Seyed Mahdi Latifi*, Alireza Salehirad, Atefeh Soltani and Javad Bakhshi Azghandi

Bio-based polymer from heterogeneous catalytic polymerization of vegetable oils

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Abstract: Recently, printing ink ingredients have been provided from vegetable oils as a renewable, non-toxic, and biodegradable resource. In this work, to produce bio-based polymer potentially exploitable in printing ink vehicles, tris(ethylenediamine)nickel(II) nitrate and bis(ethylenediamine)copper(II) nitrate complexes were synthesized, characterized, and then used as heterogeneous catalysts for polymerization of soybean oil. Also, nickel and copper oxide catalysts were fabricated through thermolysis of the mentioned complexes and, after characterization, were employed for the polymerization reaction. The results showed that the presence of nickel and copper complex catalysts favored the reaction progress as the viscosity of the reaction product was increased 4 and 1.3 times, respectively, compared with polymerization without a catalyst. Also, the results obtained from using nickel and copper oxides indicated that these metal oxides do not have a significant effect on the reaction process.

Keywords: bio-based polymers; catalytic properties; chemical synthesis; printing ink; vegetable oils.

1 Introduction

Printing inks are typically composed of the ingredients such as the colorant, solvent, vehicle or binder, and additives [1]. The ink vehicle or binder plays such roles as pigment wetting and transferring, forming a film after printing and during drying to prevent the pigments from agglomerating and being glued to the surface and, finally, protecting the pigments from corrosion, moisture, and temperature [2, 3]. In the last century, the vehicles derived from petroleum have been used in the printing ink industry, but the environmental concerns, such as emission of volatile organic solvents and also the issues pertaining to recycling or waste disposal of the residues [4], as well as the fluctuation of the petroleum price, prompted the technologists and researchers to revert to renewable resource-based vehicles [5]. Among the renewable resources, vegetable oils due to environmental advantages, including non-toxicity, biodegradability, preventing volatile organic compounds (VOC), plus availability, and reasonable price, have attracted considerable attention for use as raw materials for producing various polymeric materials [5–10]. Vegetable oils mainly include a mixture of triglycerides – esters of glycerol with three long-chain fatty acids with compositions varying depending on the source of the oil [11–13]. The existence of the carbon-carbon double bonds in vegetable oils provides this potential for them to be polymerized for use in such applications as printing ink vehicle [6]. The vehicles derived from vegetable oils have the advantages of capability for ink formulation over a wider range of viscosities demanded by various printing applications, lower rub-off characteristics, and also decreasing VOC emission [4, 14]. Soyink® is an example of a successfully commercialized vegetable oil-based ink in which the vehicle produced from soybean oil polymerization is used in ink formulation. This type of ink, due to the transparency of the soybean oil-derived vehicle, which results in reducing pigment loading, has been particularly found to be cost effective for colored systems [1, 3]. It is well known that the time-consuming thermal polymerization that occurs in temperatures above 280°C accounts for the main cost in the vehicle production [3]. Therefore, to improve the economics of the process, it is necessary to reduce both temperature and time of polymerization [1]. In early work on this subject, such organic catalysts as quinones [15] and anthraquinones [16] were used to decrease the polymerization reaction time, but the results indicated that none of the used catalysts have enough activity for catalyzing the process. Mello et al. [3] used M(carboxylate)$_2$ (Mc=Fe, Cu, Ni, Co and Sn) complexes for soybean oil polymerization and achieved 60% reduction in reaction time using 0.1 mass% Ni(carboxylate)$_2$. Also, these authors employed the mentioned catalysts for the polymerization reaction of used frying oil [17] and obtained 75% higher viscosity for the catalyzed reaction product in comparison with the non-catalyzed one. In the other work, these authors [18] used Ni(Carboxylate)$_2$

***Corresponding author: Seyed Mahdi Latifi,** Department of Chemical Technology, Iranian Research Organization for Science and Technology, Tehran 3353136846, Iran, e-mail: latifi@irost.ir
Alireza Salehirad, Atefeh Soltani and Javad Bakhshi Azghandi: Department of Chemical Technology, Iranian Research Organization for Science and Technology, Tehran, Iran

complex for catalyzing soybean oil polymerization in a temperature range from 260°C to 360°C.

Literature survey reveals that few works have been reported on heterogeneous catalysts usage for the production of printing ink vehicle from vegetable oils. In this work, to accelerate the polymerization process, tris(ethylenediamine)nickel(II) nitrate and bis(ethylenediamine)copper(II) nitrate complexes were synthesized, characterized, and then used as heterogeneous catalysts for the soybean oil polymerization reaction. In addition, nickel and copper oxide catalysts were fabricated through the thermolysis of the complexes, characterized, and employed in the polymerization reaction, and the obtained results were compared with those of the complex catalysts.

2 Materials and methods

2.1 Materials

Chemical materials employed in the fabrication of samples, including nickel nitrate (Ni $(NO_3)_2.6H_2O$, Merck, Darmstadt, Germany), copper nitrate (Cu $(NO_3)_2.3H_2O$, Merck, Darmstadt, Germany), and ethylenediamine ($C_2H_8N_2$, Sigma-Aldrich, St. Louis, MO, USA) were used without further purification.

2.2 Synthesis of nickel and copper complexes

For tris(ethylenediamine)nickel(II) nitrate synthesis, at first, an aqueous solution of Ni $(NO_3)_2.6H_2O$ (1 mmol, 0.29 g) in 20 ml of deionized water was prepared and heated in a reaction flask up to 100°C. At next step, $C_2H_8N_2$ (3 mmol, 0.8 g) was added to the solution dropwise with stirring, and then, the reaction proceeded at 100°C for 3 h under reflux conditions. The precipitant was aged for 24 h at ambient temperature under stirring and then dried at 80°C for 20 h. The bis(ethylenediamine)copper(II) nitrate was fabricated using 1 mmol Cu $(NO_3)_2.3H_2O$ in 10 ml of deionized water and 2 mmol $C_2H_8N_2$ using the same procedure as discussed for the nickel complex synthesis except for the drying temperature (100°C) and the duration (30 h).

2.3 Synthesis of NiO and CuO catalysts

For both NiO and CuO catalyst fabrication, nickel- and copper-synthesized complexes were calcined at a rate of 10°C/min in open atmosphere up to 400°C and maintained at the same temperature for 3 h.

2.4 Sample characterization

For the synthesized complexes, electronic spectra were obtained using a Perkin-Elmer, Lambda 25 spectrophotometer. Infrared spectra were measured on a FT-IR PHILIPS, PU9624 spectrophotometer with KBr pellets. The crystalline structures of the NiO and CuO catalysts were studied by XRD using a EQUINOX 3000 diffractometer via Cu Kα ($\lambda = 1.5418$ Å) as incident radiation. Crystalline phases were identified through tabulated powder diffraction files of the International Center of Diffraction Data (ICDD). In addition, the sample morphology was investigated using a microscope FESEM, model ALS2100.

2.5 Polymerization reaction system

Polymerization reaction occurred in a batch reactor system including a stainless steel reactor with a volume of 1 l equipped with a thermowell. The heating power was supplied through an electrical heating jacket mounted around the reactor, and the reactor temperature was controlled using a PID controller. For each run, 400 ml of soybean oil was charged to the reactor, and after heating up to 300°C, a weighed amount of catalyst sample was added to the reactor content. The reaction was performed under agitation, and the samples were taken within specific time intervals. Kinematic viscosities of the samples taken were measured by a Ubbelohde viscometer at 20°C according to ASTM D445. It is noteworthy to mention that the viscometer was calibrated using various concentrations of sucrose solutions at 20°C. Figure 1 depicts a scheme for the polymerization reactor system.

3 Results and discussion

3.1 Nickel and copper complex characterization

The electronic spectra obtained from $[Ni(C_2H_8N_2)_3](NO_3)_2$ and $[Cu(C_2H_8N_2)_2](NO_3)_2$ aqueous solutions are presented in Figure 2. As can be seen in Figure 2A, the electronic spectra for the nickel complex indicate four electronic transitions, an intensive peak observed at 280 nm, which can be assigned to the transition of nitrate ion. Three other

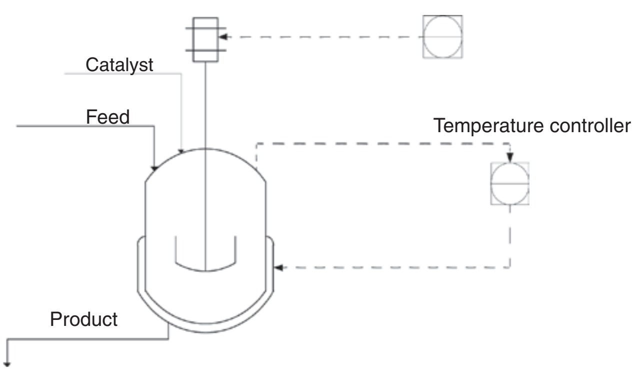


Figure 1: Scheme of the reactor system.

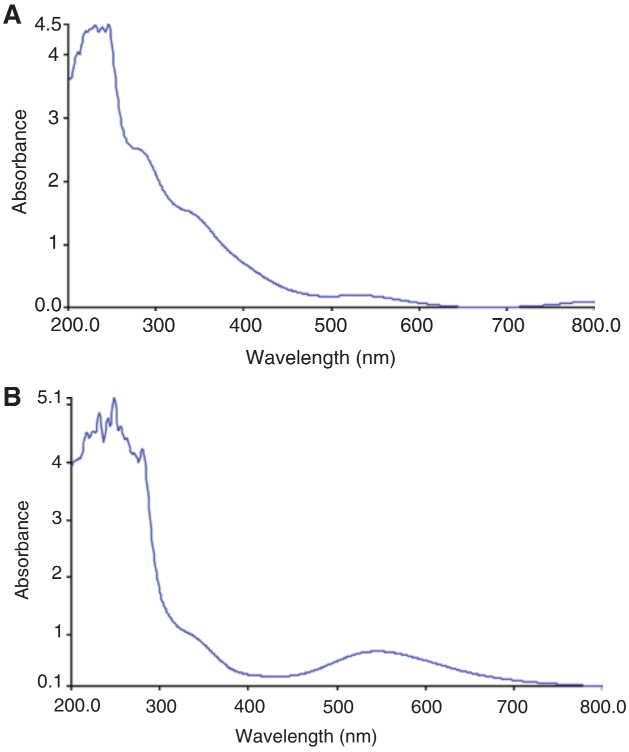


Figure 2: Electronic spectra for (A) tris(ethylenediamine)nickel(II) nitrate and (B) bis(ethylenediamine)copper(II) nitrate.

characteristic peaks at 300, 360, and 530 nm are assigned to the d-d transitions of Ni^{2+} ion, including ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. Also, in Figure 2B, the peak appearing in 280 nm corresponds to the nitrate ion, and the peak at 560 nm is assigned to the d-d transition of Cu^{2+} (${}^3E_g \rightarrow {}^3T_g$).

The IR spectra for $[Cu(C_2H_8N_2)_2](NO_3)_2$ (Figure 3A) show all absorption bands assigned to the ethylenediamine ligand, as absorption modes at 3000–3500, 2964, 1606, 1275, 1043, and 977 cm^{-1} can be attributed to υ(N-H), υ(C-H), N-H deformation, δ(NH), υ(C-N), and υ(C-C), respectively [19]. Furthermore, absorption bands at about 525 and 1382 cm^{-1} are attributed to Cu-N stretching vibration and nitrate ion, respectively [20]. Also, in the IR spectrum of $[Ni(C_2H_8N_2)_3](NO_3)_2$ (Figure 3B), all absorption bands corresponding to the ethylenediamine ligand, are observable, and absorption bands at about 500 and 1235 cm^{-1} can be attributed to the Ni-N stretching vibration and the nitrate ion existence, respectively [21].

3.2 Nickel and copper oxide characterization

The XRD pattern for the NiO catalyst (Figure 4) implies the presence of nickel oxide (JCPDS No. 78-0423) and nickel (JCPDS No. 3-1043) phases in the product. Also, all diffraction lines in the XRD pattern of the CuO (Figure 5) catalyst are assigned to copper oxide (JCPDS No. 80-1916). Also, the SEM image of the Ni/NiO and CuO catalysts are depicted in Figure 6, from which it can be seen that the spherical shape for the metal oxide particles has a rather high degree of agglomeration.

3.3 Soybean oil polymerization

It is well known that the polymerization reaction take place at temperatures above 260°C when the dienes obtained from the conjugation of double bonds react via Diels-Alder reaction to form a cross-link between chains or through the combination of free radicals. Scheme 1 depicts the possible polymerization reaction of vegetable oils.

On the other hand, the occurrence of the reaction at temperatures above 350°C leads to thermal cracking of triglycerides that results in the production of such compounds as hydrocarbons, carboxylic acids, and other oxygenated materials [18]. Therefore, the reaction temperature was set at 300°C, which is within the two above-mentioned limitations.

Soybean oil polymerization occurred at 300°C with various catalyst samples, including nickel and copper complexes and oxides, and the reaction progress was plotted as viscosity (cSt) versus time (h) in Figures 7–9. As can be seen in Figure 7, by thermal polymerization, without using any catalyst, after 3 h, the viscosity of the oil increased 4 times. By adding 0.1 wt% tris(ethylenediamine)nickel(II) nitrate to the reaction, the viscosity of the reaction product was enhanced about 75% in comparison with the non-catalyzed thermal polymerization. By increasing the nickel complex loading to 0.25 and 0.5 wt%, the product viscosity increases 2.3 and 2.7 times compared with the non-catalyzed thermal polymerization, respectively, suggesting trivial enhancement in viscosity by increasing the catalyst loading from 0.25 to 0.5 wt%. The kinematic viscosity obtained using a 0.1 wt% nickel complex catalyst is close or slightly higher than the reported results with the same amount of catalyst [3].

An acceleration in viscosity increase is observed for almost all catalytic runs after passing 2 h from the beginning of the reaction, which can be ascribed to the formation of molecules with longer chains as a result of the combination of molecules with longer chains and also the formation of cross-link bonds [22]. Figure 8 presents the enhancements of 43%, 65%, and 130% in product viscosity compared with thermal polymerization for 0.1, 0.25,

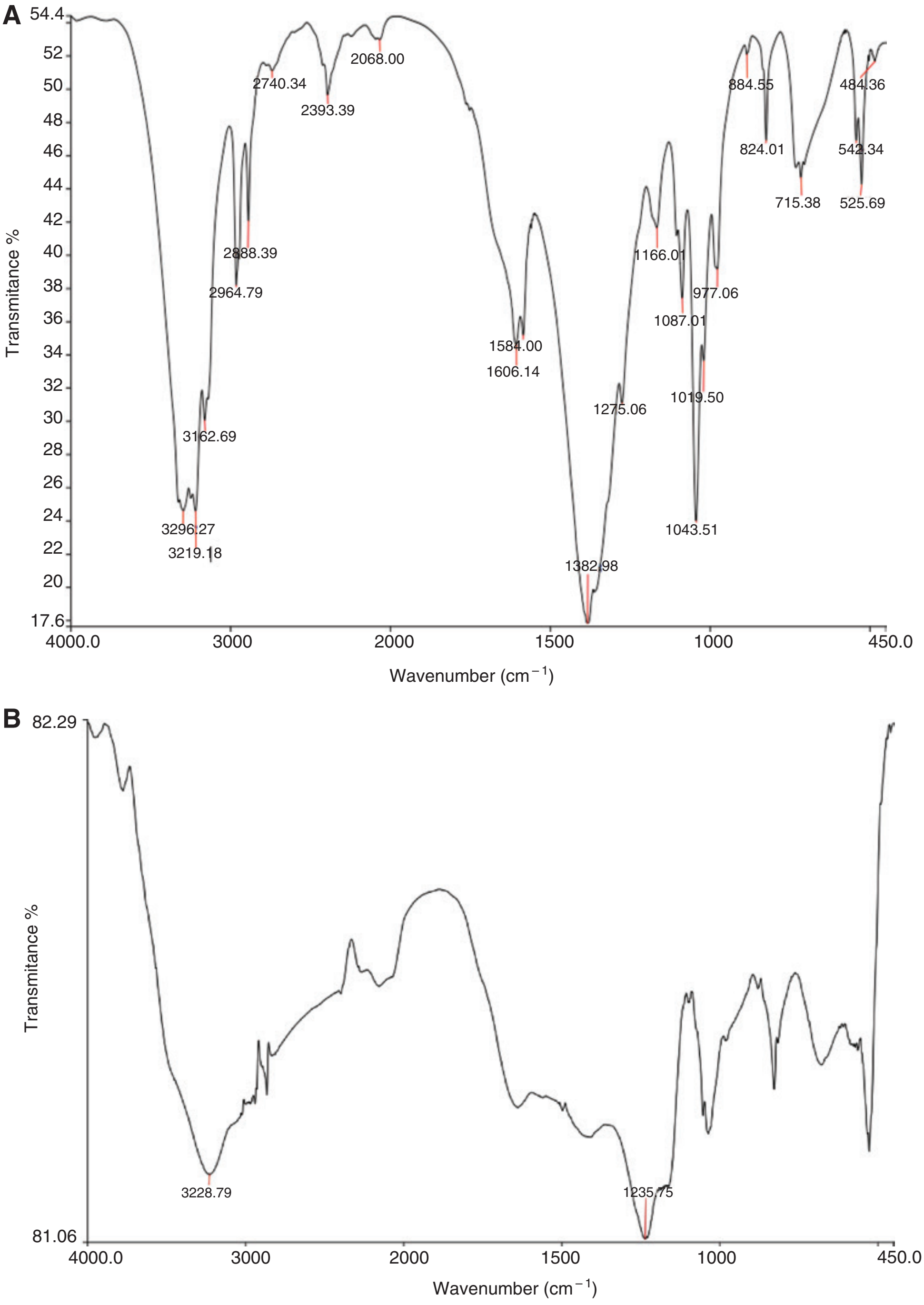


Figure 3: FT-IR spectra of (A) bis(ethylenediamine)copper(II) nitrate and (B) tris(ethylenediamine)nickel(II) nitrate.

and 0.5 wt% loadings of bis(ethylenediamine)copper(II) nitrate, respectively.

As shown in Figure 9, compared to the complex catalysts, the presence of nickel and copper oxide catalysts does not have significant influence on the reaction progress and only leads to a slight increase in the viscosity for the nickel oxide catalyst. Better activity of the complex catalysts compared with the metal oxides can be ascribed to the complex chemical structure and their intrinsic reactivity. It can be postulated that, first, the ethylenediamine ligand separates from the metal ions, and in the next step, the reaction was catalyzed by the metal ion with oxidation states [23], whereas the metal oxide catalysts, because of their stability, are needed to be reduced before catalyzing the reaction, demanding more energy that can be supplied at temperatures above 300°C.

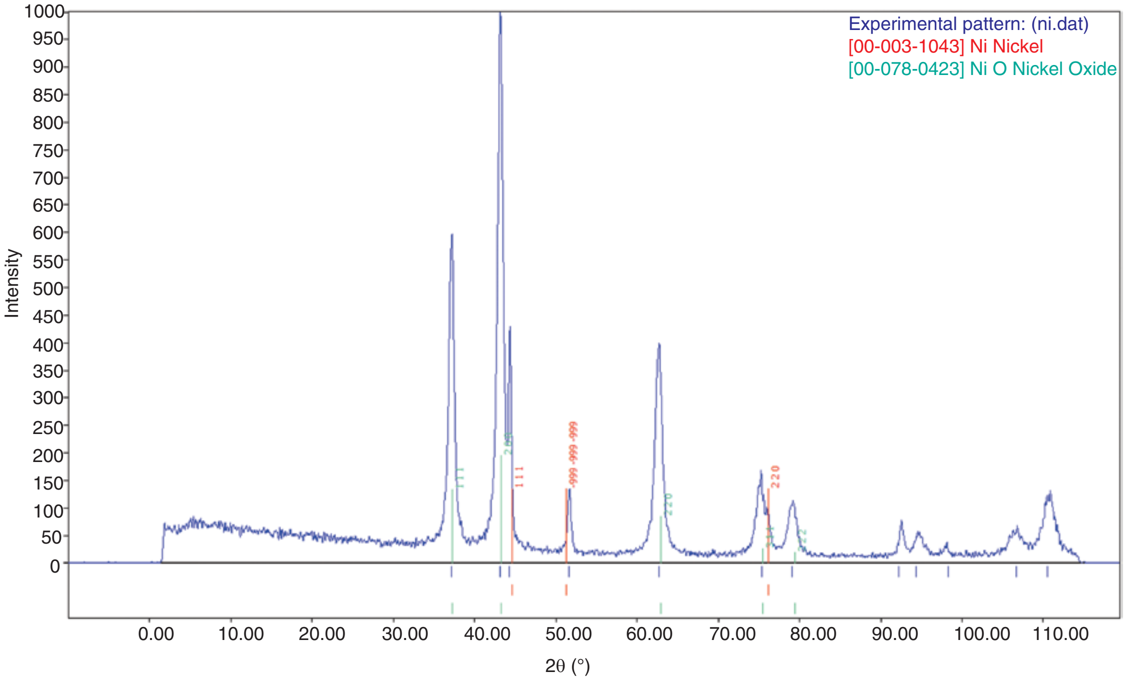


Figure 4: XRD pattern of synthesized nickel oxide.

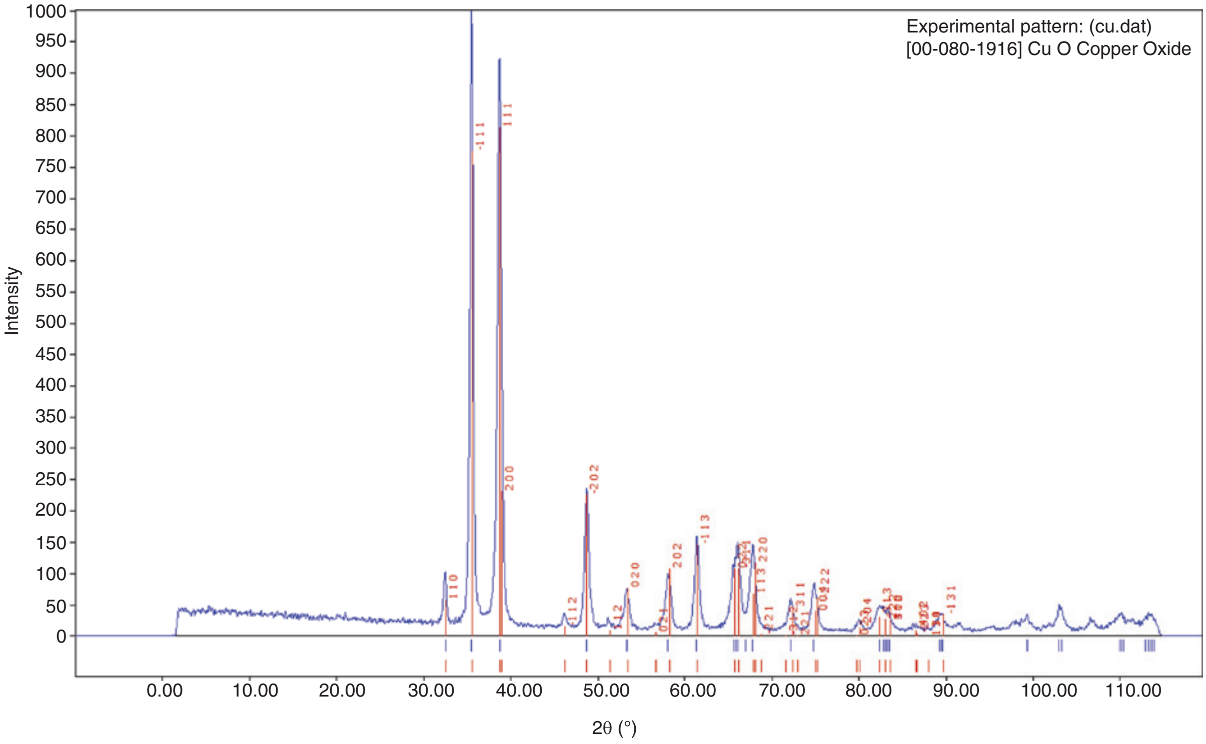


Figure 5: XRD pattern of synthesized copper oxide.

Also, comparing the results shown in Figures 7 and 8 reveals that the nickel complex catalyst exhibited a better performance in the soybean oil polymerization reaction. This observation can be justified by the fact that, despite more oxidative potential of Cu^{2+} compared with that for Ni^{2+}, Cu^{2+} is not able to act as an effective oxidative agent

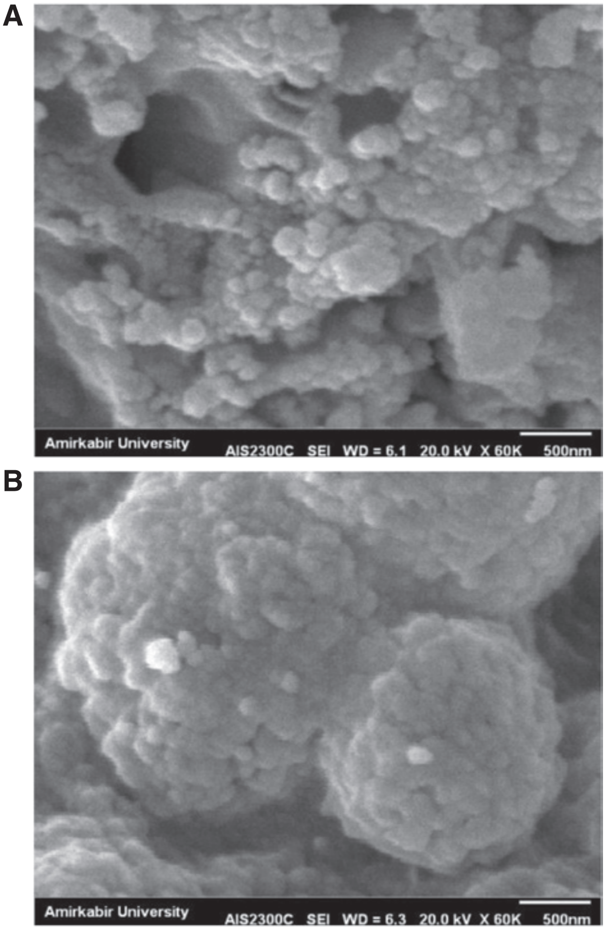
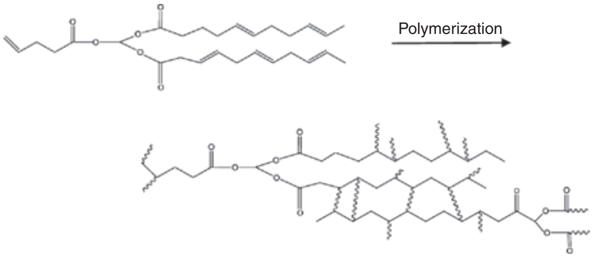


Figure 6: SEM images for (A) synthesized nickel oxide and (B) synthesized copper oxide.



Scheme 1: The polymerization of vegetable oil.

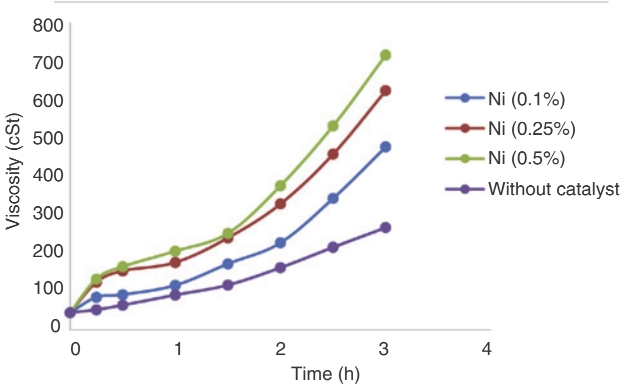


Figure 7: Soybean oil polymerization by Ni complex catalyst at 300°C.

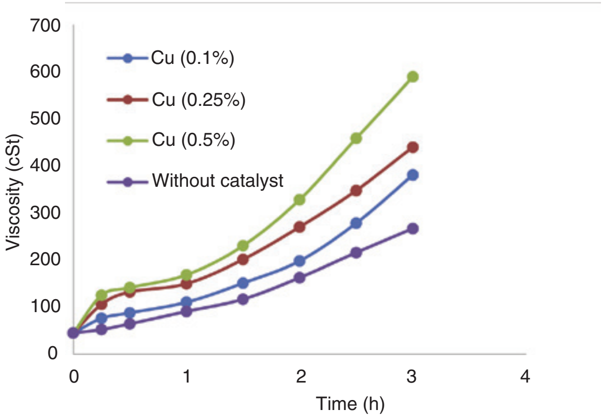


Figure 8: Soybean oil polymerization by Cu complex catalyst at 300°C.

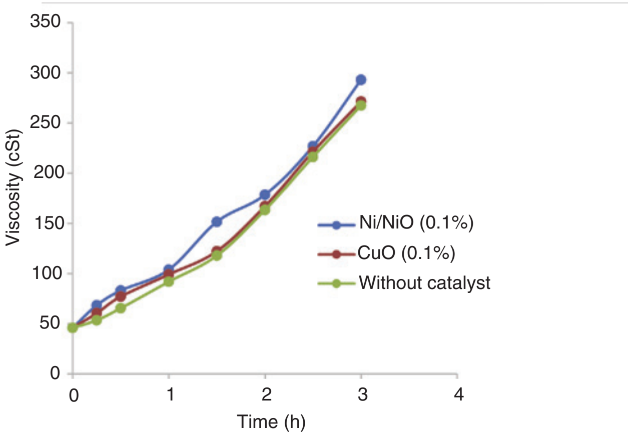


Figure 9: Soybean oil polymerization by Ni/NiO and CuO catalysts at 300°C.

due to instability and oxidative sintering at temperatures above 200°C [24].

Figure 10 presents the polymerization progress of soybean oil in the presence of nickel and copper complexes after 2.5 h from the beginning of the reaction using FTIR analysis.

As can be seen in the IR spectrum, the C=C and C-H alkenes bands appeared at 1650 and 3015 cm^{-1}, respectively [25]. For both samples, the strength of the mentioned bands decreases, indicating breaking double bands and progressing the polymerization reaction. Also, weaker C=C and C-H alkenes bands in the IR spectrum of the sample polymerized by the nickel complex reveals a

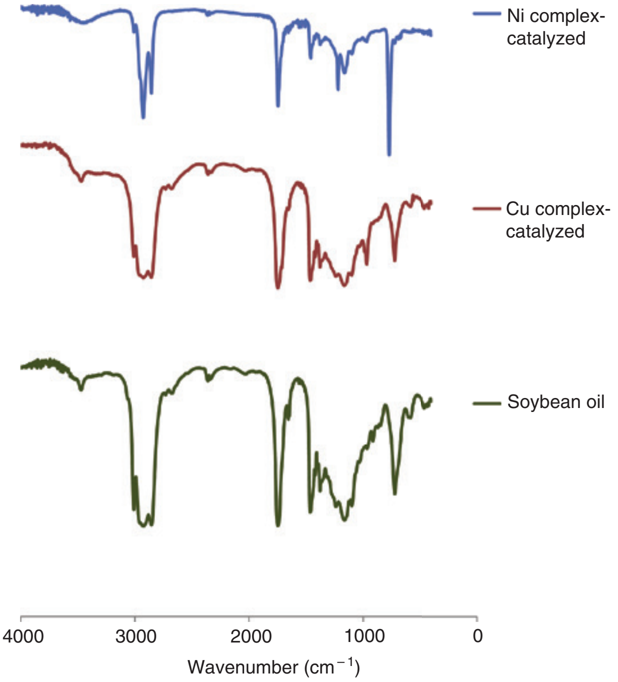


Figure 10: FT-IR spectra of non-polymerized and polymerized soybean oil by Ni and Cu complex catalysts.

greater amount of broken double bonds in the polymerization process compared with the process catalyzed by the copper complex, indicating a higher degree of polymerization when using the nickel complex catalyst. This observation is in accordance with higher magnitudes of kinematic viscosity resulting from the polymerization process catalyzed by the nickel complex catalyst (Figures 7 and 8).

4 Conclusions

Tris(ethylenediamine)nickel(II) nitrate and bis(ethylenediamine)copper(II) nitrate complexes as well as Ni/NiO and CuO were fabricated, characterized, and employed for catalyzing soybean oil polymerization reaction. The soybean oil polymerization effectively progressed in the presence of the nickel and copper complexes, suggesting that the use of these catalysts can reduce time and energy consumption of the reaction. Better capability of the metal complexes compared to the metal oxides can be attributed to the demand of the metal oxides to be reduced before catalyzing the reaction, which cannot be achieved at the reaction temperature.

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Bionotes

Seyed Mahdi Latifi

Seyed Mahdi Latifi finished his PhD in Chemical Engineering (2010) from Amirkabir University of Technology (Tehran Polytechnic). He worked at the Research and Technology Department of the National Petrochemical Company (NPC-RT) as a process researcher. He joined the Iranian Research Organization for Science and Technology as an assistant professor of Chemical Engineering in 2012. He has participated in research projects pertaining to chemical catalytic processes. He is now working on the application of heterogeneous catalysts in environmental processes.

Alireza Salehirad

Alireza Salehirad is an Assistant Professor of Inorganic Chemistry in the Iranian Research Organization for Science and Technology (IROST). He has published more than 20 papers in national and international journals. His current research interests include synthesis and characterization of nanomaterials, refractory ceramics, biomaterials and their applications, ceramic and polymer composites, heterogeneous catalysts, inorganic pigments, surface chemistry, adsorbents, and particle technology.

Atefeh Soltani

Atefeh Soltani finished his MSc in Chemical Engineering (2016) from the Iranian Research Organization for Science and Technology (IROST). Her field of study has been polymer materials. She has conducted some research on lubricant oils, including characterization and selection for industrial applications, and also using vegetable oils for substituting the petroleum-based raw materials. Also, she has been involved in the synthesis of inorganic complexes and nanomaterials for use in green processes.

Javad Bakhshi Azghandi

Javad Bakhshi Azghandi finished his MSc in Chemical Engineering (2015) from Semnan University. He conducted some research on the synthesis of nanocomposites for use as sorbents in environmental processes, mainly hydrogen sulfide removal from the gaseous hydrocarbon streams produced in petrochemical plants. Also, he worked on the catalytic reaction for hydrogen production from natural gas. He has been involved in the design and manufacturing of various experimental setups for research uses.