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Effect of extraction mediums: water vs toluene in porous epoxy

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ABSTRACT

Porous epoxy was fabricated using latex as the voids template through extraction method. The porous epoxy was prepared using mechanical mixing method. In this study, mixing was followed the sequences of epoxy, latex then hardener (ELH). Latex composition was varied at 0.5, 1.0, 1.5 and 2.0 phr, respectively. The system exhibited phase separated with latex particles dispersed in epoxy matrix. Two different types of extraction mediums were used which were toluene and water for latex extraction. Density, porosity, mechanical, dielectric and morphology were done for both soaking medium samples. Toluene revealed the lower value in dielectric constant which prefer for electronic packaging application. However, flexural strength and modulus of this porous epoxy were reduced. This was attributed to more porous structure in epoxy and was proven that toluene is more effective to be the extraction medium as compared to water. From morphology result, more porous structures were observed by using toluene as an extraction medium.

INTRODUCTION

Epoxy resin has been widely used in electronic packaging industries due to their ease of processing and low cost. Besides, they also exhibited excellent heat, moisture, and chemical resistance[1 - 2]. Low dielectric constant materials are the subjected of intense investigation and development in order to replace conventional SiO_2 dielectrics for the manufacturing of future generation microelectronic devices[3]. The primary method of lowering the dielectric constant is to make the dielectric film less dense by introducing porosity[4]. There are two fundamental routes to porosity in polymers: blowing due to sudden gas expansion (as with polymer foams) or removal of one or more disperse phases[5]. This paper utilizes the latter, which encompassed the technique to form porous epoxy based on template method by a mixture with epoxide, amine, and latex to produce disperse phase in an epoxy matrix, then removed the dispersed by extraction using two different extraction mediums. The advantages of the present technique over other methods are severalfold. First, the chemistry is limited to only three or four inexpensive chemicals, all of which are relatively stable to water and oxygen, relatively nontoxic, and very forgiving to alterations of the preparation method[6]. Second, the porous structure produced by the present template method can be easily adjusted by controlling the viscosity of latex to produce smaller pores. Third, the epoxy and amine used in this study are available in a wide range of molecular weights, can be easily exchanged to induce significant changes in the mechanical and electrical properties of the final epoxy[7]. The latex used in this study was not gone through crossking process, therefore it can be removed using water and then compared to the conventional solvent which is tolu-

TABLE 1 : Composition of ingredients

Epoxy (phr)	**100**	**100**	**100**	**100**	**100**
Hardener (phr)	60	60	60	60	60
Latex (phr)	0	0.5	1.0	1.5	2.0

ene. Ultimately, the purpose of this paper is to highlight a simple method to introduce porosity in epoxy system in order to lower the dielectric constant.

EXPERIMENTAL

Materials

Epoxy resin DER 331 (supplied by Euro Chemo-Pharma Sdn. Bhd.) was used as matrix in this study with density of $1.16gcm^{-3}$. The resin was mixed with latex (supplied by Getah Hindus Sdn Bhd) to form immiscible system of epoxy-latex that having latex particles dispersed in epoxy matrix. The hardener used was hardener A062 which was supplied by Hasrat Bestari Sdn. Bhd. with density of 0.96 g/cm^3.

Sample preparation

The epoxy resin and hardener were added according to 100 phr and 60 phr, respectively. The latex content was evaluated from 0.5 to 2phr, respectively. The mixing was followed by the sequence of: epoxy, latex then hardener (ELH). Epoxy resin was stirred using mechanical stirrer and then latex was added using dropper then the hardener was added in the mixture of epoxy and latex until homogenous. The mixture was poured in container and placed in oven for curing at 100°C for 1 hour. The cured epoxy was extracted using different extraction mediums. Then samples were extracted using toluene and water to remove latex from epoxy, respectively. Porous epoxy was then obtained after latex was fully extracted.

Testing and characterization

Three-point bend test was performed using an Instron (ID Number 5569P7531) universal testing machine (UTM). Samples were tested with a crosshead speed of 0.5 mm/min. The test was carried out in accordance with ASTM D790. The specimens used for flexural testing were bars of rectangular shape with measurement of 60 mm x 13 mm x 3 mm.

The flexural modulus and strength were calculated using Eq. 1 and 2. The results were taken as the average value of 5 samples.

Calculation of the flexural stress σ_f

$$\sigma f = \frac{3PL}{2bd^2} \quad (1)$$

Calculation of flexural modulus E_f

$$Ef = \frac{L^3m}{4bd^3} \quad (2)$$

Where:

σ_f = Stress in outer fibers at midpoint (MPa)

E_f = Flexural modulus of elasticity, (MPa)

P = Load at a given point on the load deflection curve, (N)

L = Support span, (mm)

b = Width of test beam, (mm)

d = Depth of tested beam, (mm)

m = The gradient of the initial straight-line portion of the load

Dielectric constant is the property of a dielectric which determines the electrostatic energy stored per unit volume for unit potential. The ratio of the capacity of a condenser having a dielectric material between the plates to that of the same condenser when the dielectric was replaced by a vacuum. This can be calculated using Eq. 3:

$$\text{Dielectric constant} = \frac{\text{Capacitance, material as dielectric}}{\text{Capacitance, air or vacuum as dielectric}} \quad (3)$$

SEM was used to analyze the morphology of the selected samples. Samples were characterized using JEOL JSM-6460 LA. The cross section of the fractured surface of the porous epoxy after fractural testing was studied using SEM. The density of the porous sample was tested using ACCUPYC II 1340 Gas Displacement Pycnometer according ASTM D6226. Then the porosity was determined by the Eq. 4:

$$\textbf{Porosity \%} = \left(1 - \frac{density\ porous}{density\ bulk}\right) X\ 100\% \quad (4)$$

$$= (1 - \rho_0 / \rho_1) \times 100\%$$

Where: ρ_0 and ρ_1 are the densities of the dense polymer and the porous epoxy, respectively.

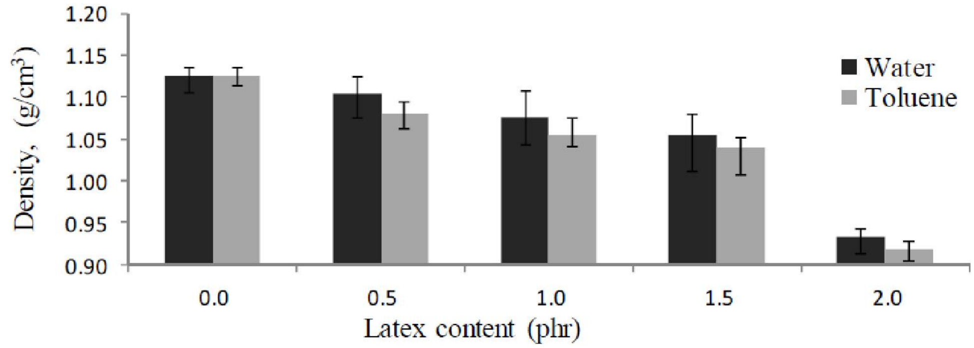

Figure 1 : The density properties of porous epoxy with different latex contents extracted using water and toluene, respectively

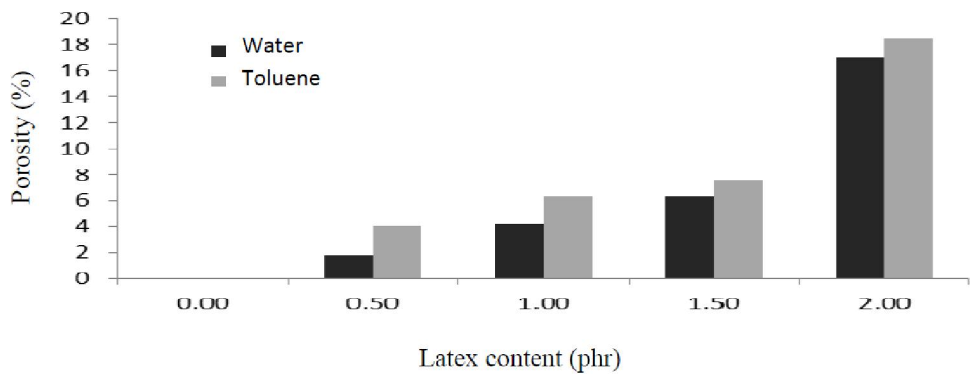

Figure 2 : The porosity properties of porous epoxy extracted with different latex contents using water and toluene

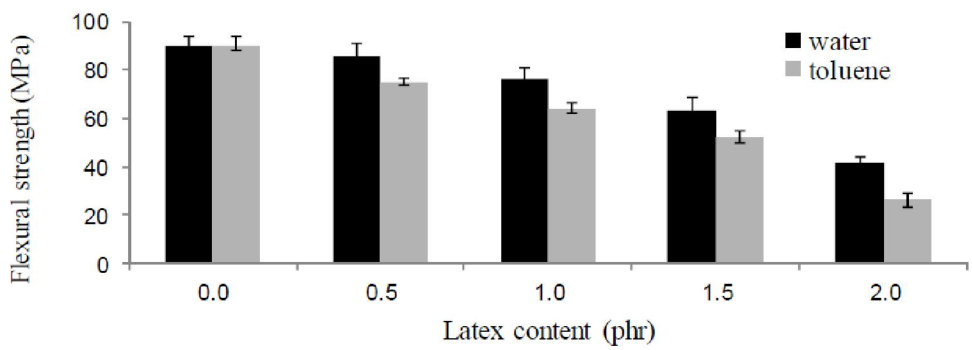

Figure 3 : Flexural strength of porous epoxy with different latex contents extracted using water and toluene, respectively

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of latex content on the density of the porous epoxy using water and toluene as the extraction medium. The density of the porous epoxy decreased when the amount of latex content was increased for both extraction mediums. As referring to Figure 2 higher porosity % was observed in porous epoxy when toluene was used as extraction medium. It can be seen that, the higher amount of voids, causing the lower of density. Tagliavia et al.[8] have reported the same observation, the reduction of density in composites was attributed to the entrapment of air in the matrix material during the process of mechanical mixing of microballoons in the resin.

Figure 2 shows the porosity % data for porous epoxy extracted using water and toluene as extraction medium, respectively. The porous epoxy sample extracted using toluene exhibited higher porosity % as compared to sample extracted using water as medium. It is proven that toluene is more effective as the extraction medium as compared to water.

Figure 3 shows the flexural strength with different water and toluene as extraction mediums. The

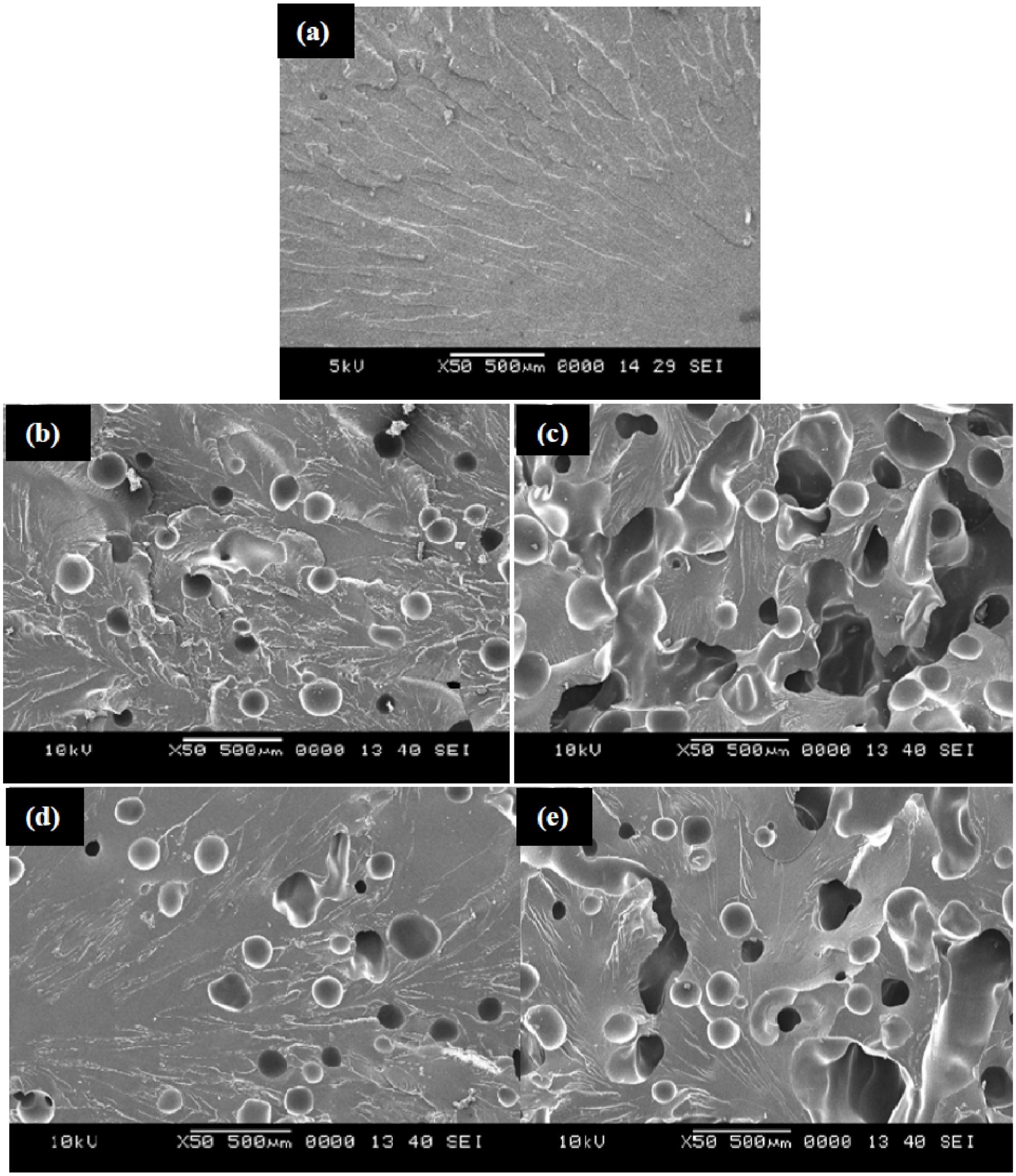

Figure 4 : SEM micrograph showing the flexural surface morphology porous epoxy with (a) 0 phr (b) 1.0 phr and (c) 2.0 phr of latex content using toluene as extraction medium and (d) 1.0 phr and (e) 2.0 phr of latex content using water as extraction medium, respectively

latex content were varied from 0 to 2 phr, above 2 part of latex content has led to latex particle agglomeration in the epoxy resin. As shown in Figure 3, the flexural strength decreased with increasing of latex content. The flexural strength of the porous epoxy is generally lower than the flexural strength of the neat resin. This results show that latex was successfully removed using water and toluene leading to a porous structure. Higher latex content produced more voids inside the samples when latex was extracted out from the sample. The flexural strength of porous epoxy extracted using water as extraction medium exhibited higher flexural strength as compared to toluene at the same latex content.

SEM micrographs in Figure 3(b) and (c) show that there is an increased of porous structure in samples using toluene which led to decrease in flexural properties. The porous structures formed when the latex particles were extracted from the sample after extracting in toluene for 6 hours. Tagliavia et al. studied about the analysis of flexural properties of hollow-particle filled composites. They found that the strength decreases as the inclusion volume fraction increases, which implies that the composite strength decreases as the resin volume content decreases. These findings suggest that interface debonding followed by matrix cracking is the primary mechanism of synthesis foam failure[9]. R. Thomas et al.[10] studied about epoxy resin toughened with a liquid rubber. In their study, they found that the addition of rubber particle in epoxy resin can occupy positions in between the reaction centers thereby separated the cross-linking points. Thus the addition of liquid rubber reduced the cross-linking

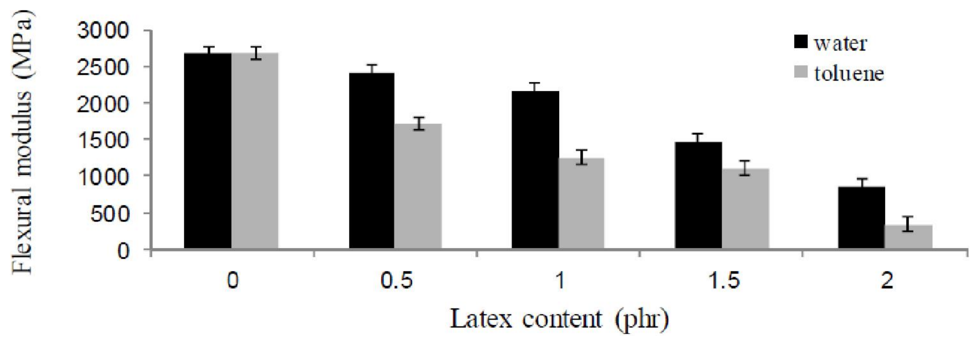

Figure 5 : Flexural modulus of porous epoxy with different latex contents extracted using water and toluene, respectively

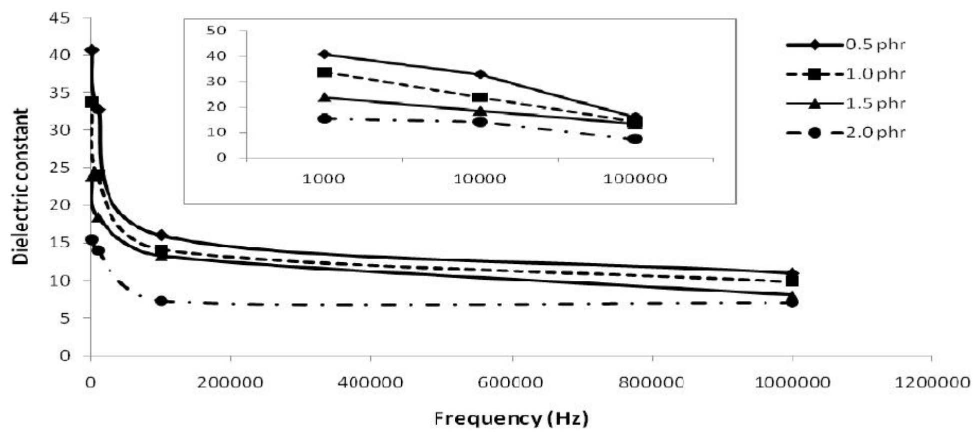

Figure 6 : The dielectric constant value of porous epoxy with different latex contents extracted using water

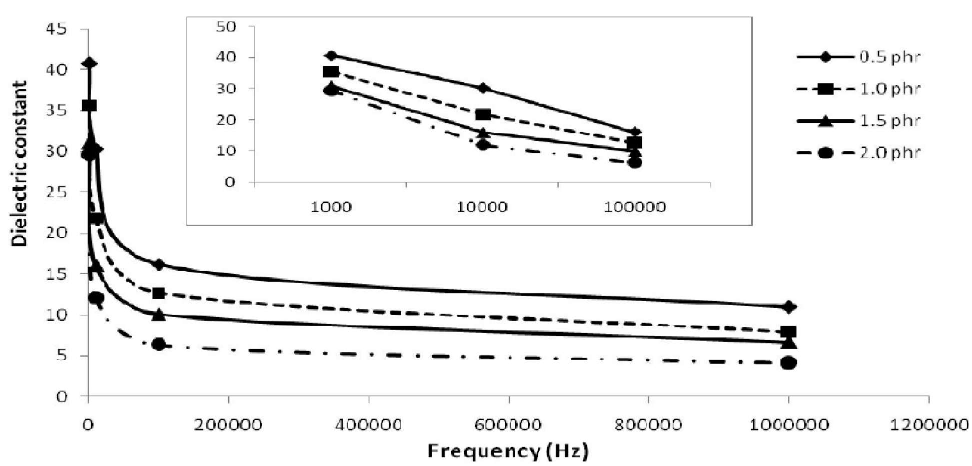

Figure 7 : The dielectric constant value of porous epoxy with different latex contents using toluene.

density, hence reduced the flexural strength.

SEM micrograph of neat epoxy in Figure 4(a) shows the smooth and flat surface. This indicating that neat epoxy exhibited brittle behavior under flexural load and weak resistance to crack propagation. Figure 4(b) and (c) show the SEM micrograph of the fracture surface of porous epoxy with 1.0 and 2.0 phr of latex content using toluene as the extraction medium. It can be observed that the porous structure created are more than porous epoxy using water as extraction medium at the same latex content, as shown in Figure 4(d) and (e).

In mechanics, the flexural modulus is the ratio of stress to strain in flexural deformation, or the tendency for a material to bend[11]. It is an intensive property. As shown in Figure 5, porous epoxy extracted using toluene exhibited lower modulus than using water at the same latex content. The flexural modulus is inversely proportional to the latex content. Modulus decreased as the latex content increased from 0 to 2 phr. The decreased flexural modulus is associated with the porosity content in the porous epoxy. Higher porosity content causing the porous epoxy become less stiff. It is clear that the flexural strength and modulus decreased with increasing porosity, which is explained by the fact that the porous structure led to the decrease of carrying capacity of materials hence weakening the interface strength and decreased the mechanical properties of the composites[12].

Low dielectric constant materials are believed to be necessary to allow signal to be transferred without delay in integrated circuits[13]. Figure 6 and 7 show dielectric constant values with different latex content as a function of frequency from 1 kHz to 1MHz using water and toluene as extraction medium, respectively. As shown in both figures, dielectric constant decreased when the frequency was increased at the same latex content. This can be explained by the fact that an increase in frequency induced weakening or disappearing of ionic polarization, and consequently decreases the dielectric constant values[14]. Porous epoxy using toluene as extraction medium exhibited lower dielectric constant value as compared to water. It can be seen that there is a strong correlation between the increase in porosity and the decrease in the dielectric constant. As the conclusion, the main microstructural parameter affecting the dielectric constant is the porosity of the samples[15]. The porosity content caused the porous epoxy to have low dielectric constant. The dielectric constant is predicted to drop even lower when the latex content and frequency is higher. Low polymer volume fractions result in a low dielectric constant, presumably because of the residual porosity of the composites[16].

CONCLUSION

Porous epoxy thermosets were successfully prepared followed the sequence of epoxy: latex: hardener (ELH) system using toluene and water as extraction medium. From the results, toluene showed the higher porosity compared to water and it can be concluded that toluene is the better extraction on forming the porous epoxy. As a latex content increased from 0 to 2.0 phr, the microstructure of the epoxy systems changed from dense to porous. Both the flexural strength and modulus for porous epoxy decreased with increasing the latex content. This was due to the increase in porosity % in the porous epoxy and correlated well with morphological observations obtained by SEM. Lastly, dielectric constant value for porous epoxy was found to decrease with decreasing the density of material.

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