CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2021,
Vol. 15, No. 2, pp. 183–190

Chemistry

GREEN POLYMERIZATION OF VINYL ACETATE USING MAGHNITE-Na^+, AN EXCHANGED MONTMORILLONITE CLAY, AS AN ECOLOGIC CATALYST

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https://doi.org/10.23939/chcht15.02.183

Abstract. In this work, the green polymerization of vinyl acetate is carried out by a new method which consists in the use of clay called Maghnite-Na^+ as an ecological catalyst, non-toxic, inexpensive and recyclable by a simple filtration. X-ray diffraction and scanning electron microscopy showed that Maghnite-Na^+ is successfully obtained after cationic treatment (sodium) on crude maghnite. It is an effective alternative to replace toxic catalysts such as benzoyl peroxide and azobisisobutyronitrile which are mostly used during the synthesis of polyvinyl acetate (PVAc) making the polymerization reaction less problematic for the environment. The synthesis reaction is less energetic by the use of recycled polyurethane as a container for the reaction mixture and is considered as a renewable material and a good thermal insulator maintaining the temperature of 273 K for 6 h. The reaction in bulk is also preferred to avoid the use of a solvent and therefore to stay in the context of green chemistry. In these conditions, the structure of obtained polymer is established by ^{1}H NMR and ^{13}C NMR. Infrared spectroscopy (FT-IR) was also used to confirm the structure of PVAc. Thermogravimetric analysis showed that it is thermally stable and starts to degrade at 603 K while differential scanning calorimetry showed that this polymer has a glass transition temperature T_g of 323 K.

Keywords: polyvinyl acetate, ecologic catalyst, Maghnite-Na^+, polymerization, green chemistry, thermal stability.

1. Introduction

The chemistry is now moving towards the use of less polluting polymers and synthetic methods that involve low energy and low toxic reagents and therefore are environmentally friendly. Polyvinyl acetate (PVAc) meets these requirements, it is non-toxic [1] and biodegradable under specific conditions [2]; it attracts considerable attention in the pharmaceutical industry [3], as anti-tumor [4], in cosmetics [5, 6], in the food and food packaging [2, 5, 7], as the cheese coating [8] and gum base for chewing gum [9]. This polymer is also used in the building industry as paint and glue for wood, paper and in the textile industry as well [10-13].

PVAc can be polymerized using various catalysts. Indeed, Madras *et al.* [14] polymerized vinyl acetate using benzoyl peroxide (BPO) as a catalyst at a temperature of 328 K, while Tewari *et al.* [15] used azobisisobutyronitrile (AIBN) in benzene as a solvent at a temperature of 333 K. Vinyl acetate was also polymerized by Shaffei *et al.* [16] in emulsion; the reaction was catalyzed by potassium persulfate in the presence of surfactants at 343 K. However, these catalysts are not recyclable and require treatment of waste, they are toxic and harmful to human health; they can be dangerous if swallowed and cause skin and eye irritation [17-19]. In addition, the polymer synthesis in the presence of these catalysts is carried out at high temperature requiring more energy which is less attractive from economic and environment standpoints.

In this perspective, in our laboratory we developed a new method for the PVAc synthesis with a sustainable way based on the principles of green chemistry. For these reasons, we used rigid polyurethane as a container for the reaction mixture that we recovered and recycled. Moreover, it is a material that remains undamaged for a very long time and is considered today as the best thermal insulation [20] maintaining a low temperature (273 K) for several hours.

The advantage of this new polymerization method is also the use of Maghnite-Na^+ catalyst that promotes the synthesis reaction. It is available, green, non-toxic, inflammable and inexpensive because it can be separated from the system by a simple filtration and reused in other reactions [21]. Unlike natural clay minerals, Maghnite-Na^+ has high crystallinity, controllable composition and fewer impurities [22]. For these reasons, the use of such

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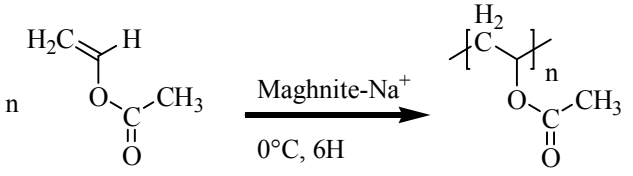
modified Maghnite as host materials is expected to be more advantageous than the use of raw natural clay minerals [23]. In the past years, this catalyst has been used successfully as an initiator for the anionic polymerization of several acrylamide and vinyl monomers [24-26], as well as for the synthesis of nanocomposites/clay [27, 28]. The polymerization of vinyl acetate catalyzed by Maghnite-Na^+ is carried out under mild conditions, in the bulk without solvent and with the minimum of reagent, reducing the waste treatment.

2. Experimental

The vinyl acetate has been polymerized by using different solvents and toxic initiators [14-19]. In our work we achieve a heterogeneous polymerization based on the principles of green chemistry, and assume that it proceeds according to the anionic mechanism (Scheme 1) PVAc.



Scheme 1. Schematic representation of the PVAc synthesis

2.1. Materials

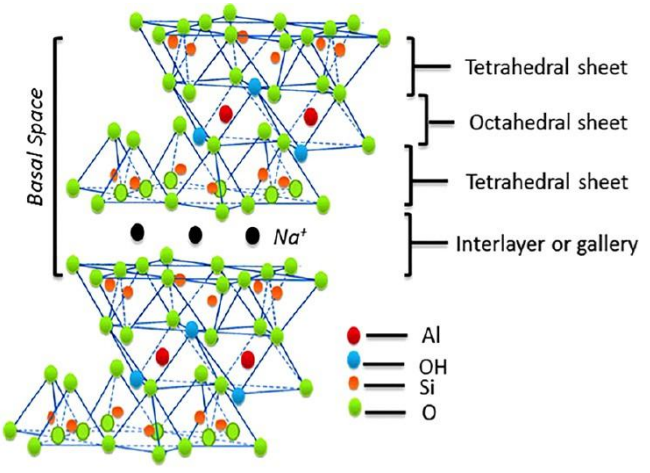
Vinyl acetate monomer (Sigma Aldrich, ≥ 99%), diethyl ether (Sigma Aldrich, ≥ 99%) and NaCl were used as received without further purification. Raw-Maghnite (Algerian montmorillonite clay) was procured from BENTAL (Algerian Society of Bentonite). Deionized water was used for the preparation of Maghnite-Na^+.

2.2. Preparation of Maghnite-Na+

In an Erlenmeyer of 1 l, 15 g of crude Maghnite is put in 400 ml of distilled water and the mixture is stirred at room temperature for 2 h. Then 600 ml of a sodium chloride solution (1M, NaCl) is added to the mixture and left stirring for 48 h at room temperature. After this time, the product is filtered and washed with distilled water until complete removal of the Cl^- ions. This is confirmed by the silver nitrate test. The last step is to crush the obtained Maghnite-Na^+ after drying in the oven at 378 K. Its structure is established by FT-IR, XRD and SEM. Scheme 2 shows the structure of the catalyst.

2.3. Synthesis of Polyvinyl Acetate (PVAc)

The polymerization of vinyl acetate is carried out in the bulk in two steps: the first step is the activation of the monomer by the catalyst. A small amount of vinyl acetate (1 g, 0.012 mol) is mixed with Maghnite-Na^+ (eco-catalyst) at various weight percentages (3, 4, 6, 7, 10 and 12 % w/w) in a sealed tube for one hour at a temperature of 273 K. The low temperature is maintained using a container which does not require energy to cool; it is made from polyurethane waste (it is a thermal insulator) which allowed the reaction to proceed smoothly under mild conditions in accordance to the principles of green chemistry. Then, in the second step, the remaining amount of the monomer (4 g, 0.046 mol) is added to the previous mixture and the polymerization is conducted at various times, still at 273 K. At the end of the reaction, solid Maghnite-Na+ is removed from the mixture by filtration, then the polymer is obtained by precipitation of the filtrate in diethyl ether. Scheme 1 describes the synthesis reaction of PVAc.



Scheme. 2. Schematic representation of Maghnite-Na+ structure [29]

2.4. Characterization

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra are recorded on a Bruker-Advance 300 MHz apparatus in deuterated chloroform ($CDCl_3$). FT-IR (Fourier transform infrared spectroscopy) absorption spectra are recorded on an Alpha Bruker FT-IR spectrometer based on Bruker Optics patented RockSolid™ design, flexible sampling and transmission, attenuated total reflection (ATR), external and diffuse reflection FT-IR sampling accessories. Thermo-gravimetric analysis (TGA) is carried out on a PerkinElmer STA 6000 under nitrogen in the temperature range of 303–963 K with a rate of 20 K/min. X-ray diffraction (XRD) studies of the clay are done using Bruker AXS D8 diffractometer with the VÅNTEC-500 detector using Cu-Kα radiation (λ = 1.5418 Å). The clay morphology is characterized by scanning electron

microscopy (SEM) using Hitachi S 2500 apparatus. Differential scanning calorimetry (DSC) measurements are carried out on a TA instrument Q500, the heating rate is 10 K/min from 253 to 473 K under N_2 and the sample weight about 20 mg.

3. Results and Discussion

3.1. Catalyst Structure

Maghnite-Na^+ is analyzed by FT-IR spectroscopy which confirmed the structure of montmorillonite. A broad band between 3200 and 3500 cm^{-1} characteristic of the OH group bonded to octahedral aluminum is observed in Fig. 1. The band at 1629 cm^{-1} corresponds to the stretching vibration of H_2O. The FT-IR spectrum also shows the presence of an intense band at 984 cm^{-1} attributed to the Si–O–Si stretching vibration in the tetrahedral layer. The characteristic bands of Si–O–Al and Si–O–Mg groups appear at 516.46 and 439.20 cm^{-1}, respectively.

The X-ray powder diffraction profiles, illustrated in Fig. 2 show that there is an increase in a basal spacing (001) from 9.98 Å in the Raw-Maghnite to 12.70 Å. This increase in the interlayer distance is explained by the adsorption of a water molecule on the surface of the montmoriollonite sheets reflecting the changes in an interlayer cation as a result of the basic treatment. The other weak peaks are related to the structure of aluminum-oxygen octahedron and silicon-oxygen tetrahedron in the montmoriollonite.

The SEM micrographs of the untreated Maghnite and Maghnite-Na^+ are illustrated in Fig. 3 and suggest that the clay has maintained its morphology even after being modified with Na^+ cations. The micrographs also show that Maghnite-Na^+ is a very cohesive material in which forming micron-size fragments are aggregated in a disordered way. These results confirm that the structure of this clay is formed from intercalated layers containing an interlayer space (already shown by XRD).

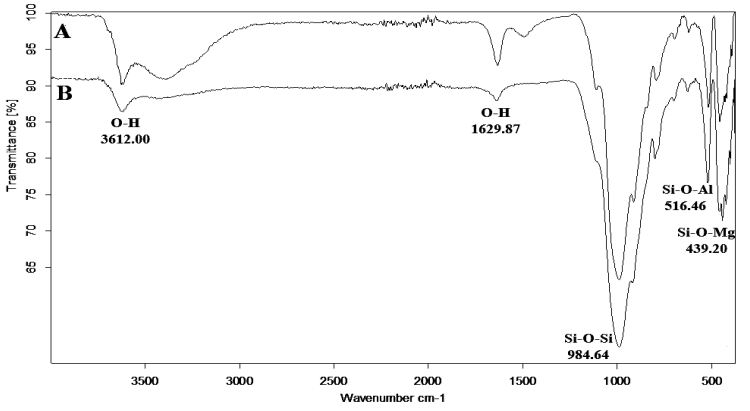


Fig. 1. FT-IR spectra of Raw-Maghnite (A) and Maghnite-Na^+ (B)

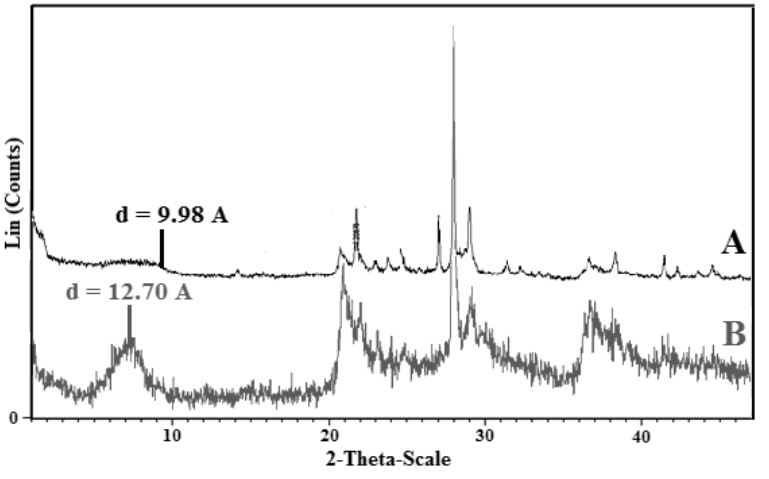


Fig. 2. XRD of Raw-Maghnite (A) and Maghnite-Na^+ (B)

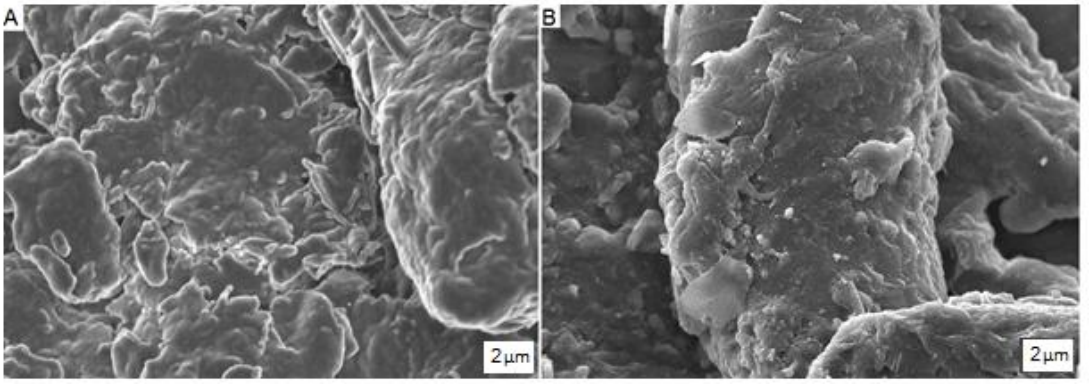


Fig. 3. SEM micrographs of Raw-Maghnite (A) [30] and Maghnite-Na^+ (B)

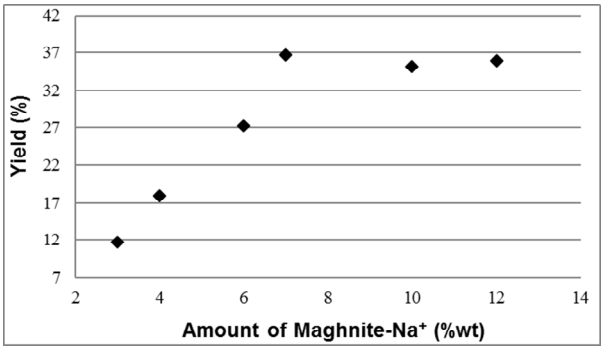


Fig. 4. Effect of Maghnite-Na^+ amount on the PVAc yield (reaction time is 6 h, reaction temperature is 273 K, in the bulk)

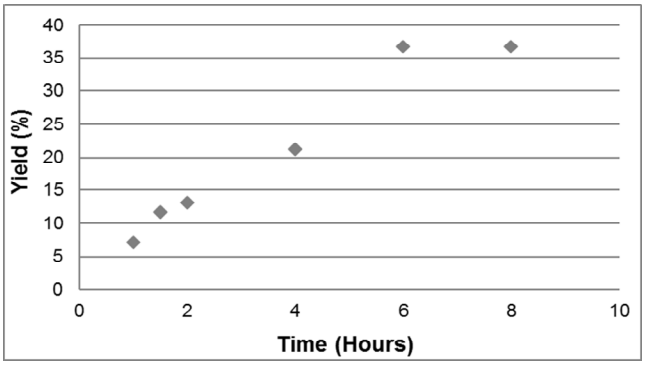


Fig. 5. Effect of time on the PVAc yield (reaction temperature is 273 K, Mag-Na^+ = 7 wt %, in the bulk)

3.2. Effect of Maghnite-Na^+ Amount and Time on the Polymerization of Vinyl Acetate

The effect of Maghnite-Na^+ amount expressed by using various weight ratios of Mag-Na^+/monomer, on the polymerization yield of vinyl acetate is shown in Fig. 4. The polymerization is carried out in the bulk at 273 K for 6 h using various amounts of Mag-Na^+ (3, 4, 6, 7, 10 and 12 % wt/wt). It can be noted that the PVAc yield increases with the increasing amount of the catalyst, in which the effect of Mag-Na^+ as a catalyst is clearly shown. However, the maximum yield is obtained at 7 wt % of Mag-Na^+ and from this value it remains unchanged. This phenomenon (increasing of the yield) can be attributed to the active sites available in the catalyst which are responsible for the initiation and acceleration of the polymerization reaction until the saturation of these sites (stabilization of the yield).

Fig. 5 shows the effect of time on the PVAc yield. The polymerization of vinyl acetate is carried out at different times in bulk at 273 K using 7 wt % of Maghnite-Na^+. The obtained results show that the yield increases slightly during four hours of reaction; this can be considered as an induction period. From that time, the yield begins to increase rapidly until it stabilizes, reaching a maximum value of 37 % after 6 h of reaction.

3.3. Polymer Structure

The structure of PVAc is analyzed and confirmed by ^{13}C NMR and ^{1}H NMR spectroscopy. The peaks at 21.04, 39.16, 66.98 and 170.38 ppm observed in the ^{13}C NMR spectrum (Fig. 6) are assigned to the CH_3, CH_2, CH and C=O groups of the polymer, respectively. The ^{1}H NMR spectrum (Fig. 7) also confirms the PVAc structure by the presence of two peaks centered at 1.52 and 1.78 ppm corresponding to the methylene group (CH_2) corroborated by the disappearance of the peaks (two doublets) at 4.56 and 4.87 ppm corresponding to the $H_2C{=}CH_2$ double bond [31]. The peaks situated between 2.01–2.05 ppm are assigned to the methyl group (CH_3) and the broad peak located at 4.88 ppm – for the CH group. These results are similar to those obtained by Itab *et al*. [32] and Poljansek *et al*. [33].

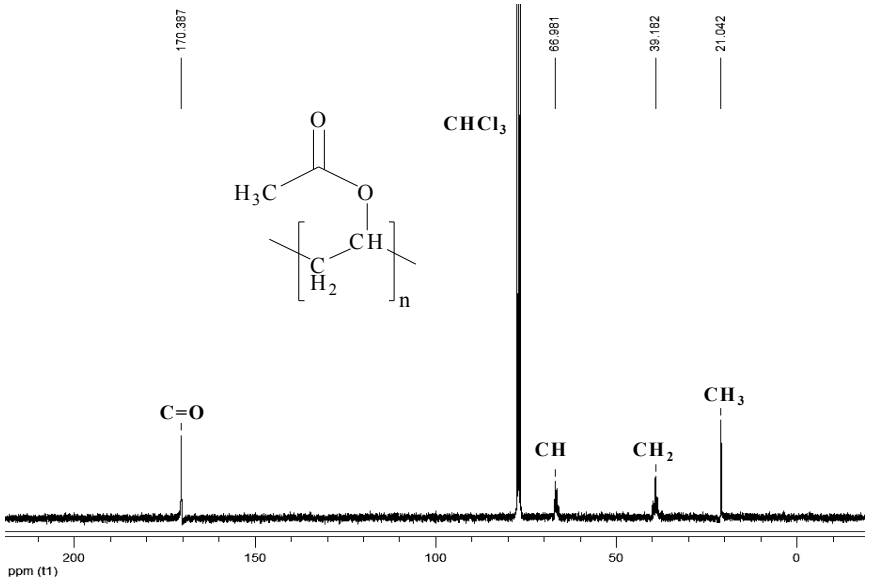


Fig. 6. ^{13}C NMR spectrum ($CDCl_3$) of PVAc

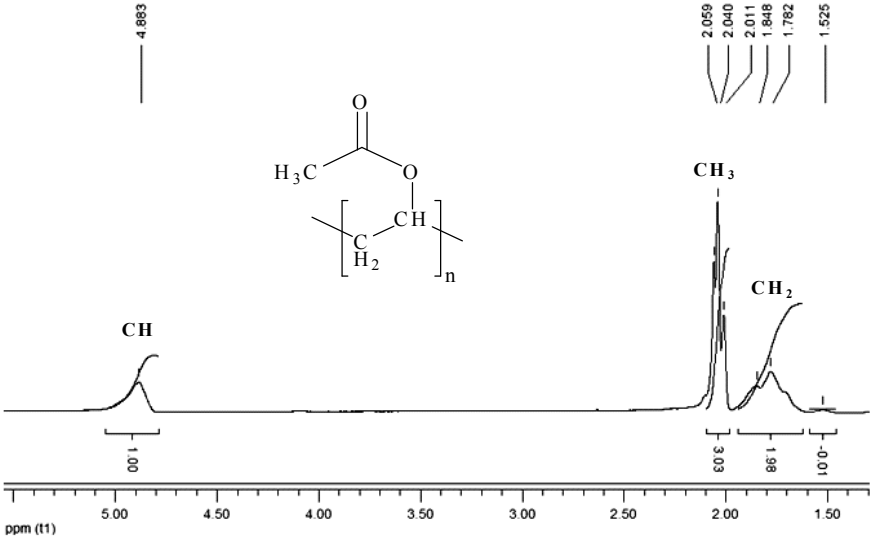


Fig. 7. ^{1}H NMR spectrum ($CDCl_3$) of PVAc

The polymerization of PVAc is also established by the FT-IR analysis. Indeed, the characteristic bands of the vinyl group at 1664.07 cm^{-1}, the stretching bands at 949 and 873 cm^{-1} corresponding to C=C and the stretching vibration at 1132.99 cm^{-1} corresponding to the =C–O–C group observed in FT-IR spectrum of vinyl acetate (Fig. 8) disappear in FT-IR spectrum of PVAc (Fig. 9) confirming that the polymerization of the monomer catalyzed by Maghnite-Na^+ (7 wt %) has been successfully completed. In addition, the stretching vibration C=O and the band corresponding to the ester group of vinyl acetate which appear, respectively, at 1728.97 and at 1206.74 cm^{-1} shift to 1755.89 and 1224.83 cm^{-1} for PVAc. The stretching vibrations of CH (2923.82 cm^{-1}), CH_2 (2923.82 cm^{-1}), CH_3 (3017.66 cm^{-1}) and $COCH_3$ (1018.77 cm^{-1}) are observed in the spectra of PVAc.

3.4. Thermal Properties

The TGA analysis is used in order to study the thermal stability of PVAc. The obtained thermogravimetric curve which is the representation of the relative weight loss depending on the heating temperature is given in Fig. 10 and shows that there are two weight loss stages. The first and intense weight loss between 573 and 673 K (69 wt %) corresponds to the deacetylation step

which consists in smaller fragments corresponding to the acetic acid mother molecule. Also during the deacetylation process, $(CH)_n$ fragments evaporate from the polymeric material indicating scission of the polymer main chain at the end. At the temperature of 673 K the PVAc decomposes into a highly regular unsaturated material or polyene. The second weight loss observed at high temperatures, in the range of 673–773 K (19 wt %), can be attributed to the complete degradation of the formed polyene through chain scission reactions. These results are similar to those obtained by Rimez *et al.* [34].

DSC analysis determines the thermal properties of PVAc and in particular its glass transition temperature, T_g, which corresponds to the passage of the polymer from the vitreous to the rubbery state. The hermetic capsule containing a mass of the polymer is introduced into the oven at room temperature and then the temperature is lowered to 253 K by a flow of N_2 gas. After that, a temperature gradient of 253–473 K is achieved with a rate of 10 K/min. At 473 K, the temperature is again lowered to 253 K, again with 10 K/min through the N_2 gas flows, before a second temperature rise in the same conditions. The DSC thermogram thus obtained allows to determine the T_g value. The first passage in temperature gives an enthalpy relaxation peak which depends on the internal tensions, resulting from the synthesis process and the thermal history of the polymer and cannot be taken into consideration. To eliminate the "thermal history" of PVAc, T_g is determined from the second pass. The obtained curve (Fig. 11) shows that T_g is about 323 K which is in agreement with the data from the literature [35].

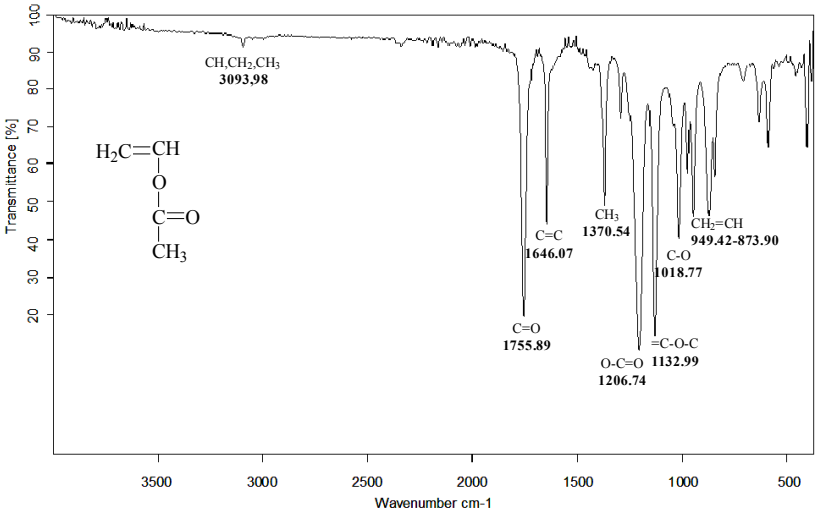


Fig. 8. FT-IR spectra of vinyl acetate

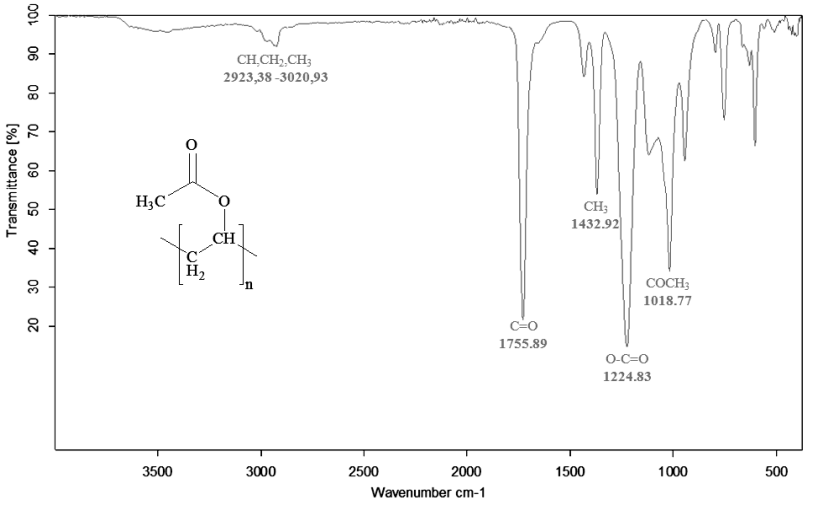


Fig. 9. FT-IR spectra of PVAc

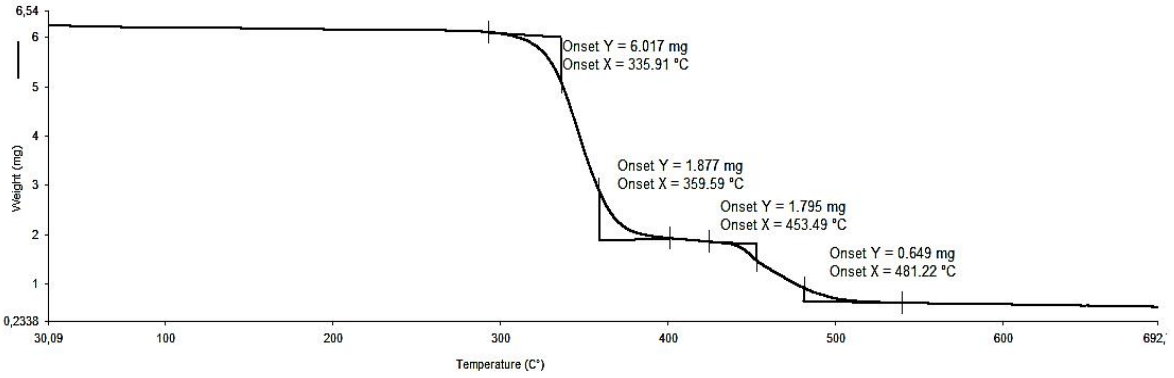


Fig. 10. TGA thermogram of PVAc catalyzed by Maghnite-Na^+ (under N_2)

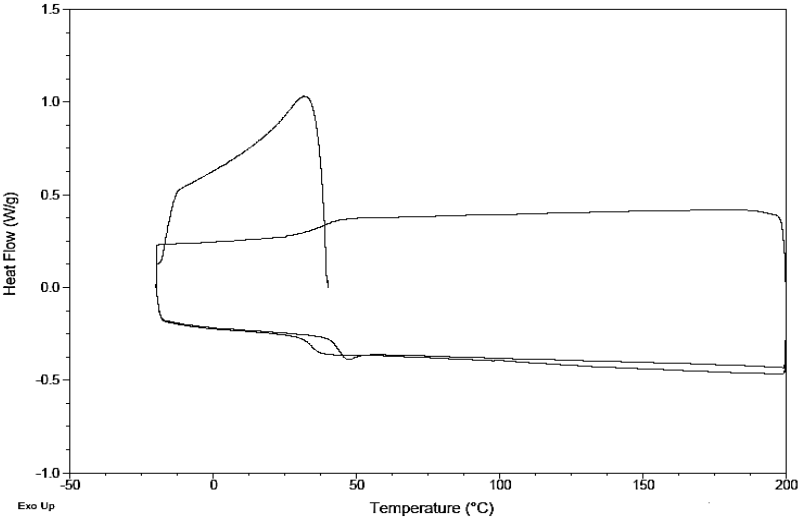


Fig. 11. DSC thermogram of PVAc catalyzed by Maghnite-Na^+ (under N_2)

4. Conclusions

In this work, polyvinyl actete (PVAc) is synthesized and structurally characterized. The synthesis of this polymer is carried out successfully by highlighting a completely ecological process by integrating the principles of green chemistry. This new approach allows developing an energy-efficient process by using a recycled polyurethane-based as a container for the reaction mixture which is an excellent thermal insulator and thus let it possible work at low temperature for a long time. In addition, PVAc is synthesized for the first time in the bulk using an efficient green catalyst called Maghnite-Na^+ under heterogeneous conditions. The polymerization proceeds *via* anionic mechanism due to the presence of intercalated sodium ion (Na^+) in the lamellar structure of the montmorillonite. The morphology of the catalyst is characterized by FT-IR spectroscopy, XRD and SEM which confirm the structure of montmorillonite and show that the layer structure remained intact after the cationic modification. The kinetic study of the PVAc synthesis shows that the best yield of this polymer is obtained by using 7 wt % of Maghnite-Na^+ with a reaction time of 6 h and a temperature of 273 K. FT-IR, as well as ^{1}H NMR and ^{13}C NMR spectroscopy establish and confirm the structure of PVAc. TGA thermograms show that the obtained polymer is thermally stable with a degradation temperature higher than 573 K and its glass transition temperature is 323 K which was obtained by DSC analysis. Thus, Maghnite-Na^+ shows that it is an attractive eco-catalyst with many advantages, such as cheapness, safety and reusability. Moreover, it can be easily separated from the polymer products and regenerated by heating to a temperature above 373 K.

References

[1] Cui H., Du G.: Adv. Polym. Technol., 2012, **31**, 130. https://doi.org/10.1002/adv.20244
[2] Amann M., Minge O.: Adv. Polym. Sci., 2012, **245**, 137. https://doi.org/10.1007/12_2011_153

[3] Chen J., Zhao X., Zhang L. *et al*.: J. Polym. Sci. Pol. Chem., 2015, **53**, 1430. https://doi.org/10.1002/pola.27582
[4] Karakus G., Polat A., Yenidunya A. *et al*.: Polym. Int., 2012, **62**, 492. https://doi.org/10.1002/pi.4341
[5] Andersen F.: J. Am. Coll. Toxicol., 1996, **15**, 166. https://doi.org/10.3109%2F10915819609043794
[6] Abdollahi M., Bigdeli P.: Polym. Bull., 2018, **75**, 1823. https://doi.org/10.1007/s00289-017-2130-z
[7] Kattner H., Buback M.: Macromol. Chem. Phys., 2014, **215**, 1180. https://doi.org/10.1002/macp.201400095
[8] Pennarun P.-Y.: Pat. EP2552243A1, Publ. Febr. 06, 2013.
[9] https://www.sciencepresse.qc.ca/blogue/2011/08/08/faut-craindre-gomme-macher
[10] Morin A., Detrembleur C., Jerôme C. *et al*.: Macromolecules, 2013, **46**, 4303. https://doi.org/10.1021/ma400651a
[11] Geng S., Shah F., Liu P. *et al*.: RSC Adv., 2017, **7**, 7483. https://doi.org/10.1039/c6ra28574k
[12] Zhang Y., Pang B., Yang S. *et al*.: Materials, 2018, **11**, 89. https://doi.org/10.3390/ma11010089
[13] Dubininkas M., Buika G.: Chinese J. Polym. Sci., 2013, **31**, 346. https://doi.org/10.1007/s10118-013-1220-0
[14] Madras G., Chattopadhyay S.: Polym. Degrad. Stabil., 2001, **73**, 33. https://doi.org/10.1016/S0141-3910(01)00064-7
[15] Tewari N., Srivastava A.: Can. J. Chem., 1990, **68**, 356. https://doi.org/10.1139/v90-052
[16] Shaffei K., Moustafa A., Hamed A.: Int. J. Polym. Sci., 2009, **2009**. https://doi.org/10.1155/2009/731971
[17] http://www.labchem.com/tools/msds/msds/LC20070.pdf
[18] https://pubchem.ncbi.nlm.nih.gov/compound/benzoyl_peroxide#section=Toxicity
[19] https://pubchem.ncbi.nlm.nih.gov/compound/aibn#section=Human-Toxicity-Excerpts
[20] https://snpu.fr/un-polyurethane-durable-contre-le-rechauffement-climatique/
[21] Belbachir M., Bensaoula A.: Pat. US 6274527B1, Publ. Aug. 14, 2001.
[22] Benharrats N., Belbachir M., Legrand A. *et al*.: Clay Miner., 2003, **38**, 49. https://doi.org/10.1180/0009855033810078
[23] Breen C., Madejovii J., Komadel P.: Appl. Clay. Sci., 1995, **10**, 219. https://doi.org/10.1016/0169-1317(95)00024-X
[24] Ayat M., Belbachir M., Rahmouni A.: Bull. Chem. React. Eng. Catal., 2016, **11**, 376. https://doi.org/10.9767/bcrec.11.3.578.376-388
[25] Bensaada N., Ayat M., Meghabar R. *et al*.: Current. Chem. Lett., 2015, **4**, 55. https://doi.org/10.5267/j.ccl.2015.3.002
[26] Rahmouni A., Belbachir M., Ayat M.: Bull. Chem. React. Eng. Catal., 2018, **13**, 262. https://doi.org/10.9767/bcrec.13.2.1308.262-274
[27] Kim B., Jung J., Hong S. *et al*.: Macromolecules, 2002, **35**, 1419. https://doi.org/10.1021/ma010497c
[28] Abd El-Ghaffar M., Youssef A., Abd El-Hakim A.: Arab. J. Chem., 2015, **8**, 771. https://doi.org/10.1016/j.arabjc.2014.01.001
[29] Nuruzzaman Md., Rahman M., Liu Y. *et al*.: J. Agric. Food Chem., 2016, **64**, 1447. https://doi.org/10.1021/acs.jafc.5b05214
[30] Zenasni M., Benfarhi S., Merlin A. *et al*.: Nat. Sci., 2012, **4**, 856. https://doi.org/10.4236/ns.2012.411114
[31] https://www.chemicalbook.com/SpectrumEN_108-05-4_1HNMR.htm
[32] Itab Y.: Doct. thesis. The University of Lorraine, 2012.
[33] Poljansek I., Fabjan E., Burja K. *et al*.: Prog. Org. Coat., 2013, **76**, 1798. https://doi.org/10.1016/j.porgcoat.2013.05.019
[34] Rimez B., Rahier H., Van Assche G. *et al*.: Polym. Degrad. Stabil., 2008, **93**, 800. https://doi.org/10.1016/j.polymdegradstab.2008.01.010
[35] Daniels W.: Vinyl Acetate Polymers, Encyclopedia of Polymer Science & Engineering, 2nd edn. Wiley Interscience 1990, 402-442.

Received: July 25, 2019 / Revised: October 15, 2019 / Accepted: November 13, 2019

«ЗЕЛЕНА» ПОЛІМЕРІЗАЦІЯ ВІНІЛАЦЕТАТУ З ВИКОРИСТАННЯМ ЯК ЕКОКАТАЛІЗАТОРА МОНТМОРИЛОНІТОВОЇ ГЛИНИ MAGHNITE-Na^+

Анотація. *Проведено «зелену» полімеризацію вінілацетату новим методом, який полягає у використанні глини під назвою Maghnite-Na^+ як екологічного, нетоксичного, недорогого каталізатора, що регенерується простою фільтрацією. За допомогою рентгенівської дифракції та скануючої електронної мікроскопії доведено, що Maghnite-Na^+ можна отримувати катіонним обробленням (натрієм) сирої глини maghnite. Показано, що такий каталізатор є ефективною альтернативою токсичним каталізаторам пероксид бензоїлу та азобісізобутиронітрилу, які в основному використовуються для синтезу полівінілацетату (ПВА). Встановлено, що синтез стає мени енергозатратним завдяки використанню як ємності для реакційної суміші утилізованого поліуретану, який є поновлюваним матеріалом та хорошим теплоізолятором, що підтримує температуру 273 К протягом 6 год. В контексті «зеленої» хімії, з метою уникнення використання розчинника реакцію проводили в масі. Структуру отриманого полімеру встановлено методами ^1H та ^{13}C ядерно-магнітної резонансної спектроскопії. Для підтвердження структури ПВА застосовано Фур'є-спектроскопію. За допомогою термогравіметричного аналізу показано, що синтезований полімер є термічно стабільним і починає руйнуватися за 603 К, а визначена за допомогою диференціальної скануючої калориметрії температура склування становить 323 К.*

Ключові слова: *полівінілацетат, екологічний каталізатор, Maghnite-Na^+, полімеризація, «зелена» хімія, термічна стабільність.*