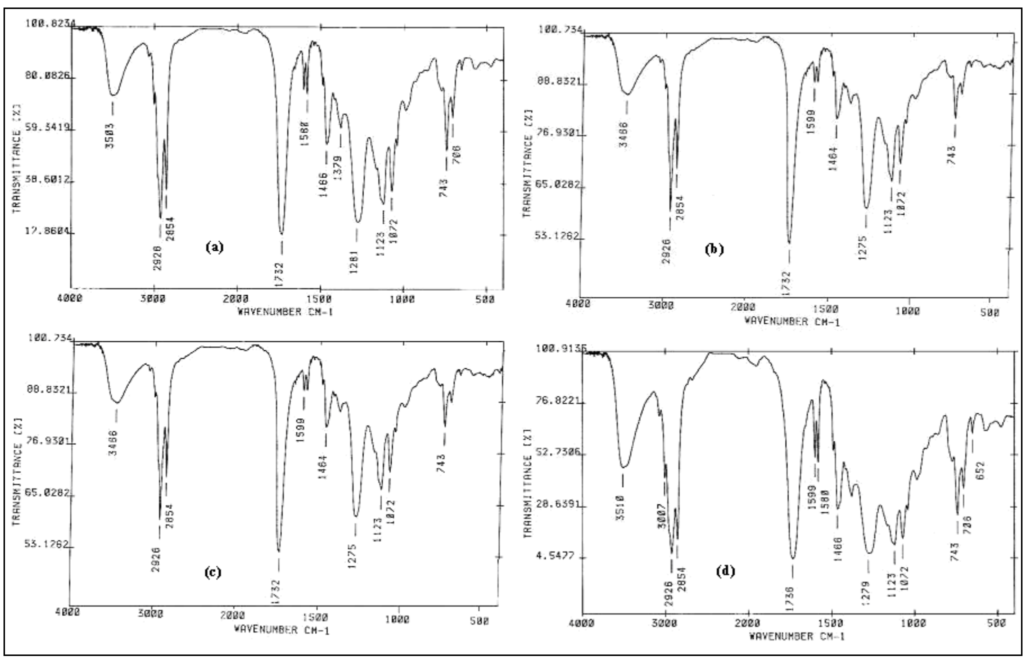

Figure 1: FTIR spectra of long oil alkyd resin for Re (a), N1 (b) N2 (c) and N3 (d)

Notification on FTIR spectra of long oil alkyd resins shows many similarities for all resins; for example hydroxyl peak in around 3500 cm^{-1} or peak of carbonyl group in 1730 cm^{-1}. In addition, more important peaks belong to finger print region (Pavia *et al*. 1996) including peaks 1123 cm^{-1} and 1072 cm^{-1} which proved that all long oil resins synthesized using different poly basic acid catalyst have same chemical nano structures. Chemical shift on some peaks of FTIR spectra happened for particularly different between poly basic acid catalyst formulations and those chemical shifts do not much effectively on behaviors of long oil alkyd resins properties.

The intensity of some peaks of FTIR spectra for long oil alkyd resins was different. The intensity of most of peaks for N3 resin is lesser than other resins, for example peaks of –OH functional group in 3500 cm^{-1} for Re, N1 and N2 resins were close but intensity for N3 resin was much lower than others. An important reason of different intensity of peaks in FTIR spectra can be attributed to different viscosity of resins as N3 resin viscosity is lower than other resin.

Broadness of some peaks, for example peak of –OH functional group in 3500 cm^{-1} for Re resin or peak of carbonyl group in 1730 cm^{-1} for N3 resin were related to the progress of reaction percent for those resins. Some carbonyl group of carboxylic acid which did not react, consequently peak shifted from 1730 cm^{-1} to higher wave length which is 1738 cm^{-1}.

FTIR spectra of long oil alkyd resins show a little different nano structures of the resins. Some of the FTIR bands for the air drying varnishes completely disappeared. This means that there are some differences between structure of resins when varnishes were prepared (Figure 2).

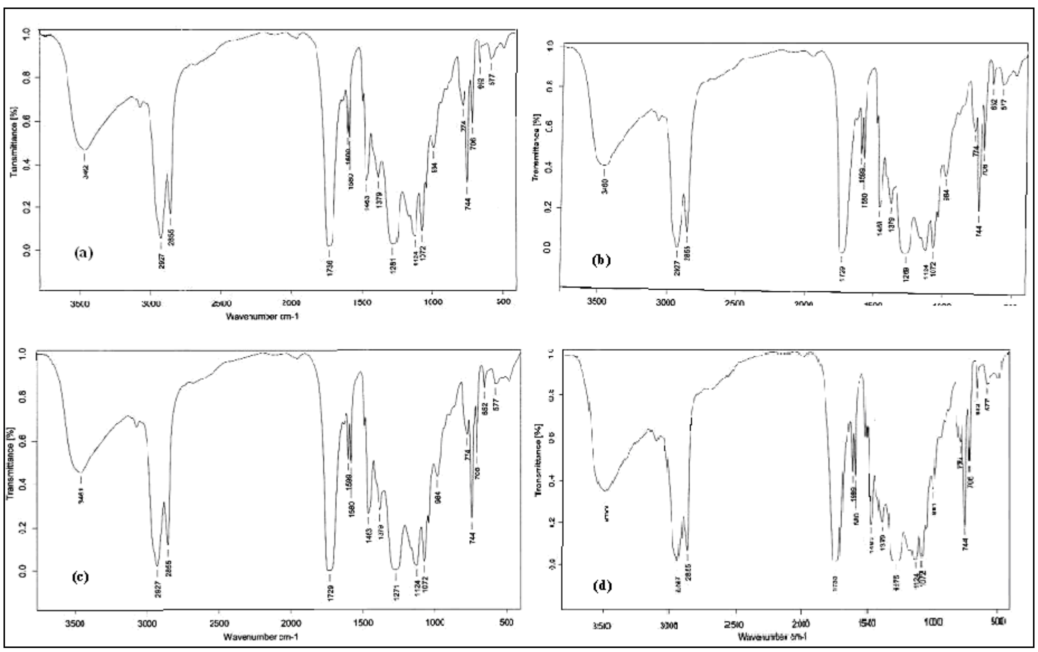

Figure 2: FTIR spectra of air drying varnishes Ref. (a), sam.1 (b) sam.2 (c) and sam.3 (d).

Table 3 shows the rheological properties of air drying varnishes of long oil alkyd resins. In dry film, thickness 40 µm for all varnishes, viscosity of sam.2 is higher and sam.1 is lower than others. All varnishes have a same surface drying time but deep drying time for sam.3 is longer than other resins. Glossary of Ref. resin is less than all but rate of decreasing glossary was similar to that of sam.3. The glossary of sam.2 was higher than others and sam.1 had the lowest rate of decreasing glossary. Observations on results of mechanical properties of varnishes show that: when the dry film thickness for all varnishes was same (40 µm), not only indirect impact, adhesive test on Iron and hardness for sam.3 is the highest value but also direct impact test of sam.2 is the lowest value.

Table 3: Rheological properties of varnishes Re, N1, N2 and N3

Rheological Tests	Standard Code (ASTM)	Name of varnishes			
		Ref.	Sam.3	Sam.2	Sam.1
Viscosity Ford Cup 4 (Seconds)	D-1200	**180**	**180**	**190**	**170**
Surface Drying Time (Minutes)	D-1640	**95**	**95**	**95**	**95**
Deep Drying Time (Minutes)	D-1640	**260**	**280**	**265**	**260**
Glossary after One Day (%)	D-523	**151.2**	**160.8**	**159.9**	**157**
Glossary after One Week (%)	D-523	**141**	**147**	**146**	**149**
Dry Film Thickness (Microns)	D-1186	**40**	**40**	**40**	**40**

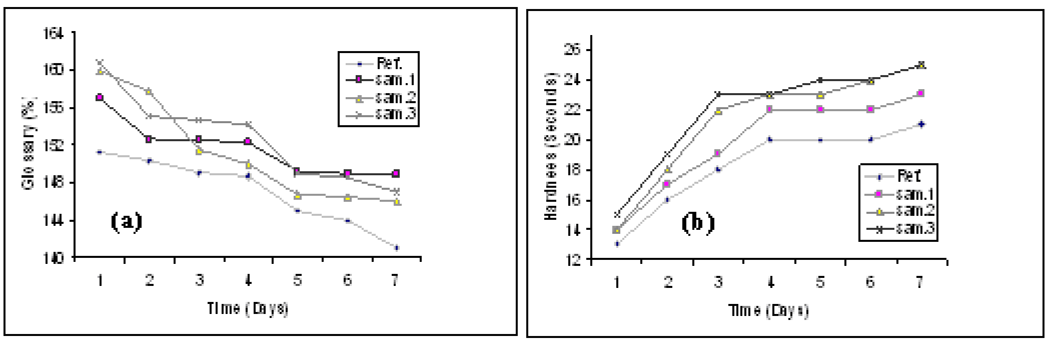

Figure 3: Glossary (a) and hardness (b) of varnishes Ref., sam.1, sam.2 and sam.3 within a week.

Figure 3(a) shows the procedure of decreasing glossary of varnishes; Ref. and sam.3 varnishes show steady procedure of decreasing glossary. For sam.2 varnish in three days, procedure of decreasing glossary is constant. Sam.1 varnish has two steps procedure of decreasing glossary after first day and after fourth days. Sam.3 and sam.2 had higher glossary for first day and Ref. varnish had the lowest glossary after one week.

Increasing hardness of varnishes product within one week is shown in figure 3(b). Hardness curve of varnishes describe that the behaviors of Ref. and sam.1 varnishes is the same; sam.2 and sam.3 show the same behaviors for first three days period and after a week but their producer of increasing of hardness for second third days period is very different (Table 4).

Table 4: Mechanical properties of varnishes Ref., sam.1, sam.2 and sam.3

Rheological Tests	Standard Code (ASTM)	Name of varnishes			
		Ref.	Sam.3	Sam.2	Sam.1
Direct Impact (lbm/in^2)	D-2794	**100**	**100**	**80**	**100**
Indirect Impact (lbm/in^2)	D-2794	**80**	**20**	**60**	**100**
Bending Test (mm)	D-522	**4**	**4**	**4**	**4**
Hardness after One Day (seconds)	D-4366	**13**	**14**	**14**	**15**
Hardness after One Week (seconds)	D-4366	**21**	**23**	**25**	**25**
Adhesive on Iron	D-3359	**1B**	**1B**	**4B**	**5B**
Dry Film Thickness (Microns)	**D-1186**	**40**	**40**	**40**	**40**

CONCLUSION

The investigations of this research revealed that: although nano chemical structures of long oil alkyd resins which were used for preparation of air drying alkyd varnishes were a little bit different, the chemical nano structure of varnishes was similar. Comparison of rheological and mechanical properties of vanishes showed that sam.3 is better than sam.2 and both are better than conventional varnishes.

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