Synthesis and Characterization of Polyester-Based Nanocomposite

Sudirman[a,b,*], M. Anggaravidya[c,d], E. Budianto[a], I. Gunawan[b]

[a]Department of Chemistry, University of Indonesia, Kampus Baru UI, Depok, Indonesia
[b]Center for Technology of Nuclear Industrial Material, National Nuclear Energy Agency, Kawasan Puspiptek, Serpong, Indonesia
[c]Department of Materials Science, University of Indonesia, Kampus Baru UI, Depok, Indonesia
[d]Industrial Assessment Center Process, Agency for the Assessment and Application of Technology,
Kawasan Puspiptek, Serpong, Indonesia

Abstract

Recently, unsaturated polyester resin (UPR) and silica nanocomposite prepared by mechanical process is the one of the promising composite materials. In this study, the effects of silica as filler on mechanical, thermal, and morphological properties of unsaturated polyester-based composite were investigated. Mechanical properties such as tensile strength, elongation and Young's modulus increase with the addition of silica nanoparticle up to 1.0 wt%, and then decrease, over 1.0 wt%. Morphological surface of composite reveals that well-dispersed silica in the matrix occurred in low concentration. However, increasing of silica concentration causes aggregation of particles. Enhancement of mechanical properties strongly corresponds to strong adhession force of silica with the matrix and it influnced by well-disperse silica particles on the whole surface of composite. Thermal characterization and analysis of major functional group of the composites were also performed and described in this paper.

1. Introduction

In materials research, very rapid development of polymer nanocomposites appears on the various multidisciplinary sciences with wide applications that have many advantages for industry. Polymer nanocomposite is a polymer that has been reinforced with small quantity (less than 5% by weight) of nano-sized particles [1]. Nanocomposites are a new class of materials that have high physical, thermal,

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* Corresponding author. Tel.: +62-21-756-0922; fax: +62-21-756-0926
  E-mail address: sudirman@batan.go.id

and mechanical properties compared with conventional composites (microcomposites), due to the much stronger interfacial interactions between the dispersed nano-sized particles and the matrix [2-7].

Polyester is a long-chain polymer which chemically composed of an ester, a dihydric alcohol and a terephthalic acid, formed by the esterification condensation of polyfunctional alcohols and acids. Unsaturated polyesters refer to that family of thermosetting polyesters with alkyl resins as the backbone. They are mostly used in reinforced plastics used in the marine and transportation industries. Several studies of silica as filler in composites materials were carried out to improve the strength, to reduce the production cost, to adjust the viscosity and to make smooth surface [8-10]. Yoshida, *et al*. showed that the addition of silica in a particular composition of the composite materials increases the tensile strength of materials [8]. The particle size of silica also affects the properties of the composite materials such as the Young's modulus increased by 40% [9-10]. The addition of nanosilica improves the thermal, rheological, mechanical and adhesion properties of polyester due to the formation of hydrogen bonds between the silanol groups on the nanosilica surface and the ester carbonyl groups in soft segments [11–15]. In that type of nanocomposites nanosilica enhances the incompatibility between hard and soft segments favouring the phase separation [15,16]. The addition of nanosilica increases the polyester chain mobility allowing this segment to become more ordered in relation to the pure polymer [13]. It has been shown that the introduction of the nanosilica up to 3 wt% can significantly enhance both tensile and elongation at break of polymer films.

Recently, polyester using unsaturated polyester resin (UPSR) reinforced using nano-sized silica particle is being developed. The effect of silica nanoparticle at low concentration on the formation of unsaturated polyester-based (UPR 108) composite was investigated in this study. The existing waste materials such as rice husk ash was utilized to synthesize silica nanoparticle. The composites were prepared by mechanical process and then characterized their physical properties such as mechanical, thermal and structural properties using appropriate instruments. The dispersion of silica in the matrix was observed by scanning electron microscope (SEM) and its effect on the overall characteristics such as mechanical, thermal and structural properties is discussed in this paper.

2. Experiment

3.1. Materials

Unsaturated polyester (UPR 108) was purchased from Justus Chemical Company, Indonesia and used as polymer matrix of composite in addition of methyl ethyl ketone peroxide (MEKPO) as catalytic reaction. Nanosilica used as filler in composite was synthesized from rice husk ash.

3.2. Methods

Preparation of nanosilica. Silica was extracted from sodium silicate solution using a soda caustic. Subsequently, carbon dioxide was allowed to pass through the reaction system containing silicate solution at a certain flow rate. Magnetically stirring was continuosly applied to the solution during the process. Filtration of the solution by washing with water was then conducted until a neutral pH to remove soluble salt. Finally, precipitation left on the surface of filter paper was collected as nanosilica and then dried in oven at 70 °C for 48 h. According to X-ray diffraction analysis, particle size of silica is about 70-80 nm.

Preparation of silica nanoparticle – unsaturated polyester (UPR) composites. The preparation of nanosilica – UPR composite was carried out by mixing nanosilica as filler with UPR as a matrix in addition of MEKPO. The reaction was performed by mixer at room temperature for 30 min. The weight

ratio of nanosilica and UPR varied at 0.5, 1.0, 1.5, 2.0 and 2.5 wt%. In the preliminary study, low content of nanosilica in the composite was considered as the best appearance of composite. Composite film was then produced by casting of the solution and dried at room temperature.

Characterization of silica nanoparticle – unsaturated polyester (UPR) composites. Mechanical properties of composite were performed by Strograph VGS5E according to ASTM D-638 at room temperature and crosshead speed of 50 mm/min. Prior to tensile test, dumbbell-shaped specimens were cut for each film according to ASTM D638, type V in dimension of $4 \times 4.75 \times 3$ mm^3. Fracture surface of sample was put on the surface of a sample holder and then coated with gold for electron microscopy measurement. Morphological surface of cross-sectional fracture of composite was analyzed by scanning electron microscope (SEM), JEOL JSM 6510 LA, operated at accelerating voltage of 25 kV. Further characterization, i.e. thermal behavior of composite was carried out by using differential scanning calorimeter (DSC), DSC 910. This analysis was performed by heating of $5.0 – 5.7$ mg of sample from 50 to 300 °C with scanning rate of 20 °C/min in nitrogen gas atmosphere. Differences in functional group between the composites and UPR as a control were analyzed by Fourier transform infra red (FTIR) spectrometer, A JASCO spectrometer.

4. Results and Discussion

The influence of silica nanoparticle in the formation of silica-UPR composite was evaluated based on the analysis of mechanical, thermal and morphological properties of composites. Figure 1 shows the tensile strength and elongation properties of composite compared with UPR as a control. It is shown that the initial value of UPR, the tensile strength is 54 MPa and the elongation is 2.7%. Addition of silica concentration up to 1.0 wt% causes the tensile strength and elongation increased up to 64 MPa and 4.2%, respectively, compared with UPR itself. Further addition of silica concentration over 1.0 wt% causes the tensile strength and elongation returned to the initial value of UPR, 42 MPa and 2.4%, respectively at 2.5 wt% of silica concentration.
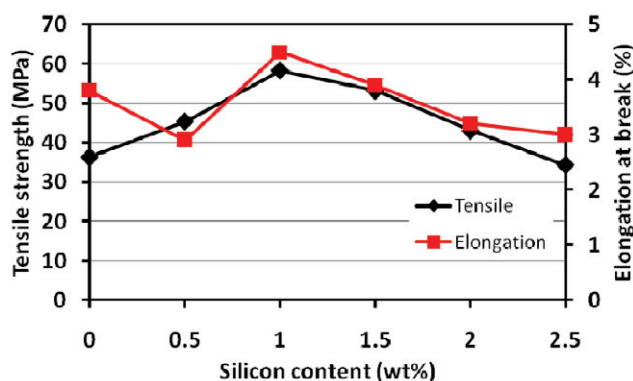

Fig. 1.   Tensile strength and elongation of composite in the variation of silica concentrations

Increasing of mechanical properties of composite on the concentration range of 0.5 and 1.0 wt% was due to easy of homogeneously dispersed silica in the polymer matrix. Increase in mechanical properties of composite compared with the UPR itself indicate the presence of good reinforcement of silica to form composite network [17]. Otherwise, decreasing of mechanical properties with further addition of silica (over 1.0 wt%) most likely caused by the aggregation of silica. Aggregation of silica is stricly associated

to the inhomogeneous distribution of silica in matrix and reduced the interaction between silica as filler and UPR as matrix. Another possibility is due to high viscosity of mixture at high concentration of silica which caused improper mixing process. However, lower tensile strength at 0.5 wt% silica compared with intial value constitutes abnormal condition, presumably due to inadequate mechanically mixing to create a homogeneous dispersion of silica.

Slightly different tendency was indicated in Young's modulus of composite, shown in Figure 2. Fistly, greatly increase of Young's modulus (1590 Mpa) was evidently observed on the small amount of silica, 0.5 wt%. The concentrations above 0.5 wt%, Young's modulus change in the fluctuations and finally decrease to 1180 MPa at 2.5 wt%, slightly higher than UPR itself. Young's modulus reduction at concentrations above 0.5 wt% might be caused by exfoliation of silica nanoparticle from the matrix which resulted in porous surface. However, these overall results explain that the addition of silica to polymer matrix enhances mechanical properties of composites.
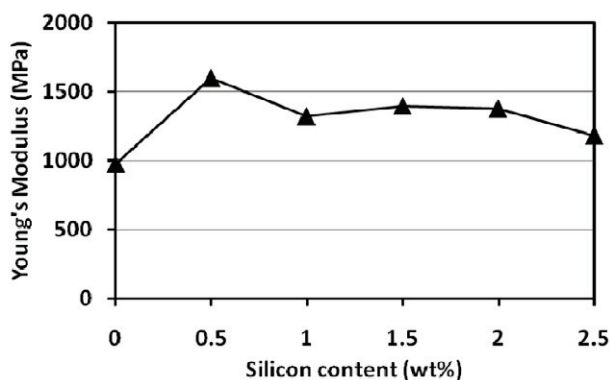

Fig. 2. Young's modulus of composite in the variation of silica concentration

The tendency result of mechanical properties is well explained from the SEM images. Fracture of mechanical properties measurement was used as object of SEM observation to further ensure the close relationship between morphological structure and its mechanical properties (Figure 3). Smooth surface was clearly observed on fracture of UPR. The facets on fracture surface of sample seem glassy. It indicates that the material is highly brittle. In the case of 0.5 wt% of silica dispersed in the polymeric system gives a description of surface to be rough with fine facets. This indicates the formation of strong bonding between silica and polyester resin. Increasing of silica, fracture becomes more rough. In the images, good dispersion of silica nanoparticle was observed untill 1.0 wt% of silica whereas high strength of nanocomposite system was formed at 1.0 wt%. Above 1.0 wt%, weak interaction of phase occurred as a result of particle aggregation, shown by the existence of larger particles, shown as the white particle. Weak interaction between silica particles and the polymer phase causes some voids on the matrix surface. This condition significantly reduced the mechanical properties of composite, particularly at 2.5 wt% due to less continue polyester phase. Good dispersion in low concentration of silica in the UPR matrix plays an essential role to provide well-formed interpenetrating network (IPN) structures. In addition to the aggregation of silica, concentrations above 1wt% also shows immiscible composite due to the existence of phase separation between silica nanoparticle and UPR matrix. Therefore, mechanical process is very important tool to form miscible composite, especially related to nanoparticle. However, this study explain that the whole morphological structure importantly contributes in strength of composite network.
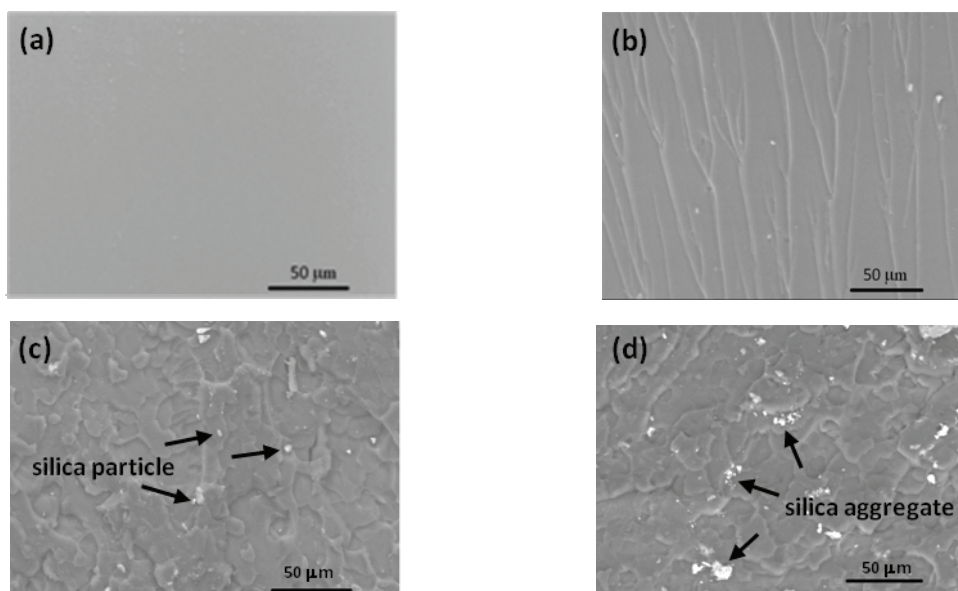
Fig. 2. Morphological fracture of UPR and composite in the variation of silica concentrations (a) UPR; (b) 0.5 wt%; (c) 1.0 wt%;
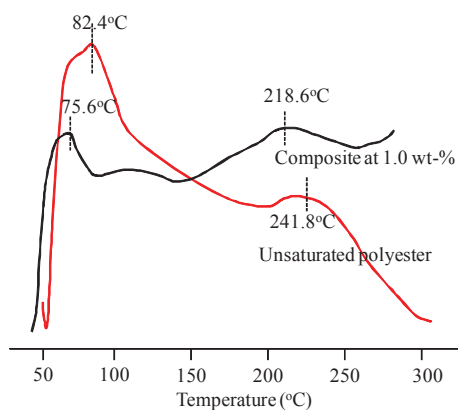(d) 1.5 wt% (black arrows : silica particles)

Fig. 4. Thermal properties of UPR and nanocomposite at 1.0 wt% of silica concentration

Thermal behavior of polymer composites is one of the most important factors for polymer processing and applications. Figure 4 shows profiles of thermal behavior of UPR and composite at 1.0 wt% of silica as representative of composite due to almost similar profile of them. Description of thermal behaviors including glass transition, melting point and enthalpy of composite are given in detail in Table 1. Basically, addition of silica nanoparticle to the UPR matrix reduce melting point and glass transition of composite. Firstly, addition of 0.5 wt% of crystalline nanosilica into amorphous polymeric network greatly reduced glass transition and melting point of composite. In the concentration range (0.5-1.5 wt%), these temperatures change in the fluctuation with a tolerance of 0.2-2.4% (glass transition) and 4.4-10.9% (melting point) of the initial value. Reducing of these temperatures provide an easier relaxation of molecular chain in the less continue polimeric phase which related to length of molecular chain and

molecular weight of composite. As given in Table 1, silica concentration of 0.5 wt% causes great increasing of enthalpy (48.63 J/g). On the heating, reaction in the composite structure occur and release higher energy than that's of another composites. This reveals the presence of well-formed interpenetrating network (IPN) structures and cross-linking interaction between silica and UPR in the composite matrix. Otherwise, the presence of weak interaction is indicated by decreasing of enthalpy to 40.58 J/g and 30.28 J/g at 1.0 and 1.5 wt% of silica, respectively. Based on the thermal analysis, silica nanoparticle distribution in the polymer network is believed to be an essential factor to thermal characteristic of the resulting composite.

Table 1. Glass transition, melting point and enthalpy of UPR and composites in variation of silica concentration

Materials	T_g (°C)	T_m (°C)	ΔH (J/g)
UPR	82.43	241.28	37.15
UPR/silica 0.5 wt%	75.95	214.16	48.63
UPR/silica 1.0 wt%	75.76	218.58	40.58
UPR/silica 1.5 wt%	77.76	229.48	30.28

Figure 5 shows the FTIR spectra of UPR and UPR-silica 1 wt%. Structural changes due to silica particle was identified by comparing the functional groups of UPR and composites. We selected FTIR spectrum of composite at 1.0 wt% as representating for all composites. The FTIR of UPR shows vibration band at wave number of 2931.27 cm^{-1} as aliphatic hydrocarbon (CH stretching), aromatic ring at wave number of 1596 cm^{-1}, unsaturated bonding (C=C) at 1070 cm^{-1} as deformation peak and carbonyl group (C=O) at 1735.62 cm^{-1}. Meanwhile the FTIR of composites shows additional peak at 1268-1132 cm^{-1} assigned as vibration of asymmetric stretching of Si-O-Si bonds. Si-OH groups also exist at 966 cm^{-1}. The broad strong bands around 3457 cm^{-1} are assigned to the O-H stretching vibration of silanol hydroxyls, while the absorption at 1630 cm^{-1} is assigned to the O-H bending. This proves that the existency of silica particle in the UPR matrix structural change of composite.
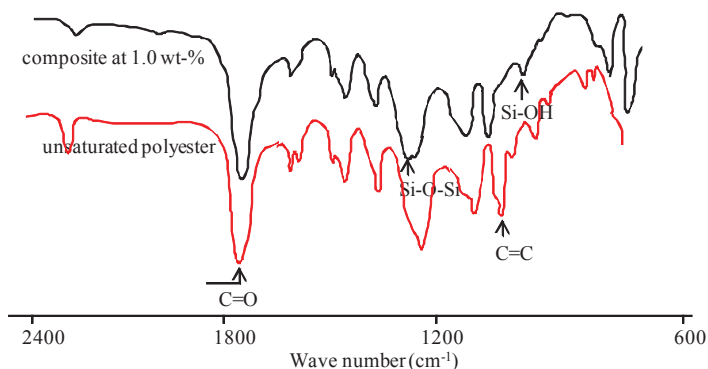

Fig. 5 . FTIR Spectra of UPR and silica-UPR nanocomposite

5. Conclusion

At silica concentration of 1.0 wt% expressed as the highest concentration that be able to achieve good dispersion in UPR matrix. Good dispersion of silica strongly creates mechanical properties of composite to be higher. Low mechanical properties might be due to aggregation of silica particle. Close relationship between mehanical properties and morphological structure of composite reveals that mechanical process importantly affects performance of composite. Crosslinkage and well-formed interpenetrating network are possible to be formed in the low concentration of silica. At low concentration of silica nanoparticle is the easiest condition to make good dispersion of nanoparticle in the matrix region. Therefore, dispersion of silica nanoparticle in UPR matrix is very important factor to determine the whole characteristic of the resulting composite.

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