CATALYSIS RESEARCH

Research Article

Coating Composition on the Basis of Carbamide-Phenol-Formaldehyde Co-Oligomer

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ABSTRACT

In order to obtain desired properties of oligomers, modification process is used to change their structure and composition. In this matter, using traditional technology equipments and methods are more suitable. Lately to eliminate deficiencies of known oligomers, the process of modification with compounds of different nature is broadly studied. It is not always possible to reach the properties given for the particular oligomer material during the synthesis of oligomer material in industrial conditions; moreover, these processes are not always economical enough. Therefore, the modification processes of traditional industrial oligomer are being investigated more intensively with the purpose of obtaining oligomer compositions on their base with the given properties. In solution of this problem, great attention is being given to oligomer materials on the base of phenol-formaldehyde oligomers having available wide raw material base and reactivity, heat-resistance, satisfactory dielectric properties and cake formation ability. However, this oligomer has a number of disadvantages: low molecular mass, high flow in uncured state, brittleness, presence of free phenol in the composition and so on. These investigations are being carried out in some directions and the more vital of them in modification of phenol-formaldehyde oligomers with the purpose of regulation of the above mentioned disadvantages and giving more functionality to these oligomers.

The development of production and the compositions based on biopolymer are expanding very fast. In order to obtain ecologically friendly composition, as a liaison modified phenol-formaldehyde oligomer and as filler, biopolymers were used. Main properties of obtained coating and adhesive compositions were studied. New composite, ecologically friendly coating and adhesive compositions are recommended to be used in many fields of industry. The need for improvement of new compositions is also very high. Main parts of molecular structure consist of cellulose and lignin. Almond shell powder taken as additive affect is on improvement of physical - mechanical features of the painting composition. Thermal properties of filler have been studied by

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means of thermogravimetric analysis (TGA). In order to identify functional groups of compounds used IR spectroscopy.

KEYWORDS: Phenol-Formaldehyde oligomers; Polycondensation process; Modification; Fillers; Binder; Biopolymers; Composite

INTRODUCTION

Ever-growing demand for the quality of oligomer materials engendered by the acceleration of the scientific and technical progress stimulates development of the investigations in the field of chemistry of phenol-formaldehyde oligomers. Compositions based on modified phenol formaldehyde oligomer and composites filled with biopolymers have individual complex of usefulness technological and functioning feature [1,2].

As mentioned before, in these investigations we studied some directions and the more vital of them in modification of phenol-formaldehyde oligomers in order to eliminate above mentioned disadvantages and giving more functionality to these oligomers.

For the first-time modification of phenol-formaldehyde oligomers was carried out by benzo-guan-amine, benzylamine, benzamide, acetamide, oxamide, terephthaldiamide, propargyl-glycidyl ether and other organic compounds. Mechanism of phenol-formaldehyde oligomers modification has been studied. Detailed investigation of the structure and properties of the obtained oligomers had been cited depending on different parameters. Modification of phenol-formaldehyde was carried out at constant phenol and formaldehyde molar ratio, 1.15:1.45 and quantity of modifier in reaction mass was changed in the 0.05-1.0 molar interval. Change of the modifier content has an effect upon the process rate strongly, consequently, on the yield of soluble fraction of modified oligomer [3,4].

It has been determined that using modifier in the 0.05-0.5 molar interval at constant phenol and formaldehyde ratio: $[C_6H_5OH]$ = 1.15 mole and $[CH_2O]$ = 1.45 mole, basic part of the reaction products are substances of viscous consistency from yellow color up to brown, well soluble in acetone, ethanol tetrahydrofuran and dioxane. When modifier is used at amount more than 0.75 mole, solid, insoluble mass is obtained. The composition and structure of synthesized modified oligomers was confirmed by the IR, NMR-methods, physical-chemical and element analyses. It has been shown that the products of phenol-formaldehyde oligomers modification are oligomers incorporating with structural fragments of phenol - formaldehyde and corresponding modifier [5-8].

It is difficult to put in one word their feature, because of various feature and multiplex formation of high molecular compounds of their feature. By molecular layout, topological structural level, supramolecular, and colloidal diffusion interconnected layout can be distinguished in four structural levels. Molecular level is identified by means of chemical chain of high molecular compounds, the elemental configuration of structural parts, the kind and location of functional groups, and the structure and contour of polymer chains [9-12].

EXPERIMENTAL SECTION

In order to prepare ecologically clean composition with high physical-mechanical features, as a filler used biopolymer such as almond shell powder and as a liaison applied resole type modified phenol-formaldehyde oligomer (MPhFO). Modification process was performed in the setup reactor in laboratory.

As reagents for chemical modification of phenol formaldehyde resin as modifiers used 37% formaldehyde water solution (formalin) and as a catalyst 25% - ammonia water. Main purpose of the chemical modification process of PhFO is to eliminate its fragility and increase its heat resistance properties. Especially nitrogen containing carbamide leads to eliminate disadvantages side such as fragility.

In order to homogeneous composition used almond shell powder was grinded in the LZM type laboratory mill. The identified particle size sifted by means of 45 μm - size sieve. Particle size studied in order to determine efficiency of coating composition preparing processes and performance of the final composition filled with biopolymer shell powder.

The size of particles has been studied by diffraction particle size analyzer Malvern master size. Almond shell powder as a biopolymer has high molecular structure. Molecular weight is about from $500 \cdot 10^3$ up to a few million. Main parts of molecular structure consist of cellulose and lignin. By taking almond shell powder as biopolymer additive effects on improvement of physical - mechanical features of the coating and painting composition. Some main parameters such as thermal properties of filler have been studied by means of thermogravimetric analysis (TGA). In order to identify functional groups of compounds, analysis performed by IR spectroscopy [13-15].

RESULTS AND DISCUSSION

By the dissolving in different solvents the performance of the solution has been investigated. It was determined that best solvents for biopolymer shell powder are dimethylformamide. Due to mixtures in almond shell powder, it has generated residue in dioxane and p-xylene solvents. Compared to shell powder phenol-formaldehyde oligomer is totally dissolved in dioxane, o-xylene, acetone, and dimethylformamide. By means of Master size analysis is has been determined that particles of the filler mostly in lower than 45μm. It was determined that, the biopolymer shell compound mainly consists of individually lignin - 50.34%, cellulose-37.7%, oil and resins -3.5%, water-soluble ingredients 7.3% and ash substances 0.6%.

By means of LECO TruSpec CHN - S Element Analyzer elements have been determined that biopolymer consists of the element such as nitrogen (N), hydrogen (H) and Carbon (C) were identified according to ASTM D 5373 - 02 standard method and the sulfur (S) element has been determined according to the ASTM D 4239 - 05 standard. The element analysis results are mentioned below in the table (Table 1).

Table 1: The results of the element analysis for the biopolymer (almond shell in %).

Sample	C	H	N	O
Almond shell	51,20	6,50	0,55	41,75

The comparative results of non-modified PhFO and modified PhFO by carbamide are tabulated below (Table 2).

Table 2: The main data on resole type non-modified and modified CPhFO.

Indicator	PhFO	CPhFO
The amount of nitrogen, %	–	8.6
The amount of free phenol, %	13 – 15	0.5
Free formaldehyde amount, %	9.7	0.8
The amount of methylol groups, %	11.2	9.8
Hydroxyl groups, %	17.5	15.2
Softening temperature (Ubbelohde), °C	56	75
Viscosity (50% - solution) by VZ – 4 device, sec	40	52
Heat resistance (by Wika device), °C	105	180
Hardness (according to Brunel), MPa	220	285
Solidification rate, %	92	98.8
Stickiness, MPa	2.2	4.8
Density, kg/m3	1200	1260

Destruction process of used additive has been studied by means of DTA and TG analysis.

The operating condition of "Perkin Elmer" 6000 STA device is 15 - 1000°C, the speed of thermal processing is 4 –25°C/secand "digital temperature controller" type cooling system. By "Pyris Manger" software program the kinetic parameters have been identified. In order to keep away from the elimination of burning product from the system and to avert condensation procedure the inert argon gas was applied and given to the system by 20 ml/min speed. For this process sample was used as standard 177.78 mg aluminum-oxide based sample.

By the results of differential thermal analysis and thermogravimetric analysis of almond shell powder samples, it is clear that the destruction procedure is going on mainly in two steps and correspondingly the weight loss is 7.243% at 67.72°C; 36.197% at 277.89°C (Figure 1).

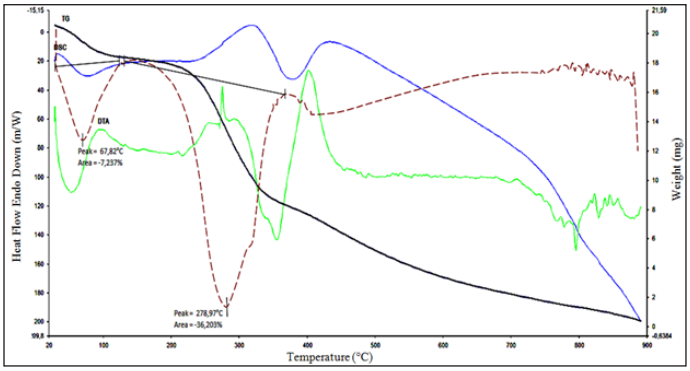

Figure 1: DTA, TG, DSC analysis of the almond shell.

At the end of the gasification process executed by argon gas in the steam atmosphere the separated mixture from biopolymer contains of hydrogen, methane, carbon monoxide and carbon-dioxide gases. At the first step *holocellulose* (hemicellulose + *cellulose*) is awaited to break. Initially, inside the polysaccharide hemicellulose begins breaking-up. In the step of hemicellulose breaking up as a result of ether groups smashing, carbon dioxide gas is released. In the step of cellulose breaking up hydroxyl groups and in the breaking down of either compound the carbon-monoxide gas is separated. In the stage of carbon monoxide emission, carbon dioxide is awaited to be separated too. Apart from this at this step methane gas is also emitted. The source of releasing of metahane is cellulose. At the initial step the separation of hydrogen happened as a result of hemicellulose, cellulose and lignin breaking up. In the second step aromatic groups and lignin are awaited to break up. Methoxy compounds, inside the lignin released methane, and hydrocarbons demand

carbon monoxide and hydrogen separation [16-19].

By the results below attached graphics of differential thermal analysis and thermogravimetric analysis of environmentally friendly coating composition prepared based on MPhFO and biopolymer almond shell powder have demonstrated the destruction action is going on mainly in two steps and respectively the weight loss is 3% at 185°C; 21% at 310°C (Figure 2).

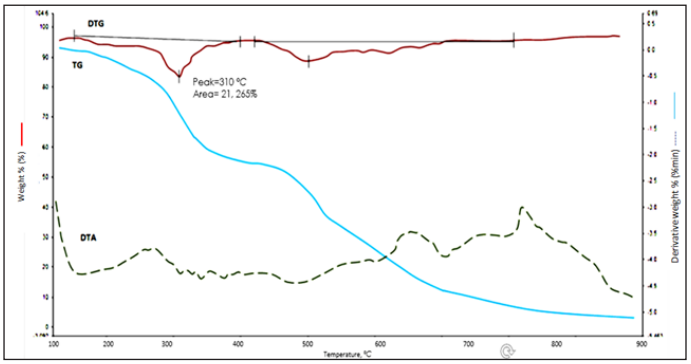

Figure 2: DTA, TG, DSC analysis of the coating composition based on CPhFO and almond shell.

From the result of the analysis, it is clear that environmentally friendly coating composition prepared based on MPhFO and biopolymer almond shell powder is much more long-lasting.

In order to determined of funcional groups that included in components and prepared compostion there was used IR analysis. Infrared Spectroscopy analysis have been performed by means of the SPECORD M 80 and NICOLET Is 10 equipment.

In the IR spectrums (Figure 3) of the modified phenol - formaldehyde resin, 3400 cm^{-1} specify amine connection in the compound and the group of peaks in-between 3189 – 2590 cm^{-1} demonstrates the absorption zone of the hydroxyl group valence swinging in the carboxyl group. 1784 cm^{-1} carboxyl group, 1599 cm^{-1} identifies the aromatic rings, 1460 cm–1existence of methyl group, at 1261.35 and 1106.56 cm^{-1} identify methyl and hydroxyl groups and 965.28 - 758.72 cm^{-1}, and 701.81 – 625 cm^{-1} peaks identify the CH2 and CH groups existing in the compound.

The studied samples of spectra have been checked with 2 cm^{-1} spectral accuracy in the mid-infrared 3500 - 500 cm^{-1} area spectrophotometer.

Absorption spectra of the compound are strictly connected with the change in the internal energy of their atoms and molecules. In infrared spectrophotometer spectrum–3800-3200 cm^{-1} area broad field of absorption band of biopolymers is strictly connected with the valence vibration of OH bond. It is clear that the low frequency strip area vOH specify stronger (intramolecular), while high frequency strip area denotes a weaker (intermolecular) OH groups binder with hydrogen bonds.

It is obvious that from the infrared spectrophotometer spectrum of almond shell (Figure 4) that 665 – 908 cm^{-1} denotes methyl group, 1020 cm–1 compound ester groups, 1508 cm^{-1}, C - CH3, 1606.33 aromatic links 1646.74 cm^{-1} NH2, 3648.35 cm^{-1} absorption of strips of OH bond valence oscillation.

Compared to IR spectrum of the component, in the infrared spectrophotometer spectrum of the compound filled with biopolimer shell powder at 3680, 3630.25 and 3600.82 cm^{-1} indicate hydroxyl group, amin groups is indicated at 3474.67, 3361.76 and 3227.78 cm^{-1} area, 3012.36 cm^{-1} denotes methyl group in alkyl compound, C = C is indicated at 1748.54 cm^{-1} area, 1651.87 cm^{-1} denotes - HC = CH –groups, C = C bonds, 1593.25 cm^{-1} denotearomatic rings, 1224.88 and C – O groups indicated at 1168.96 cm^{-1}, the peaks between 969.86 - 657.42 cm^{-1} CH = CH, and are the absorption lines of CH oscillations in $(CH_2)_n$ bonds.

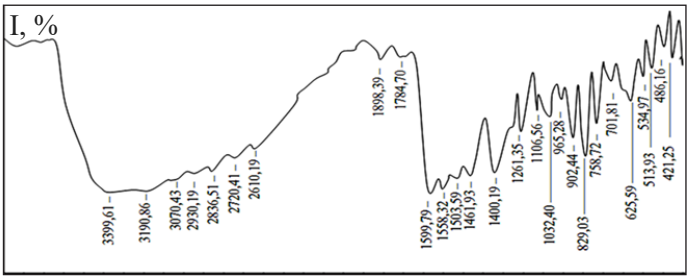

Figure 3: IR spectroscopy analysis of PhFO modified by carbamide.

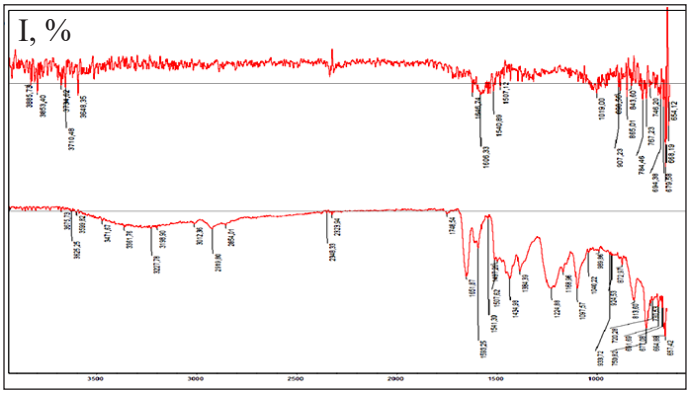

Figure 4: IR spectrums of the almond shell powder and CPhFO composition.

According to the result of analysis performed by high quality environmentally friendly coating composition has been prepared. It is evident by the results of the performed analysis for studying proporties of the prepared composition based on modified phenol-formaldehyde oligomer and filled with biopolymer have been demonstrated much more high performance [20–24].

CONCLUSION

- Phenol formaldehyde resin was modified with nitrogen containing carbamide. Physical-chemical and physical-mechanical indices of non-modified and modified phenol-formaldehyde olygomers have been studied. Is has been determined that by modification amount of the free phenol has been decreased from 13 -15 % till 0.5 %, beside it amount of the free formaldehyde has been decreased from 9.7 % till 0.8 %;
- It has been obtained that at the result of modification process viscosity, heat resistance, hardness, solidification rate increased from 92 - 98.8%, stickness has been increased from 2.2 to 4.8 MPa.
- With high performance of ecological carbamide-phenol-formaldehyde olygomer was used as a main components for preparation of composition.
- By investigation main indices of composition filled with biopolymer have been investigated. By the results of differential thermal analysis and thermogravimetric analysis of coating composition prepared based on CPhFO and biopolymer almond shell powder have demonstrated the destruction action is going on mainly in two steps and respectively the weight loss is 3% at 185°C; 21% at 310°C.
- According this result we can conclude that coating composition filled with biopolymer shell powder is much more long-lasting, has high physical-mechanical, chemical properties and it is environmentally more friendly as well.
- Having high performance it can be concluded that filled with biopolymers shell powder coating composition can be used in diffrent area especially in furniture manufacturing.

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