Thermal properties and corrosion resistance of organoclay/epoxy resin film

M Baiquni\(^1\) and B Soegijono\(^2\)

\(^1\)Graduate Materials Science Program, Dept. of Physics University of Indonesia
\(^2\)Dept. of Physics University of Indonesia

E-mail: naufal@ui.ac.id

Abstract. Hybrid materials organoclay/epoxy resin films were prepared by varying organoclay content in epoxy resin as a matrix. The film were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and thermal conductivity. TGA and FT-IR results confirmed that the melting temperature shifted to a lower point. The thermal conductivity and corrosion resistant generally increase with increasing organoclay content. The changes on these properties may due to cross link between organoclay and epoxy.

1. Introduction

Because of the properties of epoxy resin such as chemical stability, good adhesion, and excellent mechanical properties, epoxy resin have been often used as coating, adhesives, laminates, casting material [1-6], and as matrix for composite materials [7-8]. However, researcher are still searching for enhancing the properties of epoxy resin for many applications such as heat resistance, moisture resistance, material for printed board, liquid crystal displays, and plasma display panel.

By incorporating inorganic materials such as organoclay in epoxy resin, rubber or other matrix, the properties of the composite improved [9-11]. However, the role of organoclay in the enhancement of the properties is not well explained yet. The processing of the composite determined its properties, such as the dispersion of clay in epoxy resin matrix. In most cases, many researcher show that well-dispersed and exfoliated clay could enhance the properties of the polymer matrix [12-15].

Composite with more than one compound of filler are interesting, such as organoclay and rock-wool with epoxy resin as a matrix. In this paper, composite epoxy resin and different content of organoclay as a filler have been studied to understand the role of organoclay on thermal stability and corrosion resistance.

2. Experimental procedure

A commercially available two-part epoxy thermoset were used. Epoxy resin is based on a diglycidyl ether of bisphenol A/epichlorohydrin (DGEBA), while Harderner (EPH 555) is a cycloaliphatic amine. MMT organoclay functionalized with an octadecyl ammonium salt was purchased from Nanocor. Epoxy was mixed with various content of organoclay of 1, 3, and 5 phr (parts per hundred resin) and stirred at 300
rpm for 24 h at 27 °C in an Erlenmeyer flask. Hardener EPH555 was added to the mixture and it was highly degassed in a vacuum until the bubble come out from the solution. The samples were molded and cured at room temperature for 24 h.

Thermal stability of the samples was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry which was conducted from 30 to 800 °C in nitrogen atmosphere. The heating rate and nitrogen flow rate were 10 °C/min and 0.1 ml/min, respectively. The composite were subjected to salt spray test according to ASTM B-117 for 72 h to obtain information of its corrosion resistance. Corrosion resistance was obtained by observing morphology of the samples using electron microscope instead of mass difference method.

3. Results and discussion

3.1. TGA Analysis

Thermal stability information of the samples can be obtained from TGA pattern. Figure 1 shows TGA curve of organoclay/epoxy resin composite with different content of organoclay at temperature 35 to 800 °C. The onset decomposition temperature of epoxy resin is different with various content of clay. This indicates that thermal stability is shifting. There are at least three stages of decomposition as shown in figure 1.

![Figure 1. TGA pattern of organoclay/epoxy resin with different content of clay.](image)

![Figure 2. DSC pattern of organoclay/epoxy resin with different content of clay.](image)

The onset and end set temperature of the four samples for three stages decomposition are each different. It can be concluded that the addition of organoclay influenced the thermal properties. Sample with 1 phr clay, below 325 °C, show the smallest weight loss, but above 325 °C the TGA curve shows gradual weight loss of all composites. It is also noted from the TGA that increase in weight percentage of nano-clay in epoxy resin shows reduction in weight loss of material at high temperature [16]. The sample with 1 phr clay showed optimum thermal stability.
3.2. DSC analysis
Figure 2 shows DSC curve of clay/epoxy composite with different clay content. Generally exothermic peaks involving weight loss, no weight change, and weight gain are known to be a result from combustion, crystallization, and oxidation, respectively. The same goes with endothermic peaks involving weight loss indicate decomposition or dehydration [16]. In the present study, the DSC curve indicate and exothermic peak around 250 °C and endothermic peaks around 300 °C and 600 °C, accompanied by weight loss of material. This indicates that decomposition of material occurs at temperature above 300 °C. The latest is probably due to clay content (5 phr). Addition of 1 phr clay showed the least heat needed for decomposition during heating process from room temperature to 800 °C. The optimum thermal stability of the samples is the composite with 1 phr clay content. Increasing amount of organoclay in the samples (3 and 5 phr) did not show good thermal stability probably due to agglomeration of organoclay, or poor dispersion in the samples.

3.3. FTIR analysis
Figure 3 describes FTIR curve of organoclay/epoxy resin with different content of clay. From the curve, it seems that the influence of clay addition on the absorption behavior is not quite clear.

Table 1 shows detailed wave number absorption of the samples. The wave number 3389.93 coming from the clay is affected and slightly shifting to higher wave number 3361.17 when mixed with epoxy resin. However, wave number 447.05 is shifting to the right (464.96) and then back to the left (459.39). Wave number 1383.16 appears only in the sample with addition of 1 phr clay. Addition of organoclay to the epoxy resin slightly affects infrared absorption. The shift of wave number might indicate a tighter structure and stronger bonds compared to neat epoxy. A shift toward high wave numbers also indicates decreased cross-linking for any nanoclay contents [17]. Figure 3 has clearly shown the optimum absorption of the sample, e.g. with 1 phr clay.
Table 1. The absorption wave number of organoclay/epoxy resin with different content of clay.

| clay      | epoxy neat | epoxy clay 1 phr | epoxy clay 3 phr | epoxy clay 5 phr | Notes                                      |
|-----------|------------|------------------|------------------|------------------|-------------------------------------------|
| neat      | 3389.93    | 3351.35          | 3358.25          | 3354.53          | Amides bond, alcohol bond                 |
|           | 2923.42    | 2922.87          | 2923.05          | 2923.04          | sp3 C-H                                   |
| 1630.78   | 1606.79    | 1606.86          | 1606.76          | 1606.85          | alkenes bond                              |
|           | 1581.73    | 1581.73          | 1581.73          | 1581.73          | amides N-H bond                           |
|           | 1508.16    | 1508.04          | 1508.13          | 1508.10          | nitro compound                            |
|           | 1456.63    | 1456.20          | 1456.70          | 1456.58          | alkane (methylen group)                   |
|           | 1383.16    |                  |                  |                  | Aldehyde bond                             |
|           | 1361.79    | 1361.74          | 1361.51          | 1364.51          | sulfoamide bond (S=O)                     |
|           | 1294.96    | 1295.01          | 1294.90          | 1294.81          | Alcyl bond (C-O)                          |
|           | 1235.01    | 1235.10          | 1235.30          | 1235.01          | Amine bond                                |
|           | 1181.22    | 1181.22          | 1181.25          | 1181.22          | tertiary alcohol bond                     |
|           | 1105.88    | 1105.89          |                  |                  | secondary alcohol bond                    |
|           | 1034.26    | 1033.31          | 1033.65          | 1032.22          | alken bond (monosubstituted)              |
| 988.18    | 826.79     | 826.73           | 826.87           | 828.69           | alken bond (trisubstituted)               |
|           | 735.10     | 734.84           | 734.53           | 734.53           | alken bond (Cis)                          |
|           | 697.42     | 697.39           | 697.37           | 697.46           | alken bond (cis)                          |
| 673.16    | 647.97     |                  |                  |                  |                                            |
|           | 556.76     | 558.79           | 558.51           | 555.71           |                                            |
|           | 447.05     | 458.99           | 464.96           | 459.39           |                                            |
|           | 419.60     | 419.06           |                  |                  |                                            |
| 402.96    |            |                  |                  |                  |                                            |

3.4. Thermal conductivity

Table 2 shows thermal conductivity of organoclay-resin composite. The measurement was taken 8 times for each sample. From table 2, thermal conductivity of the samples increases with increasing organoclay content. This increase is due to addition of clay as a filler, and the fact that they have higher thermal conductivity than epoxy.
Table 2. Thermal conductivity of organoclay-resin composite (watt/m K).

| No | Epoxy neat | Epoxy+Clay 1 phr | Epoxy+Clay 3 phr | Epoxy+Clay 5 phr |
|----|-------------|------------------|------------------|------------------|
| 1  | 0.2553      | 0.2619           | 0.2553           | 0.2627           |
| 2  | 0.2516      | 0.2767           | 0.2677           | 0.3411           |
| 3  | 0.2519      | 0.2667           | 0.2745           | 0.3341           |
| 4  | 0.2369      | 0.2642           | 0.2540           | 0.2241           |
| 5  | 0.2452      | 0.2627           | 0.2681           | 0.3103           |
| 6  | 0.2310      | 0.2439           | 0.2407           | 0.2788           |
| 7  | 0.2301      | 0.2552           | 0.2445           | 0.2626           |
| 8  | 0.2134      | 0.2238           | 0.2526           | 0.2706           |
| AVG| 0.2394      | 0.2569           | 0.2572           | 0.2855           |

The increase in average thermal conductivity may be due to cross link and also thermal conductivity of organoclay which is higher than epoxy.

3.5. Corrosion test

Corrosion resistance test of the samples were conducted by salt spray method for 72 hours. Figure 4 show the surface morphology after corrosion test with 0, 1, and 3 phr clay addition.

![Figure 4. Surface morphology of organoclay/epoxy resin with (a) 0, (b) 1 and (c) 3 phr clay after salt spray test for 72 hours (magnification 1000x)](image)

Different surface morphology provides evidence that addition of clay influences how epoxy resin changes its corrosion resistance. All of these may due to interaction between clay and epoxy as matrix. From figure 4, it is clearly shown that the addition of 1 phr organoclay has shown the best corrosion resistance.

4. Conclusion

Composite organoclay/epoxy resins with different content of clay have been well prepared. Thermal stability of the samples with 1 phr clay content shows the best performance. Increasing organoclay content in the composite organoclay/epoxy resin also increases the thermal conductivity. Corrosion resistance of composite change with addition of organoclay 1 phr shows the best result. Overall, the influence of
organoclay on the properties of clay/epoxy resin composite are clearly seen with 1 phr organoclay. These may due to crosslink of clay and epoxy as a matrix.

Acknowledgment

This research is supported financially by “Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa University of Indonesia” through letter of decree no.630/UN2.R3.1/HKP.05.00/2017.

References

[1] Fan Q C, Wu C Z and Zhang L J 2008 Technol. Res. Dev. 23 17
[2] Teh P L, Jaafar M and Akil H M 2008 Polym. Adv. Technol. 19 308
[3] Koerner H, Hampton E, Dean D, Turgut Z, Drummy L, Mirau P and Vaia R A 2005 Chem. Mater. 17 1990
[4] Wang D, Jiang M T, Zheng D M, Cheng B and Huang Z 2006 Journal of Materials Engineering 1 417
[5] Zhang L and Wei Y B 2005 Journal of Chemical Engineering of Chinese Universities 19 720
[6] Zhang D T 2002 Thermoset. Resin 17 44
[7] Chen G X, Kim H S, Shim J H and Yoon J S 2005 Macromolecules. 38 3738
[8] Tamura K, Yokoyama S, Pascua C S and Yamada H 2008 Chem. Mater. 20 2242
[9] Fathurrohman M I, Soegijono B and Budianto E 2015 Macromol. Symp. 353 62
[10] Hussain M, Varley R J, Mathys Z 2004 J. Appl. Polym. Sci. 91 1233
[11] Zang Y, Xu W, Liu G, Qiu D and Su S 2009 J. Appl. Polym. Sci. 111 813
[12] Lee J Y, Shim M J and Kim S W 1997 Mater. Chem. Phys. 48 36
[13] Miyagawa H, Rich M J and Drzal L T 2004 J. Polym. Sci. B 42 4384
[14] Zheng Y, Chonung K, Wang G, Wei P and Jiang P 2009 J. Appl. Polym. Sci. 111 917
[15] Stone G C and Boulter E A 2004 Electrical Insulation for Rotating Machines Design, Evaluation, Aging, Testing, and Repair Chapter 1 (Canada: IEEE Press) pp 173–214
[16] Sarathi R, Sahu RK and Rajeshkumar P 2007 Mater. Sci. Eng. A 445–446 567
[17] Nyczyk A, Paluszkiewicz C, Hasik M, Cypryk M and Pospiech P 2012 Vib. Spectrosc. 59 1