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Mechanical Properties of Carbon Fiber Laminated Composite with UV-thermal Dual Curing Epoxy Resin

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ABSTRACT : *A major concern in the use of epoxy resins based on laminated composites relates to the occurrence of exfoliation or interlayer cracks associated with manufacturing defects. To improve this drawback of the epoxy resin, UV-heat dual cure resins have been developed. This paper presents UV heat dual cure resins used with epoxy acrylate oligomers, photoinitiators, thermal hardeners and thermosetting epoxy resins. Photo-DSC, DMA and FTIR-ATR spectroscopy were used to investigate the UV curing behavior and the properties of the UV heat dual curable epoxy resin. The mechanical properties of UV-thermal dual curable epoxy resin impregnated CF composite with Tensile, Flextural, ILSS and Charpy impact test. The obtained results showed that UV curable resin content improves the epoxy toughness.*

Keywords : *UV-thermal dual curing resin, tack property, toughening effect, Thermosetting composite, CF prepreg*

I. INTRODUCTION

Epoxy resins are typical thermosetting resins that can be used in a wide variety of applications. They have wide range of properties and process capability. So they are widely used in adhesives, coating agents and matrix of composite materials with electrical insulators. Epoxy resins used in the field of composites are subject to changes in the composition formulation that the properties of the mechanical properties and manufacturing process [1, 2]. The process temperature requirement and the curing time are changed and the toughness of the material can be changed to improve the temperature resistance characteristics. In the field of composite materials, epoxy resin is an important matrix but causes problems with resin brittleness when it is applied to lightweight structural materials such as automobile and aircraft despite its wide use. In order to improve the low toughness of epoxy resin, researches have been carried out by using rubber additives or adding thermoplastic polymers to improve patience[3]. However, in the case of rubber additives, their use at high temperatures is restricted to lower the glass transition temperature, the low thermal decomposition temperature and the mechanical properties[5, 7], and the use of the thermoplastic polymer is difficult to dissolve in the epoxy resin due to the high molecular weight. It is not reactive with epoxy resin and it is not part of the network structure formed by epoxy resin. So there is a problem that the content medium is lowered[4, 6]. Recently, studies are to improve brittleness that the structure, properties of rigid thermoset resin and ductile thermoplastic polymer are examined in a binary system. Also the physical properties between the polymers (semi -interpenetrating network) has been studied the miscibility of blend materials[6]. In this study UV curing resin were used to fabricate toughening effect composites using modified thermosetting resins. Figure 1 shows the schematic diagram of dual-curing mechanism of UV-thermal dual curable resin. The thermosetting hybrid resin is first cured by UV irradiation, thermally cured and finally a cross-linked structure similar to a semi-interpenetrating network can be obtained. Carbon fabrics composite was modified using UV-thermal dual curing resin in order to decreased the prepreg surface of tacky, then to improve its mechanical properties and impact energy absorbing capacity.

II. EXPERIMENTAL

2.1 Materials

The ultraviolet curable resin used was a photo-initiator Irgacure® 184 as a reactive functional diluent for bifunctional groups, epoxy acrylate and viscosity control, and a multi-functional monomer pentaerithrytol triacrylate. A diglycidyl ether of bisphenol A (DGEBA) type epoxy resin (YD-128, EEW=184~190 g/mol, density 1.16 g/cm3) was supplied by Kuk-do chemical Co. Ltd., south korea. A curing agent (Dicyanidiaminde(DICY),

Mw 84.08 g/mol) and curing acceleration agent (3-phenyl-1,1-dimethylurea, 3-(3,4-dichlorophenyl) -1,1-dimethylurea(DCMU)) were used. Table 1 shows the chemical formulation used to prepare UV-curing resin. The amount of ultraviolet curing resin added was 0, 5, 10, and 20 phr, and the mixture was thoroughly stirred at 80 ° C for 6 hours until the resin was completely blending. Carbon fabrics(TORAYCA® 3327, Plain woven, Toray Co. Ltd., Japan)with an areal density of 200g/m2 were obtained as reinforcement and to evaluate interlaminate adhesive properties to the composite resins.

2.2 Preparation of UV-thermal Dual Curable Epoxy Resin

The UV-thermal curable epoxy prepregs were prepared by hot-melt type as resin content of 40 ± 1 wt%, because impregnation method during prepreg manufacture is difficult to precisely control the resin content. UV-thermal curable prepregs were irradiated with UV-rays using a 2 kW lamp (UVACUBE2000 ACM, HONLE UV tech. Co. Ltd., USA). The treatment UV intensity at the prepreg was measured 50 kJ/cm2 over the wavelength range of 250-650 nm(UV Power Puck II, EIT instrument markets, USA).

2.3 Characterization of UV-thermal Dual Curable Epoxy Resin and Composites

The UV cured behavior of various UV curing resin content in epoxy resin was measured by photo differential scanning calorimetry (photo DSC, DSC-Q1000, TA instrument) in the radiation time of 1-3 sec at room temperature. The dynamic mechanical analysis (DMA) of the laminated composites was conducted under a single cantilever mode (ASTM D4065) in the temperature range of 25-190 °C at a heating rate of 3 °C/min and a frequency of 1 Hz. The curing kinetics of the photo-induced cross-linking was observed using FRIR-ATR spectrostcopy(Prekin Elmer system 2000). The curing behavior of the dual- curable prepreg was analyzed by observing the changes in the deformation of the C=C bonds at1635cm-1. The prepreg of tack features were characterized by Probe tack test (TXATM®, Yeonjin Co. Ltd., Korea). The Experimental conditions were contact time 60, 120, 180, 160 sec, Contact force 100 gf, Plate temperature 150 ℃, Debonding rate 1 mm / min. The basic physical properties (Resin content; ASTM D3171, Density; ASTM D792, Volatile content; ASTM D3530) of the composite material molded at 150 ° C for 10 minutes were measured according to the ASTM standard. The mechanical properties (Tensile test; ASTM D3039, Flexural test; ASTM D790, ILSS; ASTM D2344) of laminated composite tests were carried out by using a universal tensile testing machine (AG250kN, SHIMADZU). The Charpy impact test was carried out according to the ASTM D256 test method.

III. RESULTS AND DISCUSSION

3.1 UV curing behavior analysis

Fig. 2 shows the results of UV irradiation photo-induced cross-linking was measured using FTIR-ATR spectroscopy. After the photo-initiation of the dual-curable resin by UV irradiation, the specific peaks of the functional monomers or oligomers confirmed that the polymerization was carried out. The degree of cure was calculated using an equation (1), in which the measured, C = O stretching vibration (1730 cm -1) of the monomer and the relative concentration change of the C = C bond of the epoxy acrylate oligomer after UV irradiation.

$$\text{Relative concentrating of UV cured group (\%)} = \left(\frac{[A]^{UV}_{1635} / [A]^{UV}_{1730}}{[A]^{0}_{1635} / [A]^{0}_{1730}} \right) \times 100 \qquad (1)$$

$[A]^{0}_{1635}$: IR absorbance at 1635cm-1 before UV irradiation

$[A]^{0}_{1730}$: IR absorbance at 1730cm-1 before UV irradiation

$[A]^{UV}_{1635}$: IR absorbance at 1635cm-1 after UV irradiation

$[A]^{UV}_{1730}$: IR absorbance at 1730cm-1 after UV irradiation

The C = C bond peak of epoxy acrylate was decreased by ultraviolet irradiation, and it was confirmed that epoxy acrylate form a tightly cross-linked structure by UV irradiation. As a result of calculation of the curing degree after photo –induced cross-linking using the equation (2), the relative conversion ratio by ultraviolet irradiation was about 22.5%[8, 14].

The photo-curing characteristics of the resin were analyzed by Photo-DSC in order to investigate the effect of the UV curing rate. Fig. 3 shows the photo calorimetric exotherm of photo-DSC according to the addition amount of UV dual-curable resin. It was confirmed that the maximum exotherm was increased and the reaction rate was improved according to the addition amount of UV curing resin content. This means that the oligomer of the UV

irradiated hardener has improved mobility and the diffusion of radical proceeds more smoothly, thereby increasing the reaction rate.

The Dynamic thermal analysis (DMA) measured the storage modulus and loss modulus as a function of temperature. Fig. 4(a) and (b) show the relationship between the tan δ and the storage modulus of the dual-curable composite. As shown in Fig. 4, tan δ and storage modulus vs temperature curve, the glass transition temperature of the dual-curable resin blending system was 147.4 ℃, which is the highest at 5 phr. This is due to the solubility of the blending compatibility of both resins as well as the polymer entanglement between the molecules [7, 8]. The addition of 5 phr of UV cured resin increased the tan δ which means that as the monomer content increases, the reactivity increases and the curing rate is accelerated. However, when a relatively high content of 10, 20 phr of UV curing resin was added, tan δ decreased. This is due to the lower compatibility of the two resins in the two blend resin systems.

3.2 Tack properties of UV-thermal dual curing prepreg

Fig. 5 shows the results of analyzed the tack properties of the photo UV-thermal dual curable prepreg according to contact time. The tack properties of the prepreg decreased when the UV curing resin content was only 5 phr. When the UV curing resin content exceeded 10phr, the tack property was decreased to such an extent that the tacky could not be determined. This is a result of the partial curing of the surface of the prepreg as the photo induced curing reaction by UV light occurs abruptly[11].

3.3 Mechanical properties of UV-thermal dual curing composite

The laminated composites for evaluating the mechanical properties of the dual curing prepreg was manufactured at a temperature of 150°C for 10 minutes using a heating press at a pressure of 100 bar. The tensile and flexural strength specimens were laminated 9 ply and the in- plane shear strength specimens were laminated 15 ply. Table 2 shows the general properties and Table 3 shows the mechanical properties of molded specimens according to the UV curing resin content. The tensile and flexural test results showed that the strength and modulus of the specimens blending with 5 phr of UV curing resin were improved. However, as show in Fig. 6, the mechanical properties tend to decreased in the above contents. Fig. 7 shows the load-displacement curve of the ILSS test can be understood for this reason. In the composite failure mechanism, matrix crack(interfacial delamination)- crack growth - delamination - fiber breakage phenomenon was observed sequentially, whereas interlayer separation phenomenon was mainly observed as the content of the UV curable resin was increased[15]. One of the failure behavior of the fiber-reinforced composite material of interlaminar fracture is delaminated. The fracture Mode I, occurred at the interface between the weakest layers of the composite, was predominantly due to the addition of UV curing resin. When a specimen is partially formed by laminated prepregs cured by UV irradiation, delamination occurs between the prepreg layer and the layer, thereby deteriorating the mechanical properties[12, 13]. However, in the case of 5phr which is more compatibility, as a toughening agent, the interlaminar shear strength and impact strength were improved by dispersing cracks in order to compensate the matrix crazing phenomenon caused by external force.

IV. CONCLUSIONS

In this study, the UV-thermal dual cured composites were prepared with UV curing resin and thermosetting epoxy blend as a kind of toughening agent. Their UV curing behavior, Tack properties and mechanical properties were analyzed. Results were as follows:

- In the thermal analysis test, the UV curing behavior according to the addition amount of the epoxy acrylate oligomer, the monomer and the free radical photo-initiator, photo calorimetric exotherm was increased and the reaction rate was improved according to the addition amount.
- Dual curing epoxy resin showed the highest glass transition temperature at 5 phr contents, which showed excellent compatibility with the two blended resins and polymer entanglement between the molecules.
- The UV-curing reaction due to ultraviolet irradiation occurs rapidly and when an excessive amount of the UV curing resin is contained, the surface of the prepreg is partially cured to deteriorate the physical properties.
- In the composite material containing more than 10 phr of UV curing resin, delamination occurs between the layer and layer due to the partial curing of the surface of the prepreg, thereby lowering the mechanical properties. However, in the case of 5 phr of compatibility, shear strength and impact strength were improved. This study clearly demonstrates that the toughening effect with UV-thermal dual curable resin conformation significantly influences the mechanical, thermal and interfacial properties of composites. UV-thermal dual curable resin provide an easy and effective means of studying such CPMC(Chopped prepreg molding compound) manufacture and energy absorb material in automobile part.

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[17]. *Note that the proceedings title is set in italic*

Table 1. Formulation of UV-curing resin.

	Component	**Parts by weight**
Oligomer	Epoxy acrylate oligomer	62
Monomer	Pentaerithrytol triacrylayte	35
Photoinitiator	1-Hydroxy-cyclohexyl-phenyl-ketone(Irgacure® 184)	3

Table 2. Properties of prepreg sample manufactured with different UV resin contents.

Property	**UV-curing resin contents**			
	0 phr	**5 phr**	**10 phr**	**20 phr**
Total Areal Weight (g/m^2)	368.0	363.6	371.7	364.4
Fiber Areal Weight (g/m^2)	200.9	203.2	202.3	203.5
Resin Content (wt%)	45.0	43.8	45.6	44.6
Neat Resin density (g/cm^3)	1.16	1.11	1.11	1.14
Laminate density (g/cm^3)	1.49	1.51	1.49	1.48
Volatile Content (wt%)	0.91	0.87	0.90	0.90

Table 3. Mechanical properties of composites cured dual system with different UV resin contents.

UV-curing resin contents	Tensile		Flexural		ILSS
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	Strength (MPa)
0 phr	627.8(±13.4)	49.4(±5.8)	781.3(±13.1)	51.9(±7.2)	74.4(±11.9)
5 phr	627.2(±14.3)	54.7(±6.2)	806.8(±12.4)	55.9(±8.7)	78.3(±14.3)
10 phr	609.4(±12.2)	45.6(±5.4)	810.8(±15.7)	56.1(±7.3)	67.2(±15.7)
20 phr	571.8(±13.1)	46.7(±7.8)	801.8(±11.5)	54.8(±6.4)	61.9(±16.5)

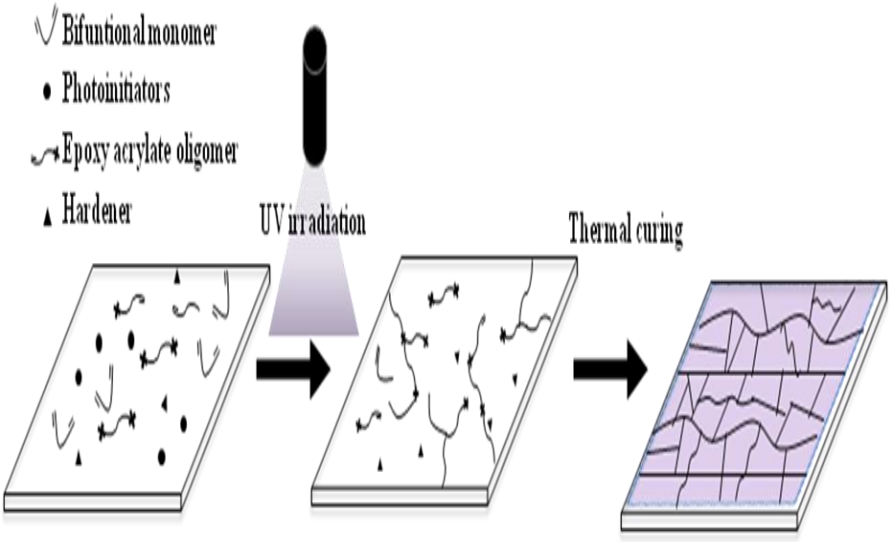

Figure 1. Schematic arrangement of dual curing process of UV-thermal dual curable resin

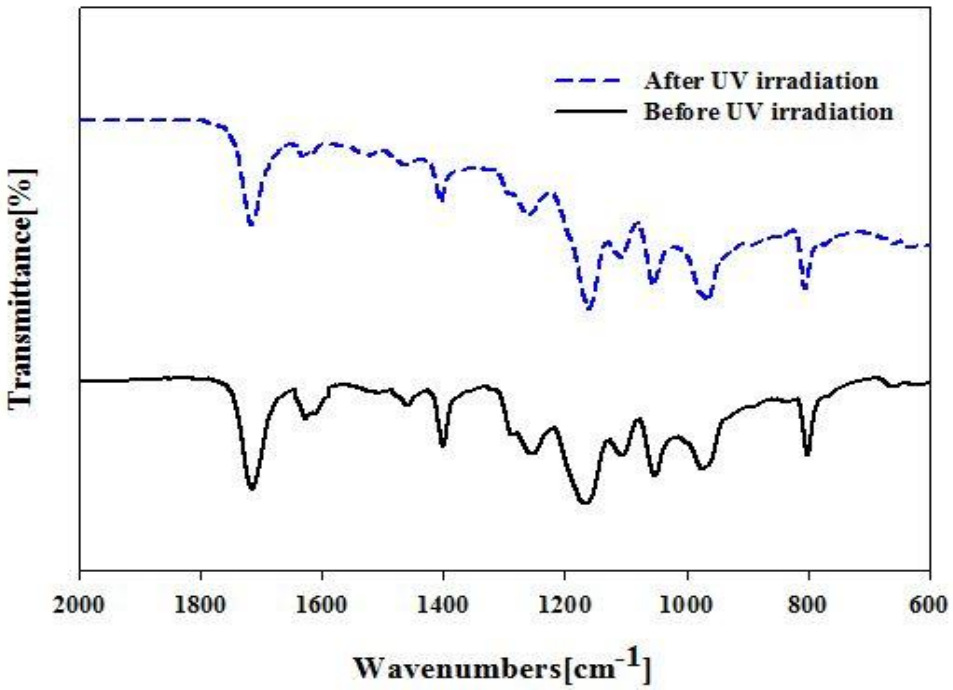

Figure 2. FT-IR curve of UV curing resin by UV irradiation.

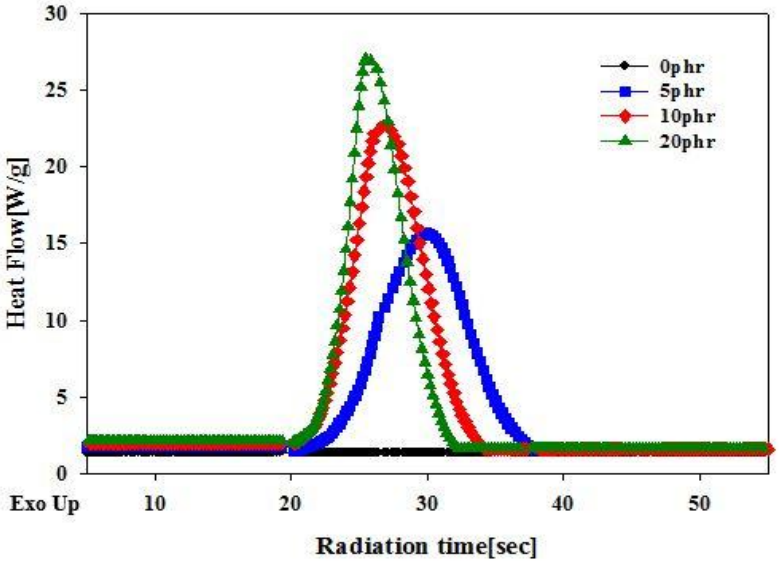

Figure 3. Photo-DSC curve of epoxy resin with different UV resin contents

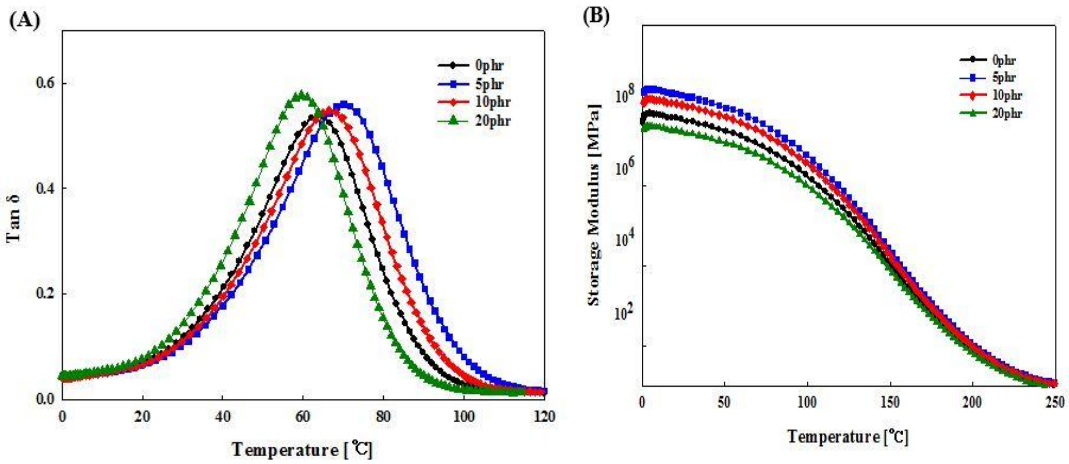

Figure 4 . Tan delta curves (A) and storage modulus curves (B) of epoxy resin cured dual system with different UV resin contents

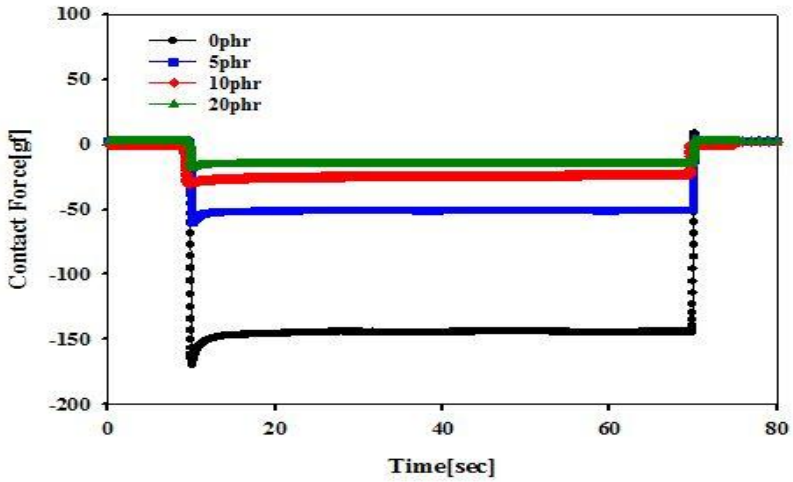

Figure 5. Probe tack test curve of composites with different UV resin contents by UV irradiation.

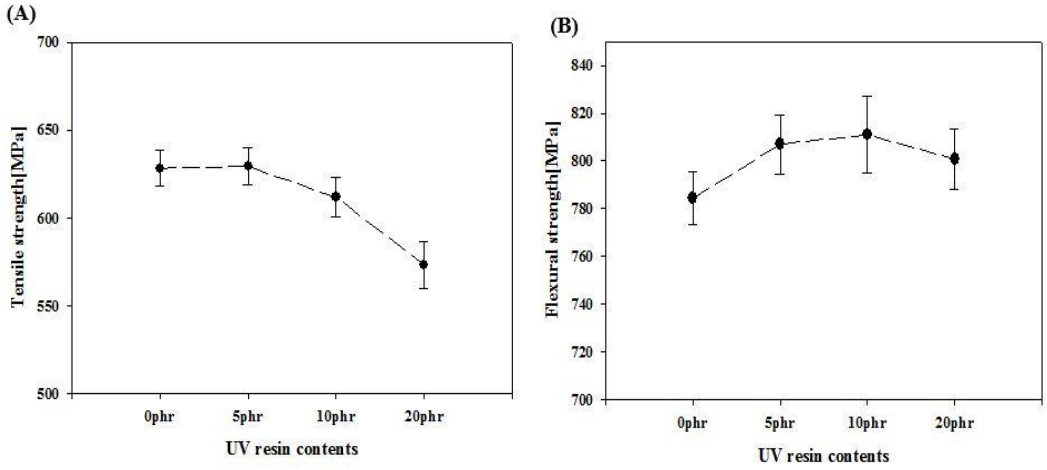

Figure 6. Tensile strength curve (A) and Flexural strength curve (B) of composites cured dual system with different UV resin contents

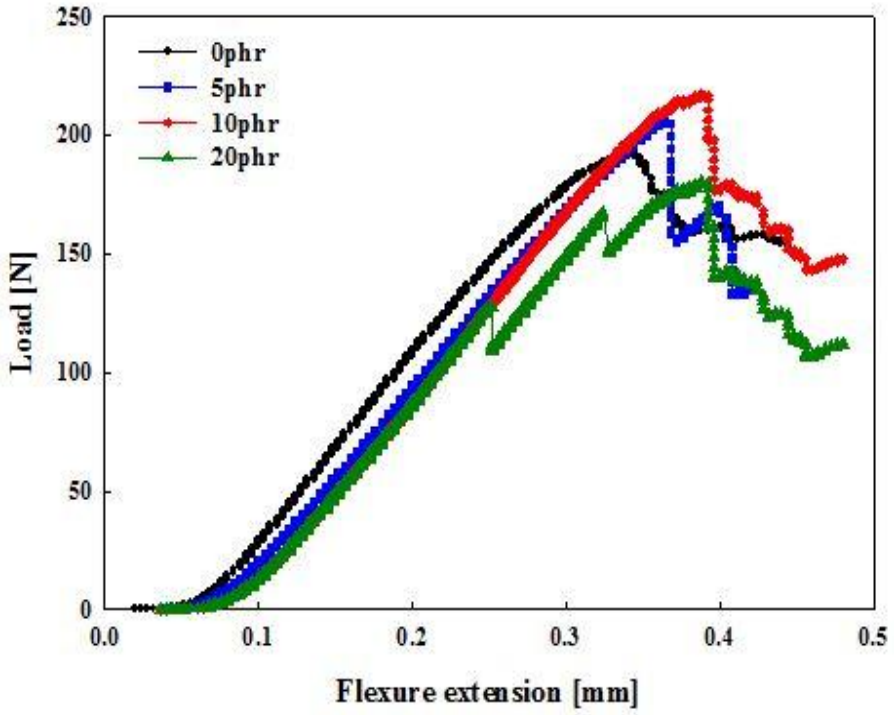

Figure 7. ILSS curve of composites cured dual system with different UV resin contents

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