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Thermal and Mechanical Properties of Carbon Fiber Reinforced Epoxy Composites Modified with CTBN and Hydroxyl Terminated Polyester

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Summary: Carbon fiber reinforced epoxy composites toughened with carboxyl terminated acrylonitrile butadiene rubber (CTBN) and hydroxyl terminated polyester (HTP) were prepared by autoclave vacuum bag molding process. The influence of compositions and blending method with toughening agents on glass transition temperature (T_g) and impact energy of cured laminates was evaluated. To improve the blending capability, different pre-treatment methods were adopted for CTBN and HTP. The toughness of the carbon fiber reinforced epoxy composite materials (C-FRP) modified with HTP showed a maximum when the HTP contents was 3.1 wt%. In case of CTBN, the maximum was 5.7 wt%. In addition, the fracture surfaces of toughened epoxy resin were examined by scanning electron microscopy (SEM) and the morphology was also discussed in this study.

Keywords: carbon fiber; carboxyl terminnated acrylonitrile butadiene rubber; composites; epoxy; hydroxyl terminated polyester

Introduction

Toughened polymer composites have attracted much interest because of their low production costs and good processability.[1,2] As is well known, epoxy resin is one of the most widely used matrices for the C-FRP by virtue of its good impregnation and adhesion to carbon fiber. Rubbers such as CTBN are used to improve the toughness of the epoxy resin. CTBN requires a pre-treatment for the good performance in the final product.[3–5]

For this paper, C-FRP toughened with CTBN and HTP were prepared by autoclave vacuum bag molding process. The influence of compositions and blending method with toughening agents on glass transition temperature (T_g) and impact energy of cured laminates was evaluated.To improve the blending capability, different pre-treatment methods were adopted for CTBN and HTP.[6] In addition, the fracture surfaces of the toughened epoxy resin were examined by SEM and and the morphology was also discussed in this study.

Experimental Part

Diglycidyl ether of bisphenol A (DGEBA, YD-128, EEW;190 g/eq, Kukdo) epoxy resin for the matrix material was modified with CTBN (Hycar 1300 × 13, Noveon) and HTP (Desmophen 1200, Bayer). The dicyandiamide (Dicy, Degussa) was used as a curing agent. The 1,1-dimethyl-3-(3,4-dichlorophenyl)urea (Diuron, Dupont) was used as a accelerator. The carbon fabric (CF3327, plain, HFG) fabricated by the polyacrylonitrile-based carbon fiber (HTA-3K, Toho) was used as a reinforcement.

For the pre-treatment, the CTBN and DGEBA were stirred for 1.5 h at 140 °C under nitrogen gas using triphenylphosphine as a catalyst. The HTP and DGEBA

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Table 1.
Formulations of epoxy resin.

Code	Ratio of components (by weight)[a]		
	DGEBA	CTBN	HTP
Control	100	0	0
C-5		5	0
C-10		10	0
C-15		15	0
C-20		20	0
D-5		0	5
D-10		0	10
D-15		0	15
D-20		0	20

[a] Ratio of Dicy introduced in each formulation was 7.8 and Diuron was 5.8.

were blended for 20 min at 60 °C.[6] Table 1 lists the formulations and composition for preparation of toughened epoxy samples. The carbon fabric was impregnated with each epoxy sample to produce prepreg with 38 wt% of resin content and a fiber areal weight of 203 ± 5 g/m^2. Figure 1 shows the vacuum bag molding process and cure cycle of autoclave designed by HFG. The cured materials were machined by the cutter equipped with diamond wheel also degined by HFG.

T$_g$ and impact energy were measured by differential scanning calorimeter (DSC 2010, TA Instruments) and Dynatub 8250 (Instron), respectively. For DSC measuring, A heating rate of 10 °C/min, sample weight of about 10 mg and nitrogen flow of 60 ml/min were maintained for all experiments. Runs were performed in temperature range 30–200 °C. The T$_g$ value was calculated automatically by interactive DSC program, picking the inflection point of the break in the heat flow curve. Impact test was performed to meet the ASTM D3763-02 and impact energy was reported in J. The quoted result is the average of determinations on five samples. The fracture surface was examined by scanning electron microscopy (PSM-75, RJ LEE Instruments).

Thermal and Mechanical Properties

With increasing the amounts of CTBN and HTP, the T$_g$ of epoxy resin decreased

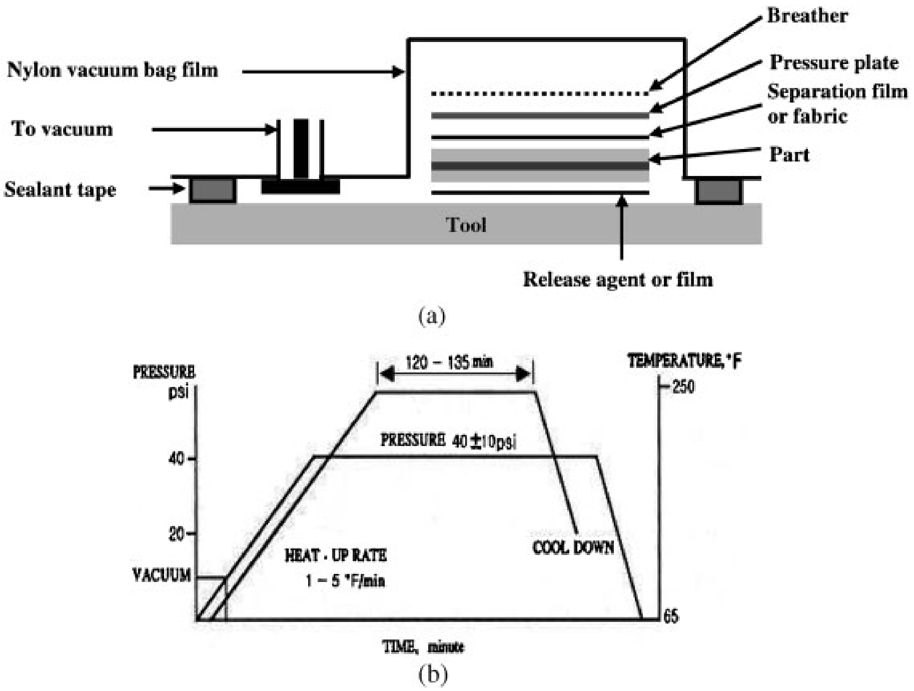

Figure 1.
Schematic illustration of the vacuum bag molding process (a) and cure cycle applied in this study (b).

Table 2.
Thermal and mechanical properties of C-FRP modified with CTBN and HTP.

Code	T_g (°C)[a]	Impact energy (J)	
		Values	S.D[b]
Control	133	4.0	0.32
C-5	125	4.7	0.37
C-10	123	5.0	0.35
C-15	119	5.1	0.43
C-20	118	6.1	0.48
D-5	115	5.2	0.39
D-10	105	5.3	0.42
D-15	95	4.3	0.33
D-20	85	3.7	0.39

[a] Measured with cured materials.
[b] S.D: Standard deviation.

(Table 2). The T_g reduction with increasing HTP content was severe. The T_g of D-5 was 115 °C which was even lower than the T_g of C-20. In case of CTBN, there was relatively little T_g reduction with C-20 having the lowest T_g as 118 °C (Figure 2). The difference in behavior of the T_g reduction between HTP and CTBN is attributed to the difference of the phase separation after curing.

The impact energy of C-FRP increased with increasing levels of CTBN and was accompanied by relatively lower T_g reduction than HTP. C-FRP containing 5.7 wt% of CTBN had the highest impact energy. The impact energy of C-FRP was also increased initially with increasing the contents of HTP.

However, the impact energy was decreased when the amounts of HTP was over 3.1 wt%. Although the T_g reduction of modification by HTP was significant, HTP was more effective than CTBN for the improvement of impact property when the contents was less than 3.1 wt% (Figure 3).

Morphology

The SEM photographs for fracture surfaces of unmodified and modified epoxy resin are shown in Figure 4. The relationship between the phase separation and impact property of the HTP modified epoxy was reported by H. Harani *et al.*[6] In the current experiments no difference was observed between Figure 4 (a) control and (b) HTP modified. For the HTP modifed epoxy, a whole series of SEM photograph showed no phase separation on the morphology. The epoxy and HTP appear like a polymer which is blended homogeneously. It is attributed to the different curing condition of epoxy resin. At the same time the CTBN modified epoxy showed the clear phase separation for the whole series (Figure 4(c)).

It has also been reported that the toughness of the toughened epoxy is

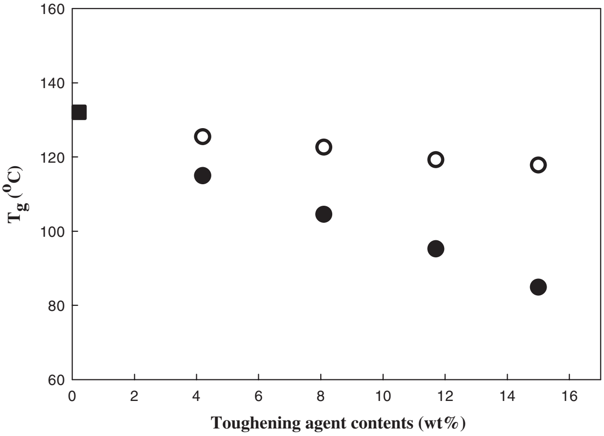

Figure 2.
Effect of toughening agents on the T_g of modified epoxy resin measured by DSC ; ■ = control, ● = modified with HTP and ○ = modified with CTBN.

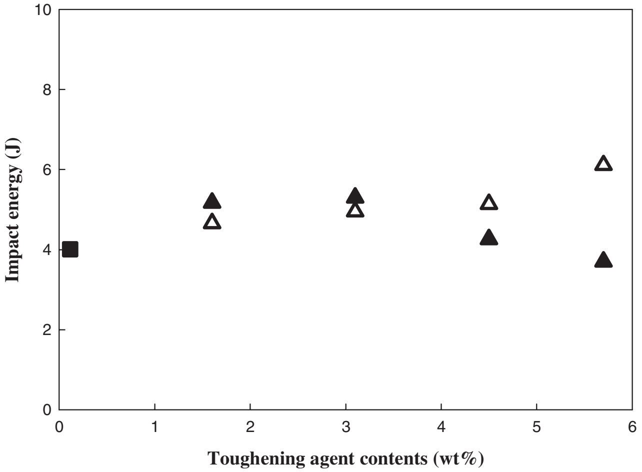

Figure 3.
Effect of toughening agents on the impact energy of modified C-FRP; ■ = control, ▲ = modified with HTP and △ = modified with CTBN.

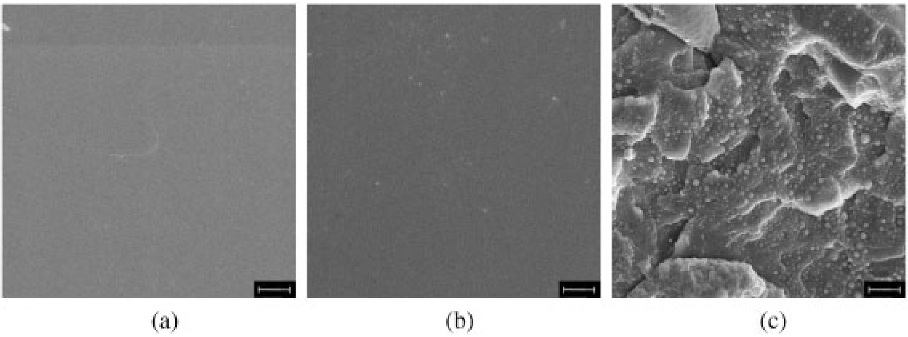

Figure 4.
SEM microphotographs of fracture surfaces for unmodified and modified epoxy resins; scale bar = 10 μm, 1000× magnification, (a) control, (b) D-20 = modified with HTP, and (c) C-20 = modified with CTBN.

strongly dependent on the morphology of the final system, dependant on the CTBN contents and size.[7] As the CTBN content level increased, an increase of the CTBN size and the impact energy value was observed.

Conclusion

The HTP was an effective additive for preparing toughened epoxy resin systems and the impact property of C-FRP modified with HTP was greater than CTBN when the HTP contents were less than 3.1 wt%. However there was too much $T_g$reduction caused by the increasing levels of HTP. On the other hand, the increased impact energy of C-FRP caused by increasing of the CTBN was accompanied by a relatively lower T_g reduction than HTP. Finally, it was concluded that the toughness of C-FRP modified with HTP showed a maximum when the HTP contents were 3.1 wt%. In case of CTBN, a maximum was 5.7 wt%.

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