

# The effect of hydrogenation of epoxy resin on the dispersion of organo-clay in the epoxy resin matrix

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# Abstract

The hydrogenated diglycidylether of Bisphenol A epoxy resin (HDGEBA) was successfully employed to prepare nanocomposites with a more homogeneous distribution of clay, compared to that of bisphenol A epoxy resin (DGEBA)/clay system. Nanocomposites, with amounts up to 7.5 wt% of Organo-clay, were synthesized by means of "slurry-compounding" method and followed by a curing process with cis-1,2-Cyclohexanedicarboxylic anhydride and Glutaric Anhydride as the curing agent. A combination of X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the dispersion behavior of organo-clay in epoxy/clay nanocomposites. It was found that, in HDGEBA/clay nanocomposites, organo-clay was uniformly dispersed and even partly exfoliated, whereas, in DGEBA/clay system, large particle aggregates were seen when examined by TEM under lower magnification. Accordingly, the rheology and compatibility experiments were carried out to investigate the interactions within each system. It turned out that, after hydrogenation, HDGEBA was endowed with stronger interactions with organo-clay, thus resulting in the enhanced dispersion behavior, which may generate more chances to be mechanically reinforced by adding inorganic clays.

## 1. Introduction

Epoxy resins are one of the most commercially successful materials known especially as composite matrix but also as coating materials and adhesives[1]. Among them, resins based on the diglycidyl ether of bisphenol A (DGEBA) are particularly well studied and most widely used.

After decades of successful production, this kind of epoxy resins now confronts an intractable safety issue. Concerns have been growing that bisphenol A (BPA), which constitutes the backbone of DGEBA, may adversely affect humans[2]. BPA is an endocrine disruptor that has been shown to be harmful in laboratory animal studies. Due to its widespread human exposure and toxicity, Restrictions on the use of BPA in certain consumer products, ranging from manufacture, sale and distributions, have been suggested and implemented in many countries[3]. Accordingly, a series of researches looking for alternatives have been carried out since then.

Many candidates alternatives have been proposed and studied, among them, Bisphenol S (BPS) and bisphenol F (BPF) are endowed with high hopes. Nonetheless, recent study shows that neither of them are safe replacements of BPA[4]. The bisphenol series of A, S and F are reported to be unsafe for human health, all of which contains aromatic rings in their backbones. These results remind us of the fact that the toxicity may derive from the aromatic rings that constitutes the backbone of the polymer. Considering this situation, we seek to hydrogenation of the BPA to transform the aromatic rings to cyclohexyl groups, thus eliminating the origins of toxicity.

The absence of aromatic rings will surely weaken the mechanical properties of the epoxy resin themselves, but, on the other hand, the hydrogenated diglycidylether of Bisphenol A epoxy resin

(HDGEBA) turns out to be a good polymer matrix to well disperse stacked clays in, which will in return generate more chances to compensate the mechanical strength loss by adding inorganic clays.

The system of epoxy-clay nanocomposites has been intensively investigated and commercialized for their unique physical and chemical properties, such as high modulus, high thermal stability, decreased flammability, and barrier properties [5–10]. The final properties of nanocomposites rely on the quality of clay dispersion in the polymer matrix. A fully exfoliated structure is most desirable but the most difficult to get. An effective approach to improve the degree of clay exfoliation is to adjust polymer/clay interaction. In our previous work, the effect of polymer/clay interaction on the clay exfoliation, clay orientation and disorientation was well elucidated by the rheology experiments, which has attracted considerable interest recently [6, 11–16]

One frequently used strategy is to modify inorganic clay using organic additives in order to ameliorate the compatibility between polymer and clay [17]. The hydrogenated resin exhibits lower polarity than DGEBA for the presence of flexible cyclohexyl groups instead of rigid aromatic rings [18]. Due to the lower polarity of the hydrogenated resin, HDGEBA is expected to be more compatible with the organically modified clay. Il-Nyoung and co-workers found that nanomaterial reinforced HDGEBA/D230 adhesives were transparent [19]. María and co-workers reported that magnetite nanoparticles of about 10 nm in diameter modified with oleic acid exhibit a good dispersion in the matrix of HDGEBA [18].

In our study, we managed to adjust the polarity of the polymer to be more compatible with organo-clay by hydrogenating the unsaturated bonds of the aromatic rings in BPA. The hydrogenated diglycidylether of Bisphenol A epoxy resin (HDGEBA) was successfully made and then employed to prepare nanocomposites with a more homogeneous distribution of clay, compared to that of bisphenol A epoxy resin (DGEBA)/clay system. Nanocomposites, with amounts up to 7.5 wt% of Organo-clay, were synthesized by means of “slurry-compounding” method and followed by a curing process with cis-1,2-Cyclohexanedicarboxylic anhydride and Glutaric Anhydride as the curing agent. The enhanced dispersion of clay in HDGEBA was investigated with a series of experiments.

In this article, we focus our attention on the effect of hydrogenation of epoxy resin on the dispersion of organo-clay in the epoxy resin matrix. Organo-clay is found more easily to get exfoliated in the matrix of hydrogenated epoxy resin by a combined characterization of X-ray diffraction (XRD) and transmission electron microscopy (TEM). Furthermore, we find there is stronger interaction between HDGEBA and organo-clay rather than DGEBA and organo-clay with the help of compatibility and rheology experiment.

## 2. Experimental

### 2.1. Materials

The commercial hydrogenated diglycidylether of Bisphenol A epoxy resin (HDGEBA), was purchased from KUKDO CHEMICAL (KUNSHAN) CO., LTD. (China), with an EEW value of 220 ~ 240 g/Eq. The commercial bisphenol A epoxy resin (DGEBA), was purchased from Zhenjiang danbao resin co., Ltd. (China), with an

EEW value of 212 ~ 227 g/Eq. Organo-clay (C18-clay (commercial name DK1)), was purchased from Tianjin OrganicClay Corp. China, which contain octadecyltrimethylammonium chloride (C18A). Two types of acid anhydrides were used as the curing agent, one of them (cis-1,2-Cyclohexanedicarboxylic anhydride) came from Aladdin Industrial Corporation, and the other, (Glutaric Anhydride) came from Sinopharm Chemical Reagent Co., Ltd (China). The accelerator (Dodecyltrimethylammonium Chloride) was purchased from Shanghai Adamas Reagent Co., Ltd.

## **2.2. Preparation of epoxy/C18-claynanocomposites**

The nanocomposites of resin/clay were synthesized by the means of “slurry-compounding” according to the method reported by Miyuki and co-workers[21].

The dried C18-clay was added to dimethylacetamide (DMAC, Sinopharm Chemical Reagent Co., Ltd (China))to prepare the slurry-clay. The weight ratio of C18-clay and DMAC was kept constant at 1:3. The mixture was stirred at 70°C and 200 rpm for 3 h.

The mixture of the slurry-clay and epoxy resin was stirred at 70°C and 300 rpm for 10 h. The deionized water at 70°C was then added to the mixture to extract the DMAC, while the solvent has a relatively low boiling point of 166°C and can reduce the viscosity of the system. The mixture was then collected and degassed at 80°C with the pressure of 0.1 MPa for 6 h. After adding a stoichiometric amount of the curing agent and the accelerator, the mixture was degassed at 80°C with the pressure of 0.1 MPa for 1 ~ 2 h. The mixture was then cured at 80°C for 20 min, 100°C for 1 h, and 150°C for 4 hat room pressure. Nanocomposites were prepared with clay contents of 2.5 wt%, 5.0 wt%, 7.5 wt% and 10.0 wt%.

## **2.3. Characterization**

### **2.3.1. X-ray diffraction (XRD)**

X-ray diffraction (XRD) experiments were performed on both clay and cured samples to evaluate the degree of exfoliation. Diffraction patterns were obtained in reflection mode in a Bruker D8 Advance X-ray powder diffractometer with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation at a generator voltage of 40 KV and a current of 40 mA.

### **2.3.2. Transmission electron microscopy (TEM)**

The microstructure of clay in nanocomposites was observed on a JEM-2100 transmission electron microscope operating at an accelerating voltage of 200 KV. The ultrathin TEM samples with a thickness of about 70 nm were cut using a microtome at room temperature. The ultrathin slices were cut from the central core of the cured bars and collected on 230-mesh copper TEM grids without staining.

### **2.3.3. Rheology experiments**

Rheology experiments were conducted on a HAAKE Rheo- Stress 600 instrument. Steady shear measurement was conducted by using a set of 35 mm diameter parallel plates with a sample thickness

of ca. 0.8 mm. The viscosities of three liquid rubbers and their clay composites at 26 °C were measured with the shear rate of 0.05 s<sup>-1</sup> for 10 min. The viscosity value was the mean value of the first Newton region.

### 3. Results And Discussion

#### 3.1. Dispersion and morphology of C18-clay in epoxy/C18-claynanocomposite bars

The HDGEBA/C18-clay nanocomposite bars, and also the DGEBA/C18-clay nanocomposite bars, were prepared with the same method under the same conditions. The HDGEBA/C18-clay nanocomposite bars were more transparent, as shown in Fig. 1, compared to those of the DGEBA/C18-clay nanocomposite bars, indicating that C18-clay may disperse more uniformly in the matrix of HDGEBA.

The degree of clay dispersion is usually characterized by XRD. The XRD patterns of the C18-clay and the series of epoxy resin/clay composites are displayed in Fig. 2. From Fig. 2a, the XRD pattern of the DGEBA/C18-clay-5.0 wt% shows a hump at around 2.3°(2θ), indicating the  $d_{001}$ -spacing of C18-clay gets greater, if compared with the XRD pattern of the C18-clay with a hump at 4.2° (2θ). While the hump on the pattern of the DGEBA/C18-clay-5.0 wt% is weak and broad, it indicates the existence of intercalated clay structure. However, the XRD pattern of HDGEBA/C18-clay displays no obvious (001) basal reflection peak, indicating possible exfoliation of the clay. The absence of the (001) peak is not due to the low quantity of clay in the nanocomposite, as the (060) in-plane reflection peak of the single-clay sheet could still be detected (the inset of Fig. 2a).

When we increase the clay content to 7.5 wt%, both the XRD patterns of the DGEBA/C18-clay-7.5 wt% and HDGEBA/C18-clay-7.5 wt% show a weak and broad hump at around 2.0° (2θ), indicating the clay was intercalated rather than exfoliated. The hump on the XRD pattern of HDGEBA/C18-clay-7.5 wt% is weaker and appears at a smaller angle, indicating the clay in the nanocomposite of HDGEBA/C18-clay-7.5 wt% is closer to the state of exfoliation, compared to that of the DGEBA/C18-clay-7.5 wt%. Therefore, these experiments clearly indicate that the hydrogenation of the epoxy resin has a significant effect on the exfoliation of the organo-clay.

As XRD generally fails to distinguish the disordered intercalated and exfoliated morphology, TEM measurements have been further performed to observe the dispersion morphologies of clay directly. The TEM micrographs of the HDGEBA/C18-clay (7.5 wt%) and DGEBA/C18-clay (7.5 wt%)nanocomposites are shown in Fig. 3. Figure 3a is a low magnification version, in which the disorderly exfoliated small cluster structure of the HDGEBA/C18-clay (7.5 wt%) was observed. Moreover, both stacked (intercalated) and isolated (exfoliated) silicate layers in the sample of HDGEBA/C18-clay (7.5 wt%) can be observed at high magnification versions as shown in Fig. 3b and Fig. 3c. The large clay blocks in DGEBA/C18-clay (7.5 wt%) were observed in Fig. 3d, which is a low magnification version.

We can see that in the sectioned samples of the C18-clay epoxy nanocomposites, the clay aggregates are fewer and well dispersed in the HDGEBA/C18-clay matrix than in the DGEBA/C18-clay matrix. These TEM observations are consistent with the XRD results above. Thus, one can get the conclusion that the clay dispersed in the nanocomposite of HDGEBA/C18-clay is easier to get exfoliated, compared to that of the nanocomposite of DGEBA/C18-clay.

## 3.2. Discussion of polymer/clay interaction

It is well-known that the polymer/clay interaction is a key factor in controlling the clay exfoliation. The epoxy/C18-clay interaction is studied by compatibility experiments and rheological measurements in our work.

The results of compatibility experiments carried out between epoxy resin and C18-clay are shown in Fig. 4. It can be observed that C18-clay can uniformly disperse in the matrixes of HDGEBA even at 150°C, while the mixture of DGEBA/C18-clay exhibit a separation state since the temperature of 100°C. From the results of compatibility experiments, one can infer that there is a stronger interaction between HDGEBA and organo-clay rather than DGEBA and organo-clay.

The viscosities of two epoxy resin and their C18-clay nanocomposites (with 5 wt% and 10 wt% of C18-clay) were measured and the results are listed in Table 1. The viscosities of DGEBA/C18-clay (5 wt%) and DGEBA/C18-clay (10 wt%) increased only 2.72 and 3.73 times, respectively, if compared with that of the pure DGEBA, indicating the absence of strong polymer/clay interaction in these two composites[6, 14]. While the viscosities of HDGEBA/C18-clay (5 wt%) and HDGEBA/C18-clay (10 wt%) increased 14.58 and  $3.41 \times 10^4$  times, respectively, if compared with that of the pure HDGEBA, indicating the presence of strong polymer/clay interaction[6, 14]. Then, it is not surprising that the C18-clay can get a homogeneous dispersion and partly exfoliation in the matrix of HDGEBA because of the existence of strong interaction between HDGEBA and C18-clay due to the hydrogenation effect.

Table 1

Steady shear viscosity at shear rate of  $0.05 \text{ s}^{-1}$  and room temperature (23°C) of different liquid epoxy/C18-clay nanocomposites

	$\eta_{\text{pure rubber}}(\text{mPas})$	$\eta_{\text{C18-clay}(5 \text{ wt}\%)}(\text{mPas})$	$\eta_{\text{C18-clay}(10 \text{ wt}\%)}(\text{mPas})$
		$\eta_{\text{pure rubber}}(\text{mPas})$	$\eta_{\text{pure rubber}}(\text{mPas})$
DGEBA	$1.67 \times 10^5$	2.72	3.73
HDGEBA	$3.49 \times 10^3$	14.58	$3.41 \times 10^4$

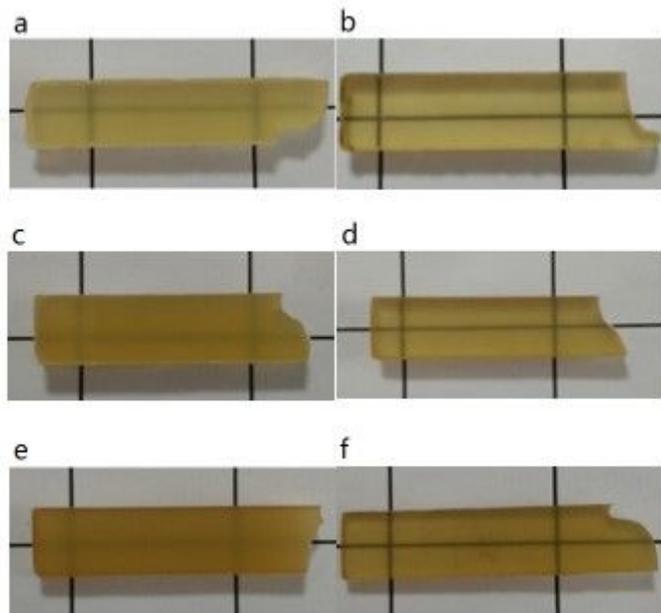
## 4. Conclusion

The hydrogenated diglycidylether of Bisphenol A epoxy resin (HDGEBA) was found to effectively exfoliate organo-clay in a clay-polymer nanocomposite. Due to the lower polarity of HDGEBA, the interaction between HDGEBA and organo-clay is stronger than that of DGEBA/organo-clay, which is confirmed by rheology and compatibility experiments. This result confirms that the match up between the polarity of the clay surface and that of the polymer matrix is an effective strategy to achieve well dispersion..

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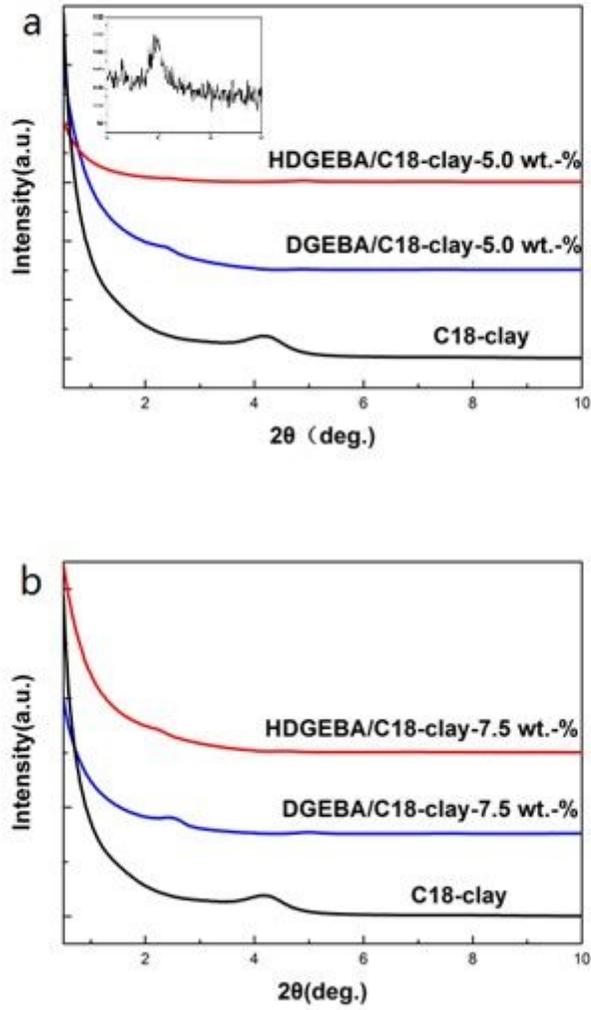
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## Figures



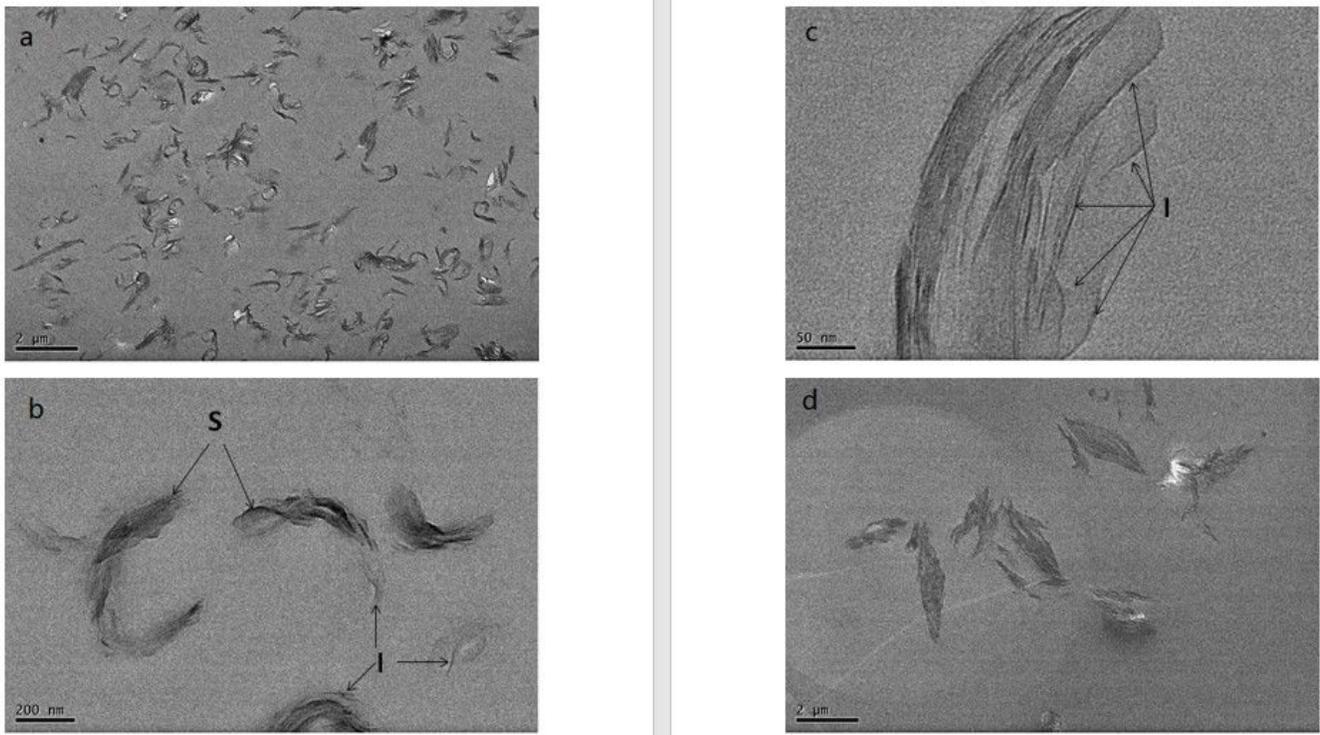
**Figure 1**

The comparison of transparency of (a) DGEBA/C18-clay (2.5 wt%), (b) HDGEBA/C18-clay (2.5 wt%), (c) DGEBA/C18-clay (5.0 wt%), (d) HDGEBA/C18-clay (5.0 wt%), (e) DGEBA/C18-clay (7.5 wt%), (f) HDGEBA/C18-clay (7.5 wt%). The thickness of all the bars is about 4mm.



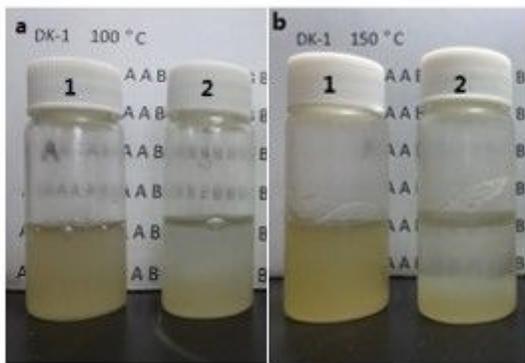
**Figure 3**

XRD patterns of resin/C18-clay nanocomposites with the clay contents of (a) 5.0 wt% and (b) 7.5 wt%. These samples are prepared by the method of “slurry-compounding”. The inset of Fig. 2a displays the in-plane 060 clay reflection of HDGEBA/C18-clay (5.0 wt%).



**Figure 5**

The TEM images of HDGEBA/C18-clay (7.5 wt%) nanocomposite with (a) low and (b), (c) high magnifications. I=individual silicate layer and S=stacked silicate layers. (d) The TEM image of DGEBA/C18-clay (7.5 wt%) nanocomposite with low magnification.



**Figure 7**

Images of the compatibility of (1) HDGEBA/C18-clay and (2) DGEBA/C18-clay mixtures at (a) 100°C and (b) 150°C.