

The variations ITO concentration for observed properties of conductivity of polymer liquid crystal of cholesteryl acrylate-indium tin oxide

A Afrizal^{1*}, A Rahman¹, Y Al¹ and E Handoko²

¹ Department of Chemistry, Universitas Negeri Jakarta, Jakarta, Indonesia

² Department of Physics, Universitas Negeri Jakarta, Jakarta, Indonesia

*afrizal@unjac.id

Abstract. Liquid crystal polymer of Cholesteryl Acrylate-Indium Tin Oxide (PolyChoA-ITO) in this study has been successfully synthesized by UV curing method, which variations of ITO concentrations i.e. 0, 10, 20, 30, 40, and 50% w/w. This research using ITO as a doping on a cholesteryl acrylate monomer and subsequently polymerized. Characterization of PolyChoA-ITO using FTIR, that resulted a peak at 1600-1750 cm⁻¹ that identifies the stretching vibration of the C=O group. The peak of the wavelength also shows the interaction of ITO with cholesteryl acrylate in PolyChoA-ITO. Characterization of PolyChoA-ITO using X Ray Diffraction (XRD) showed some peaks at $2\theta = 7,53^\circ$; $15,27^\circ$; $8,10^\circ$; and $30,40^\circ$; which is the typical peak of ITO and the typical peak of cholesteryl acrylate. SEM image of PolyChoA-ITO shows that ITO is agglomerated on the surface of cholesteryl acrylate polymer that uniform. Conductivity properties of PolyChoA-ITO shows that the higher concentration of ITO is added the greater the conductivity value. The maximum conductivity value of PolyChoA-ITO at 10% ITO concentration is 50.352×10^{-8} S/m.

1. Introduction

Liquid crystal is one type of material that has a liquid phase state and solid phase as well as depending on the temperature. Some research on liquid crystals has been studied extensively in recent years on the field of digital technology. One of type a liquid crystalline is cholesteryl acrylate that derivative of cholesterol. Based on its liquid crystalline phase, cholesteryl acrylate includes a cholesterol phase or a chiral nematik having a helical structure that can selectively reflect light [1].

Since the helical structure only appears at its mesophase temperature, it is necessary to fix the structure through the polymerization process. The process of polymerization of cholesteryl acrylate monomer was carried out using UV curing method. The process of uv curing greatly influences the resulting polymer. Several factors influence the resulting polymer yield. In this study, the monomer cholesterol acrylate was added indium tin oxide (ITO). Therefore, in this study, variation of ITO concentration was done to study the product and test the conductivity value.

The addition of ITO as a conductive dopant can alter the performance characteristics of liquid crystals, such as electro-optics and dielectric properties. Several studies have shown that doping with conductive dopants affects the properties of liquid crystal polymers such as decreasing threshold and voltage shift. ITO is a conductive oxide having unknown dielectric properties because the value is so



high and constant that it can improve the conductivity properties of the liquid-crystal cholesterol polymer composite [2, 3].

Therefore, in this research will observe the variations of concentration ITO for conductivity properties was made using UV Curing technique. Product of polymer cholesteryl acrylate-ITO (PolyChoA-ITO) will be characterized using Fourier Transmission Infrared (FTIR), Scanning Electron Microscope (SEM), and X-Ray Diffraction (XRD) and tested by using LCR Meter [4].

2. Material and methods

Materials this research were: acrylic precursor, acryloyloxy Buthyloxy benzoate (ABB), dichloromethane solvent, Indium Tin Oxide (ITO), N₂ gas. Characterizations of product of PolyChoA-ITO using Fourier Transmission Infrared (FTIR), Scanning Electron Microscope (SEM), and X-Ray Diffraction (XRD) and tested by using LCR Meter. FTIR spectrum for identifications some peaks PolyChoA-ITO, specially interaction with ITO. SEM image for identifications of surface and cross sections of thin film of PolyChoA-ITO. XRD instruments for identifications of crystalline properties products. Special apparatus LCR meter for measurements of conductivity and permittivity of thin film PolyChoA-ITO.

Methods this research by experiment that through three steps are: the first step is synthesis of cholesteryl acrylate. The second step is polymerizations of monomer cholesteryl acrylate and doped ITO. The third step is characterizations polymer cholesteryl acrylate-ITO (PolyChoA-ITO). Polymerizations of PolyChoA-ITO using UV curing method that monomer of 10 mg cholesteryl acrylate was soluted in dichloromethane solvent. Then added 0.1% (1 μ L) initiator Darocure 1173. Then added ITO with variations of concentrations. The variations concentrations ITO as follows: 0%, 10%, 20%, 30%, 40%, and 50% w/w. The homogeneous solution of cholesterol acrylate-ITO is printed on the surface of the glass plate which has been placed on a hot plate set at 75-80°C. The photopolymerization process is carried out at a temperature of 75-80°C for 30 minutes using ultraviolet (UV) radiation in the UV Curing box [5 ,6].

3. Result and discussion

Polymerization of monomer cholesteryl acrylate-ITO begin with initiation step that using the initiator benzoyl peroxide to initiation process is form radical monomer. This reaction involves a chain extension reaction which can be either free radical, the formation of a radical compound can occur when the photopolymerization process takes place resulting from the absorption of ultraviolet (UV) energy applied to the curing process. The process of photopolymerization by preparing 10 mg monomer of cholesteryl acrylate was dissolved in 0,4 mL dichloromethane pure grade and then added with initiator by 1 μ L. Then was dropped onto a glass plate measuring 2x2 cm². Initiator in this research was darocure 1173 as the initiator. Photopolymerization by UV ray areas with wavelengths between 225 nm to 375 nm [7 ,8].

Identification group function of cholesteryl acrylate and PolyChoA-ITO observed by FTIR spectrum. Based on the spectrum the peak widths of 3000-3500 cm⁻¹ indicate the presence of vibrations of hydroxyl groups (-OH). The peak at the wave number 2937.21 cm⁻¹ shows the presence of vibrations of an aliphatic C-H bond. This indicates that there is considerable C-H bonding in the sample. The sharp peak at the 1624.06 cm⁻¹ wave number of the IR spectrum of the cholesteryl acrylate monomer shows the vibration of the C=C group. However, the peak for the C=C group of the ITO-cholesteryl polymer composite had a shift to 1632.53 cm⁻¹ and the absorption peak became weak due to the vibration of the aromatic C=C bond. This suggests that in the double copolymerization photopolymerization process C=C on the cholesterol monomer of acrylate has been attacked by free radical photo initiator and becomes a single C-C bond. The absorption of UV rays on the cholesterol acrylate monomer causes free radical formation at the initiator so that the breaking of the C=C double bond. FTIR spectrum for PolyChoA-ITO have peak similar to the typical ITO peaks in the 447,49 finger print regions; 513,07; 547,78; 596.00 cm⁻¹. The peaks also experienced a slight shift from ITO which has distinctive peaks at the area 437.84; 487.99; 534.28; 619,15cm⁻¹, this indicates that the mixture contains ITO [9].

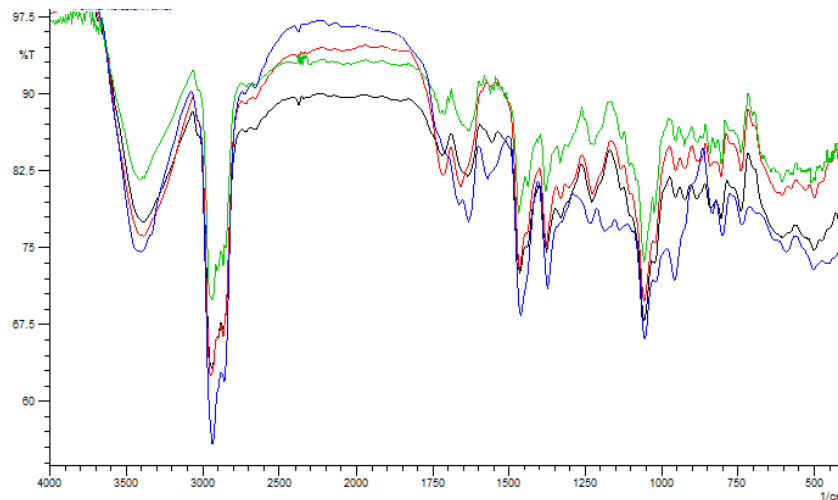


Figure 1. Spectra of PolyChoA without ITO and PolyChoA-ITO (ITO 10% green, 20% red and 30% w/w black).

Based on the XRD characterization data analyzed with the X'Pert High Score Plus application shown in Figure 2, there are sharp peaks in the 2θ areas 7.6187° ; 12.8214° ; and 15.426° which is an X-ray diffraction pattern similar to the typical diffraction pattern of the cholesteryl acrylate i.e at $2\theta = 2.71^\circ$, 5.30° , and 18.58° . However, the peaks have changed and new peaks appear on 2θ 15.426° . This indicates an interaction of cholesteryl acrylate with ITO. In addition, peaks appear with little intensity on area 2θ $15-20^\circ$ show the structure of the sample. The peaks of weaker broad 2θ at $15-20^\circ$ can be observed for the smectic, nematic and cholesteric structures. The peaks of the typical ITO diffraction at 2θ 21.40° ; 30.49° ; and 35.34° showed in the pattern XRD of the sample even though the peak intensity becomes smaller. This may also reinforce the indication of ITO interaction with the cholesteryl acrylate in the sample.

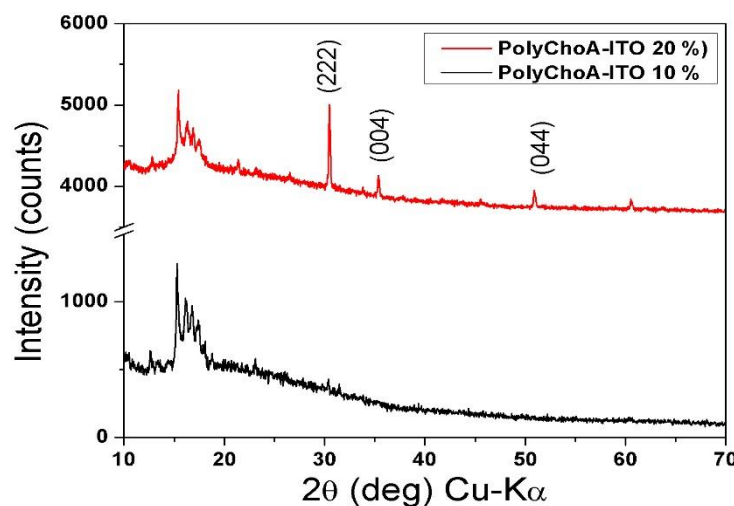


Figure 2. XRD Pattern of PolyChoA (ITO 10% w/w) and ITO (ITO 20% w/w) Polyester-Acrylate Composites (ITO 20% w/w).

XRD pattern of PolyChoA-ITO at ITO 20% w/w showed some peaks at 2θ 7.62° ; 12.82° ; 15.43° ; 21.40° ; 30.48° ; 35.34° ; and 45.56° . Therefore XRD pattern of PolyChoA-ITO at ITO 10% w/w showed some peaks at $2\theta = 7.53^\circ$; 15.27° ; 18.10° ; and 30.40° . The peak at 2θ $15-20^\circ$ of PolyChoA-ITO showed greater intensity. This indicates that ITO can alter the orientation of the crystal plane of the PolyChoA-

ITO. Therefore the smaller the percentage of ITO given, the more crystalline peaks present in the polymer and reinforced by Mindyuket al. [7] that the liquid crystal can be doped by a conductive oxide with a smaller percentage so that the crystalline peak of the liquid crystal is formed [10].

Figure 3a SEM image of cholesteryl acrylate that clearly with shape the bars with the fibers branching off and the morphological structure forming a crosslinked network. This indicates that the photopolymerization process has been successfully performed. Figure 3b showed image SEM of PolyChoA-ITO at ITO 10% w/w. Surface image that similar and equally morphological structure. This result indicates that happened interaction of ITO with cholesteryl acrylate and. ITO particle was stuck between on chain of polymer cholesteryl acrylate that formed crosslinked structure [11, 12].

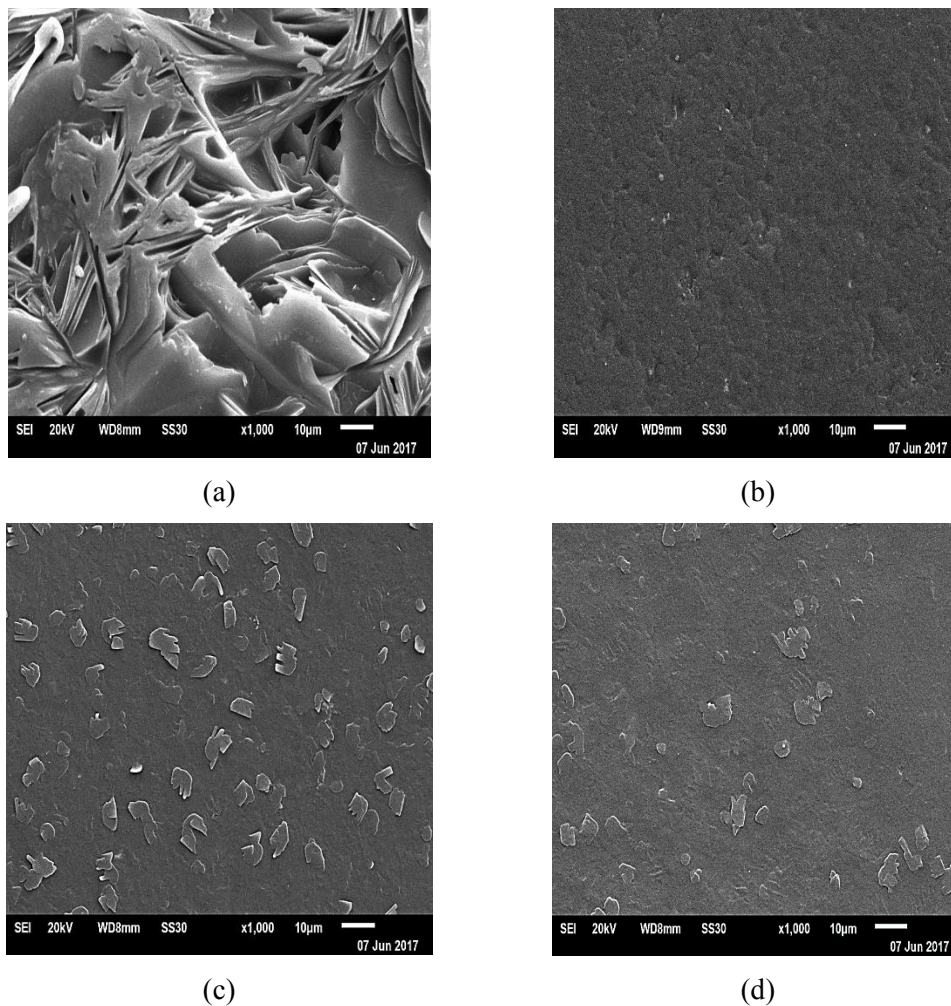


Figure 3. SEM image PolyChoA-ITO with variations concentration of ITO (a) 10% (b) 20% (c) 30% w/w.

Figure 3c SEM image for PolyChoA-ITO with ITO 20% w/w, showed numerous clumps and surrounding uniformly visible structures. ITO particles has been agglomeration process due to some ITO particles cannot bond with cholesteryl acrylate polymer so that dispersed ITO is increasing. The threshold value allows ITO no longer to fill the cavity contained in the cholesteryl-acrylate polymer. Figure 3d SEM image PolyChoA-ITO at ITO 30% w/w, that showed a surface morphological structure similar to that of ITO 20% w/w [13,14].

Testing conductivity and permittivity of PolyChoA-ITO using LCR Meter instrument. The sample is measured by clamping it between two probes at a frequency of 1 kHz and a constant voltage of 1 Volt.

Based on conductivity value of the PolyChoA-ITO above that according to SEM image of PolyChoA-ITO, specially at the ITO 10% w/w, surface of PolyChoA-ITO uniform and evenly distributed structure. Since particle of ITO filling is the cavities which causes the electron transport from the sample so that the conductivity of PolyChoA-ITO will increase. However, PolyChoA-ITO with ITO 20% w/w surface composite has a non-uniform morphological structure and there are forms of clumps. This happens because the ITO that fills the cholesterol cavity of PolyChoA-ITO has reached the threshold causing the electron transportability to decrease resulting in a decrease in the conductivity value of the sample. According to Petkoska and Jacobs study [8], each doped material has a threshold value against dopant concentration. This results in a decrease in the conductivity value of the ITO 20% w/w of PolyChoA-ITO [15,16].

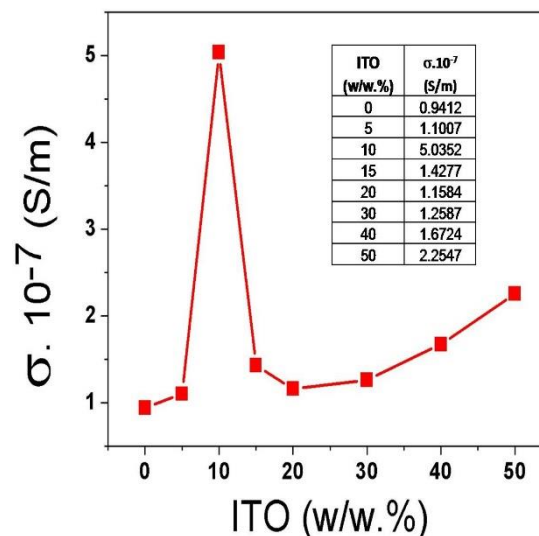


Figure 4. Graphic relation of electric conductivity to ITO dopant concentration.

4. Conclusion

The results of the ITO dopant impact test on the conductivity properties of the ITW-cholethyl-acrylate polymer composite were performed using LCR Meter instrument at a frequency of 1 kHz and a constant voltage of 1 Volt, indicating that the addition of ITO as a dopant in a cholesterol acrylate polymer may increase the conductivity of the composite. ITO-cholesterol-acrylate polymer composite with ITO concentration of 10% w/w has the highest conductivity value of 50.352×10^{-8} S/m.

Acknowledgments

This research was supported by Program Hibah Penelitian Dasar from Kementerian Riset Teknologi Dan Pendidikan Tinggi Republik Indonesia, LPPM UNJ Number : 8/SP2H/DRPM/LPPM-UNJ/II/2018.

References

- [1] X He, Y Gao, J Zheng, X Li and F Meng 2016 Chiral photosensitive side-chain liquid crystalline polymers - synthesis and characterization *Colloid Polym. Sci.* pp. 1823–1832
- [2] S Ma, X Li, L Bai, X Lan, N Zhou and F Meng 2015 Synthesis and characterization of imidazolium-based polymerized ionic liquid crystals containing cholesteryl mesogens pp. 2257–2268
- [3] S Hirano, A Kishimoto, V Chaudhari, H Chandekar, A Erkli, M Alsaadi and M Bulut Synthesis and Characterization of Composite UPR / Fe₃O₄ for Its Use as Electromagnetic Wave Absorber pp. 4–8
- [4] M Thirumoorthi and J T Joseph 2016 Journal of Asian Ceramic Societies Structure, optical and

- electrical properties of indium tin oxide ultra thin films prepared by jet nebulizer spray pyrolysis technique *Integr. Med. Res.* **4**(1) pp. 124–132
- [5] K Kumar, P Kumar, A Kumar and R Manohar 2018 Results in Physics UV response on dielectric properties of nano nematic liquid crystal *Results Phys.* **8** pp.1119–1123
- [6] F Ying, Y Cui and G Xue 2016 Preparation and properties of an antistatic UV-curable coating modified by multi-walled carbon nanotubes *Polym. Bull.* **73**(10) pp. 2815–2830
- [7] M Suen, J Gu, J Hwang, C Wu and H Lee 2018 In-situ polymerization and characteristic properties of the waterborne poly (siloxanes-urethane) s nanocomposites containing graphene
- [8] M Sadej, H Gojzewski and E Andrzejewska 2016 Photocurable polymethacrylate-silica nanocomposites : correlation between dispersion stability, curing kinetics, morphology and properties *J. Polym. Res.* pp. 1–11
- [9] M Ciprian, R Christophe, G Van Assche and B Van Mele 2012 Influence of temperature and UV intensity on photo-polymerization reaction studied by photo-DSC pp. 287–294
- [10] I Son, J H Kim, B Lee, C Kim, J Y Yoo, K Hyun, J Wu and J H Lee 2016 Vertical Alignment of Liquid Crystals Using an In Situ Self-Assembled Layer of an Amphiphilic Block Copolymer **24**(3) pp. 235–239
- [11] Z Zhao, X Mu, J Wu, H J Qi and D Fang 2016 Effects of oxygen on interfacial strength of incremental forming of materials by photopolymerization *Extrem. Mech. Lett.* **9** pp. 108–118
- [12] J Ban, L Zhu, S Chen and Y Wang 2016 The impact of liquid crystal fillers on structure and properties of liquid-crystalline shape-memory polyurethane composites *J. Mater. Sci.* **51**(22) pp. 10229–10244
- [13] Q Luo, Y Li, L Pan, L Song, L Wu and S Lu 2016 Effective reinforcement of epoxy composites with hyperbranched liquid crystals grafted on microcrystalline cellulose fibers *J. Mater. Sci.* **51**(19) pp. 8888–8899
- [14] M Jafari, A Rahimi and P Shokrolahi 2014 Synthesis of antistatic hybrid nanocomposite coatings using surface modified indium tin oxide (ITO) nanoparticles **11**(4) pp. 587–593
- [15] K Yonetake, T Takahashi, K Yonetake and T Takahashi 2006 New material design for liquid crystals and composites by magneto-processing New material design for liquid crystals and composites by magneto-processing,” **6996** pp. 5–10
- [16] R Yang, C Chu, Y Peng, and H Chueng 2012 Effects of Organic Compounds on Microstructure, Optical, and Electrical Properties of ITO Thin Films Prepared by Dip-Coating Method