

PREPARATION AND CHARACTERIZATION OF POLYBLEND PS WITH PVL OBTAINED USING BIS(DIBENZOYLMETHANE)ZIRCONIUM(IV) CATALYST

**Muhammad Yusuf[✉], Rahmayani Siregar, Marisa Hafifah Nasution
and Rudi Munzirwan Siregar**

Department of Chemistry, Universitas Negeri Medan, Jl. Willem Iskandar Psr V Medan,
Indonesia 20221

[✉]Corresponding Author: myusuf@unimed.ac.id

ABSTRACT

Polystyrene (PS) is a type of plastic that is often used in daily life as plastic bags, food containers, and medical equipment. However, PS has a drawback in that it is difficult to degrade. To overcome this problem, PS plastic is modified by mixing it with biodegradable synthetic polymers such as poly(δ -valerolactone) (PVL) to produce polyblends. The PVL used in this work was produced through the polymerization of δ -VL with involve a bis(dibenzoylmethane) zirconium(IV) ($\text{bis}(\text{dibzm})_2\text{Zr}$) catalyst. This research was conducted to prepare a PS/PVL polyblend with various compositions to produce a more compatible polyblend. The mixing is done by using a blending technique with a PS/PVL ratio of 10/0, 10/1, 10/2, 10/3, and 10/4, respectively. The best mixing results were obtained at the PS/PVL 10/2 ratio, where the tensile strength data was 5.97 MPa and the elongation was 2.51%. In addition, the results of the Fourier transform infrared spectra (FTIR) test indicate that there has been a secondary interaction between PS and PVL. Last, the differential scanning calorimetry (DSC) test showed that when PS was mixed with PVL, its thermal properties decreased.

Keywords: Polystyrene, Poly(δ -valerolactone), bis(dibenzoylmethanato)zirconium(IV), Polyblend, Compatible.

RASAYAN J. Chem., Vol. 16, No.1, 2023

INTRODUCTION

Plastic is an example of a synthetic polymer that has a high molecular weight and a long molecular chain. Due to its thermoplastic and thermoset properties, plastic is usually made into a product in the form of a thin film. In general, plastic is difficult to decompose because the primary component is derived from petroleum. The plastic decomposition process takes a long time, and it takes about 300-500 years to completely decompose. As a result, the stability of the environmental ecosystem is disturbed. the present, PS is a type of plastic that is widely used as food containers, glasses, plates, bowls, cardboard, membranes,⁴ and medical devices. This is because PS has superior properties like being lightweight, flexible, durable, resistant to heat, having a high melting point, and moisture resistance.⁵ In addition, PS also has very high electrical resistance properties, which makes it a good choice for blending, copolymerization, and crosslinking with biodegradable polymers.⁶ However, PS has a disadvantage in the form of a very slow rate of biodegradation. As a result, PS persists as a waste for a very long time.⁵ Meanwhile, the δ -VL compound is a lactone group that can be used to form PVL using an acid catalyst.⁷⁻⁹ PVL belongs to the aliphatic polyester group along with poly(ϵ -caprolactone) (PCL)¹⁰, poly(butyrolactone) (PBL), and polylactic acid (PLA). On the other hand, PVL has permeability properties, breaks down easily in the body through a process called hydrolysis, and it is biocompatible with other polymers.¹¹⁻¹³ Its unique properties make it the main choice in medical fields such as tissue transplantation media, surgical sutures, orthopedic equipment, and drug delivery in the form of microspheres or microcapsules. Moreover, PVL is recommended as an anti-tumor drug delivery system because it is permeable.¹⁴ To overcome some of the lack of PS, various methods can be used. One of them is by blending it with biobased materials and biodegradable polymers such as poly lactone, including PVL.¹⁵⁻¹⁷ The lack of PS is that it is difficult to degrade. On the other hand, PS also has advantages, namely its high melting point and resistance to chemicals.¹⁸ Unlike PS, PVL has biocompatible properties and is well degraded in nature. Nevertheless, PVL also has a disadvantage i.e.

having a low melting point.¹⁹ Based on these properties, the objective of this study was to prepare a PS/PVL polyblend with certain composition variations to produce compatible polyblends.²⁰

EXPERIMENTAL

Materials and Method

Zirconium tetrachloride, δ -VL, and dibenzoylmethane ligands were purchased commercially from E-Merck. Meanwhile, PVL was obtained from the polymerization of δ -VL using a $(\text{bis}(\text{dbzm})_2\text{Zr})$ catalyst.⁸ Next, PS was obtained from PT. Trinseo Materials Indonesia (TMI). Subsequently, the characterization of the results of polyblend PS/PVL was done by using tensile tests, FTIR, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and DSC. This instrument has the same specifications as those described in our previous research.²¹

Polymerization of δ -VL Using $\text{bis}(\text{dibzm})_2\text{Zr}$ Catalyst

The PVL used in this study is the result of polymerization from previous studies with the following steps. The $\text{bis}(\text{dibzm})_2\text{Zr}$ catalyst was put into a Schlenk flask and then vacuumed. After that, the δ -VL monomer was mixed with the catalyst while N_2 gas was flowed to the Schlenk. Furthermore, the polymerization reaction was performed at 100 °C for 4 hours. The product was then dissolved using chloroform solvent. Next, the product was refluxed until a clear solution was produced. Finally, diethyl ether is used to precipitate the solution, and a white polymeric solid is formed.⁸

PS/PVL Polyblend Film Preparation

A total of 2 grams of PS were put into a flask and dissolved with xylene at a temperature of 120 °C. After that, PVL was added and refluxed for 3 hours at 120 °C. The PVL composition used in PS/PVL polyblends consists of 0%, 10%, 20%, 30%, and 40%, respectively. Next, the obtained polyblend is molded and put in the oven until the xylene solvent evaporates. Subsequently, the resulting polyblend film was printed according to ASTM D638 size. Last, the polyblends obtained were analyzed using tensile tests, FTIR, XRD, SEM, and DSC.²¹

RESULTS AND DISCUSSION

The PS/PVL polyblend plastic film was made by a blending technique using the reflux method. The purpose of blending is so that the PS and PVL components can be mixed homogeneously. Blending is the process of mixing two or more polymers in one solution phase. This method will produce a polyblend plastic film that is physically mixed. Through the blending process, it is hoped that the PVL component will fill the gaps between the PS monomers without any chemical bonds being formed.²¹

Tensile Strength Test

Tensile strength testing serves to determine the mechanical properties of PS/PVL polyblend. The mechanical properties can be in the form of elastic, plastic, strength, and stiffness properties of a material against a given load. The tensile strength and elongation tests were carried out using a tensile strength tool for each PS/PVL mixed plastic specimen.²² The polyblend was cut according to the American Society for Testing Materials (ASTM) D638 tensile test standard. Meanwhile, tensile strength (MPa) and elongation (%) were calculated from the stress and strain measurement data. The results of the mechanical properties test are listed in the Table-1.

Table-1: Mechanical Properties PS/PVL Polyblend

No.	PS/PVL (w/w)	σ (MPa)	ε (%)
1.	10/0	9.8	1.34
2.	10/1	7.35	1.16
3.	10/2	5.97	2.51
4.	10/3	5.97	1.73
5.	10/4	5.97	1.46

In Table-1, it can be seen that variations in the composition of different mixtures will produce different levels of compatibility. The most optimal mechanical properties of the PS/PVL polyblend are in the ratio of 10/2 (No. 3). The mixture at this ratio also has the best compatibility compared to the others, with tensile

strength and elongation of about 5.97 MPa and 2.51%. Meanwhile, the tensile strength and elongation of pure PS was 9.8 MPa and 1.34%. At the PS/PVL 10/1 ratio, the tensile strength and elongation decreased compared to pure PS, while at the ratio of 10/2, the elongation increased compared to pure PS. Subsequently, the elongation at the ratios of 10/3 and 10/4 also increased compared to pure PS. According to these results, the addition of PVL up to 40% in the PS matrix causes the tensile strength value of polyblend plastic specimens to decrease. On the other hand, the elongation significantly increased if the PVL composition was 20%, 30%, and 40%. This can happen because the PS and PVL components influence each other.²² As a result, the interactions between polymer molecules become weaker, thereby reducing the tensile strength of the polyblend film. Another factor that can cause a decrease in the tensile strength of plastic specimens is the presence of empty spaces due to the less homogeneous mixing of PS and PVL.²³

FTIR Analysis

FTIR analysis was conducted to determine the changes in the absorption of functional groups from PS and PVL components after being mixed into polyblend. In addition, the FTIR analysis also aims to determine the interactions that occur between PS and PVL, as shown in Fig.-1.

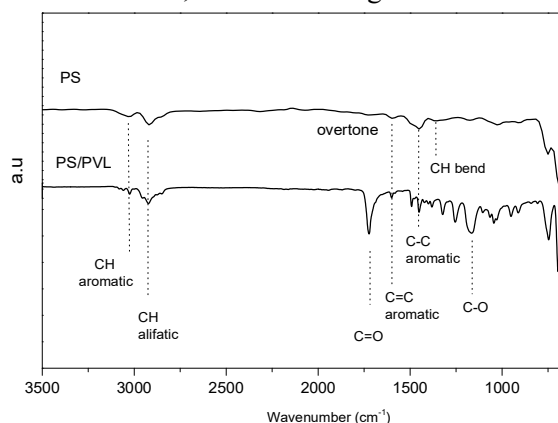


Fig.-1: FTIR Spectrum of PS, and PS/PVL Polyblend

In the PS/PVL spectrum, it can be seen that PS and PVL have been mixed. This is indicated by the appearance of functional group absorption from PVL components. At a wave number of 2922.63 cm^{-1} , the absorption of the methylene C-H group was identified. After that, at 1723.12 cm^{-1} , the presence of a carbonyl C=O group was identified. Next, at 1165.55 cm^{-1} , the presence of an ether C-O group was identified. The three δ -VL functional groups have almost the same characteristics as the functional groups that have been reported by previous researchers.¹² Furthermore, when PS with PVL is blended as in this study, the wavelength of the carbonyl group will shift from 1730 cm^{-1} to 1723.12 cm^{-1} . This happens because of a secondary interaction formed between PS and PVL.¹² Meanwhile the components of PS in polyblend are characterized by the appearance of C-H groups (aromatic) at 3024.88 cm^{-1} . In addition, the C=C (aromatic) group was identified at 1600.47 cm^{-1} . Furthermore, at 756.55 cm^{-1} , the presence of flexural vibrations or bending of aromatic C-H from PS was identified. The three PS functional groups have also almost the same characteristics as the functional groups that have been reported by previous researchers.¹⁷ According to the results of the FTIR analysis, there is an indication that PS and PVL in the polyblend have Van Der Waals interaction as shown in Fig.-2. This was evidence by the absence of new functional group uptake outside of the PS and PVL components. Additionally, in PS/PVL polyblend spectrum there is a wavelength shift in each functional group which is typical compared to pure PS and PVL. In Fig.- 2, it is shown that the ether group of PVL with a low polarity interacts with the H atom of PS. Furthermore, the carbonyl group of PVL with a high degree of polarity also interacts with the H atom of PS. As a result, dipole-nondipole interactions occur between PS and PVL.²⁴ The existence of this interaction causes changes in the thermal, physical, and crystallinity characteristics of the resulting polyblend compared to pure PS and PVL.

XRD Analysis

XRD analysis aims to identify the amorphous and crystalline structures of a polymer.²⁵ Polymers have crystalline and amorphous regions that mix randomly. The XRD diffractograms of crystalline polymers will propensity produce sharp peaks while amorphous polymers propensity to produce broad peaks. XRD diffractograms of PS and PS/PVL specimens are shown in Fig.-3. In pure PS, a wide diffraction peak appears at $2\theta = 19.16^\circ$ whereas a sharp peak appears at $2\theta = 43.94^\circ$. These two peaks are typical peaks of pure PS, as has been observed by previous researchers.²⁶

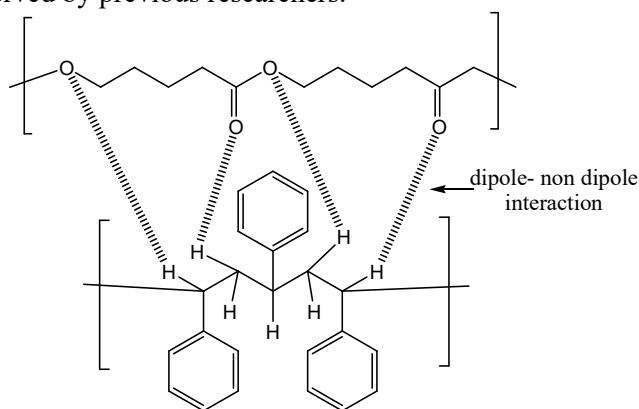


Fig.-2: Interaction of PS/PVL that Proposed

Subsequently, in the PS/PVL polyblend, a broad peak appeared at $2\theta = 21.94^\circ$ and 18.9° . These two peaks represent the amorphous phase of the polyblend while a sharp peak appears at $2\theta = 44.32^\circ$. This peak represents the crystalline phase of the polyblend. The fact that the polyblend had both amorphous and crystalline peaks showed that the PS/PVL polyblend was semicrystalline. In the XRD PS/PVL diffractograms, the changes in the shape of amorphous and crystalline peaks occurred due to the addition of pure PVL to the PS matrix. These results indicate that there has been a Van der Waals interaction between PS and PVL in polyblend. Meanwhile, pure PVL diffraction peaks have been observed by previous researchers at $2\theta = 22.2^\circ, 24.3^\circ, 30.5^\circ$ and 41.3° .^{7,10}

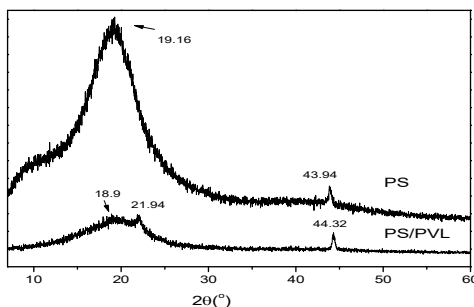


Fig.-3: XRD Diffractograms of PS, and PS/PVL Polyblend

DSC Analysis

A DSC analysis was conducted to determine the thermal properties of a polymer. The test results will be in the form of a thermogram curve that will give information about the melting point (T_m) and decomposition temperature (T_d). T_m is the condition when the polymer is in a liquid state. Furthermore, T_d is the state at which the polymer begins to break down and degrade.²² Figure-4 below shows the results of the DSC test for PS/PVL polyblend plastic film. In Fig.-4, the results of the pure PS and PS/PVL polyblend thermograms are presented. In the PS/PVL polyblend thermogram, the peak was observed at 56.03°C , and the enthalpy was 6.43 J/g . This peak was identified as the melting point of the polyblend. Because the measurement began at 27°C , the glass transition temperature (T_g) could not be detected. Whereas in pure PS thermograms, a peak was observed at 80°C , and the enthalpy was 3.41 J/g . This peak was identified as the T_g of the polyblend. These results are similar to those obtained by previous researchers.²⁷ Furthermore, pure PVL thermograms also have been observed by previous researchers, where the T_g value of 63°C , T_m

of 58 °C, and enthalpy of 63 J/g were obtained.^{7,10} The low Tm of polyblend PS/PVL makes it the potential to be used as packaging for frozen foods and beverages. Based on the DSC thermogram results, it is known that the thermal properties of PS have decreased after being blended with PVL. This can occur because of the effect of adding PVL to the PS matrix. In addition, PVL has a high level of crystallinity so that it can affect changes in the thermal, mechanical, and morphological properties of the resulting polyblend.¹²

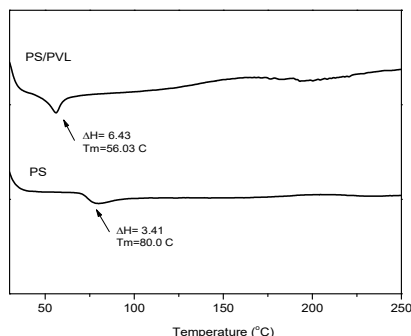


Fig.- 4: DSC Thermograms of PS, and PS/PVL Polyblend

SEM Analysis

The SEM instrument is a type of electron microscope that is used to describe the surface shape of PS/PVL polyblends, as shown in Fig.-5. In Fig.-5b, it can be seen that the surface is rough and there are lumps. This can happen because the components of PVL interact secondarily with the PS components. As a result, the aromatic chain rings of adjacent PS will be intertwined to form a lumps-like morphology.²⁰ Hence, the resulting polyblend has more elastic properties than pure PS. Meanwhile, pure PS SEM tends to be more evenly distributed than PS/PVL.

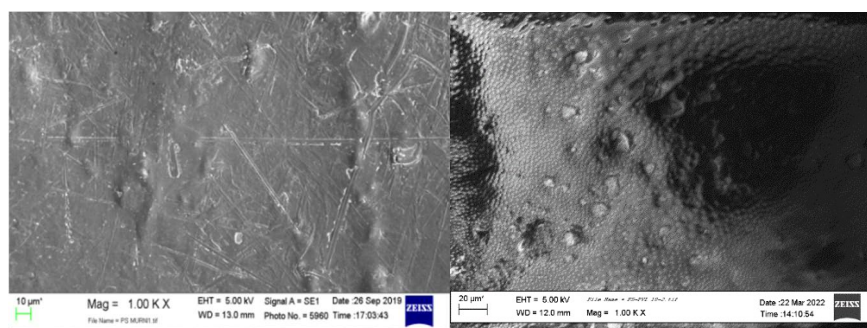


Fig.-5: SEM Images of (a) Pure PS, and (b) PS/PVL Polyblend

CONCLUSION

The mixing of PS and PVL plastic specimens using the solvent casting method to produce polyblend has been successfully carried out. Although, the addition of PVL to the PS matrix has reduced the tensile strength of the polyblend plastic specimens compared to pure PS. But, in general, the elongation of polyblend was higher compared to pure PS, and the maximum elongation was observed at a PS/PVL ratio of 10:2. This composition is a more compatible polyblend than other polyblend compositions. Based on the results of FTIR analysis, carbonyl and aromatic groups have been identified in the polyblend and no new groups have been found outside the PS and PVL components. Then, the resulting polyblend is semicrystalline polymer. Besides that, this polyblend also has lower thermal properties compared to pure PS. Furthermore, the low melting point of polyblend makes it suitable for use in frozen food and beverage packaging. Meanwhile, the SEM analysis shows that the empty PS surface has been filled by the PVL matrix. Based on the results of the FTIR, XRD, SEM, and DSC characterization analysis, it can be concluded that the mixture of PS and PVL plastic films has interacted in a Van der Waals manner.

ACKNOWLEDGMENTS

We are grateful for the financial support provided by Dana BLU Program Hibah Penelitian Terapan Universitas Negeri Medan (No. 104/UN33.8/KEP/PPKM/PT/2022).

CONFLICT OF INTERESTS

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

All authors contributed in writing the draft manuscript. Muhammad Yusuf performed writing manuscript review. Rahmayani Siregar and Marisa Hafifah Nasution performed δ -VL polymerization with a bis(dibzm)₂ Zr catalyst, PS/PVL polyblend film preparation, and tensile strength testing. Muhammad Yusuf and Rudi Munzirwan Siregar performed FTIR, XRD, DSC, and SEM analysis. The author's ORCID id profile is:

Muhammad Yusuf  <https://orcid.org/0000-0002-2119-6490>

Rahmayani Siregar  <https://orcid.org/0000-0001-5412-8227>

Marisa Hafifah Nasution  <https://orcid.org/0000-0001-6679-1114>

Rudi Munzirwan Siregar  <https://orcid.org/0000-0001-6035-4714>

Open Access: This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

REFERENCES

1. S. Agarwal, *Macromolecular Chemistry and Physics*, **221**(6), 2000017(2020), <https://doi.org/10.1002/macp.202000017>
2. S. Bahl, J. Dolma, J. J. Singh, and S. Sehgal, *Materials Today: Proceedings*, **39**(1), 31(2020), <https://doi.org/10.1016/j.matpr.2020.06.096>
3. R. E. Dibiyantini and M. Yusuf, *Journal of Physics: Conference Series*, **1811**(1), 012056(2021), <http://dx.doi.org/10.1088/1742-6596/1811/1/012056>
4. A. N. Pulungan et al., *Rasayan Journal of Chemistry*, **13**(2), 1112(2020), <http://dx.doi.org/10.31788/RJC.2020.1325616>
5. A. H. Farha, A. F. Al Naim, and S. A. Mansour, *Polymers*, **12**(9), 1935(2020), <https://doi.org/10.3390/polym12091935>
6. A. N. Sabbar, H. S. Mohammed, A. R. Ibrahim, and H. R. Saud, *Oriental Journal of Chemistry*, **35**(1), 455(2019), <http://dx.doi.org/10.13005/ojc/350159>
7. J. Jitonnorn, R. Molloy, W. Punyodom, and W. Meelua, *Songklanakarin Journal of Science and Technology*, **40**(4), 854(2018), <https://doi.org/10.14456/sjst-psu.2018.120>
8. Muhammad Yusuf; Eddiyanto Eddiyanto; Rudi Munzirwan Siregar; Rizki Dwi Irmalasari, *Egyptian Journal of Chemistry*, **65**(12), 111(2022), <https://doi.org/10.21608/ejchem.2022.107965.4942>
9. M. Yusuf, D. R. Dahniar, and M. Damanik, *Asian Journal of Chemistry*, **31**(5), 982(2019), <https://doi.org/10.14233/ajchem.2019.21662>
10. M. Yusuf, D. Roza, Nurfajriani, H. Gunawan, and N. Dari, *Rasayan Journal of Chemistry*, **12**(4), 2132(2019), <http://dx.doi.org/10.31788/RJC.2019.1245463>
11. M. Badwelan et al., *Polymers*, **13**(1), 1(2021), <https://doi.org/10.3390/polym13010046>
12. W. S. Saeed, A. B. Al-Odayni, A. A. Alghamdi, A. Alrahlah, and T. Aouak, *Crystals*, **8**(12), 1(2018), <https://doi.org/10.3390/cryst8120452>
13. Y. Ren et al., *RSC Advances*, **6**(51), 45791(2016), <https://doi.org/10.1039/C6RA09289F>
14. K. Duale, M. Zi, P. Chaber, D. Jeanne, and D. Fouque, *Molecules*, **23**(8), 2034(2018), <https://doi.org/10.3390/molecules23082034>
15. Nurfajriani, A. N. Pulungan, M. Yusuf, M. D. Tampubolon, and N. Bukit, *Journal of Physics: Conference Series*, **1485** 012055(2020), <http://dx.doi.org/10.1088/1742-6596/1485/1/012055>
16. N. Nurfajriani, A. N. Pulungan, M. Yusuf, and N. Bukit, *Journal of Physics: Conference Series*, **1811**(1), 12070(2021), <http://dx.doi.org/10.1088/1742-6596/1811/1/012070>
17. S. Ibrahim, M. Abdel Rehim, and G. Turkey, *Journal of Physics and Chemistry of Solids*, **119**(March),

- 56(2018), <https://doi.org/10.1016/j.jpcs.2018.03.030>
18. J. Lv et al., *Polymer Engineering and Science*, **59** E171(2019), <https://doi.org/10.1002/pen.24898>
19. M. Arcana, B. Tanajaya, B. Anwar, C. L. Radiman, and M. A. Sulfikar, *Proceedings ITB Sains & Teknologi*, **37**(2), 93(2005),.
20. D. D. de Souza Morais et al., *Revista Escola de Minas*, **72**(1), 87(2019), <https://doi.org/10.1590/0370-44672017720137>
21. M. Yusuf, N. Dari, R. Siregar, and D. P. F. Amne, *Rasayan Journal of Chemistry*, **15**(3), 1634(2022), <http://doi.org/10.31788/RJC.2022.1536673>
22. I. M. Arcana, B. Bundjali, I. Yudistira, B. Jariah, and L. Sukria, *Polymer Journal*, **39**(12), 1337(2007), <https://doi.org/10.1295/Polymj.PJ2006250>
23. E. B. Bezerra et al., *Polimeros*, **29**(2), 1(2019), <https://doi.org/10.1590/0104-1428.02518>
24. L. Shao, Y. Xi, and Y. Weng, *Molecules*, **27**(18), 5953(2022), <https://doi.org/10.3390/molecules27185953>
25. J. L. Sihombing et al., *Catalysts*, **10**(1), 121(2020), <https://doi.org/10.3390/catal10010121>
26. K. Tian, C. Liu, H. Yang, and X. Ren, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **397** 12(2012), <http://dx.doi.org/10.1016/j.colsurfa.2012.01.019>
27. Q. A. Kadhim, R. M. Alwan, R. A. Ali, and A. N. Jassim, *Nanoscience and Nanotechnology*, **6**(1), 1(2016), <https://doi.org/10.5923/j.Nn.20160601.01>

[RJC-8050/2023]