PROCESSING AND PROPERTIES OF FULLERENE (C-60) DERIVED CARBON/CARBON COMPOSITES

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SUMMARY: The linear PU and star C60-PU copolymers were synthesized to modify novolac phenolic resin. The improvement on the toughness of the cured modified phenolic resin was investigated. The modified phenolic resins were utilized to prepare carbon/carbon composites.

Experimental results confirm the predicted chemical structure of linear PU can be synthesized by reacting the tyramine with PU prepolymer. Furthermore, one isocyanate group of PU prepolymer can react with tyramine, and then the other isocyanate group of PU prepolymer will react with $C_{60}(OH)_{12}$. Consequently, the star C60-PU can be synthesized.

Impact strength of cured resin specimen containing 3phr linear PU is 27 % higher than that of neat phenolic resin which the impact strength of specimen containing 3phr C60-PU is 57 % higher than that of neat phenolic resin. Properties of the C60-PU modified phenolic resin based carbon-carbon composite will be discussed.

KEYWORDS: Fullerene, polyurethane, phenolic resin, Carbon-Carbon Composite, impact strength.

INTRODUCTION

Phenolic resin has been widely used in articles of everyday use and industrial applications due to its excellent flame resistance, thermal insulation, chemical resistance, dimensional stability, and low toxicity[1-3]. However the brittleness of phenolic resin is its inherent weakness which limits its applications. Therefore, improving the toughness of phenolic resin is a very important task[4].

As described in previous reports[5-6], phenolic resin provides an intermolecular hydrogen bonding as a dominant driving force to interact with other miscible polymer which containing hydroxyl, carbonyl, ether, and other functional groups with hydrogen bonding. The thermoplastic polymer with flexible functional group that contains hydrogen bond will interpenetrate into the phenolic network[7]. The fullerenols ($C_{60}(OH)_{12}$) has been synthesized

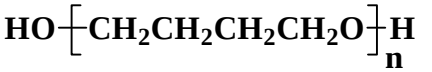
recently[8-10], that leads to a new type of star-shape polymer, which possesses several unique properties e.g. flexibility high thermal resistance, good bio-compatibility, etc.

In this present work, linear PU or C60-PU are added to modify phenolic resin and cured. X-ray, SEM, differential scanning calorimetry (DSC) of cured phenolic resin containing linear PU or star C60-PU have been used to study the miscibility between phenolic resin network and linear PU or C60-PU. These results are helpful to investigate how linear PU or C60-PU interact with the phenolic resin network. In addition, further processing and properties of carbon/carbon composite will be discussed.

EXPERIMENTAL SECTION

Materials:

1. PTMO---- Polytetramethane oxide (Tokyo Chemical, Japan)



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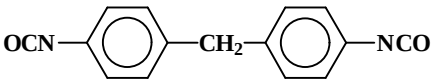
2. MDI---4,4-Diphenylmethane Diisocyanate (Tokyo Chemical, Japan)



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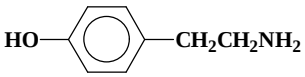
3. Tyramine---4-(2-aminoethyl)phenol (Tokyo Chemical, Japan)



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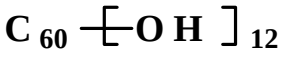
4. Fullerenols(Center for Condensed Matter Sciences, NTU, Taiwan)



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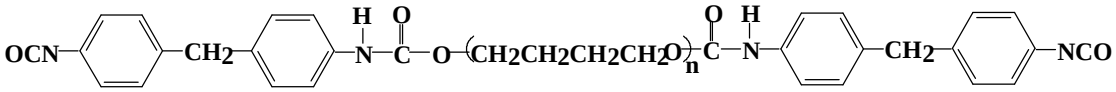
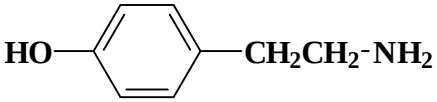
Synthesis of linear PU(LPU) and star C60-PU(SPU)

The linear polyurethane(LPU) was prepared by reacting PU prepolymer with tyramine as the following equation.

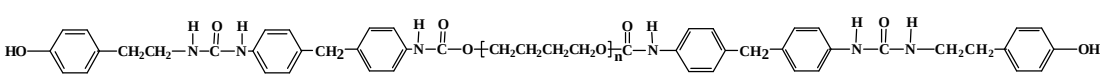


PU prepolymer

+

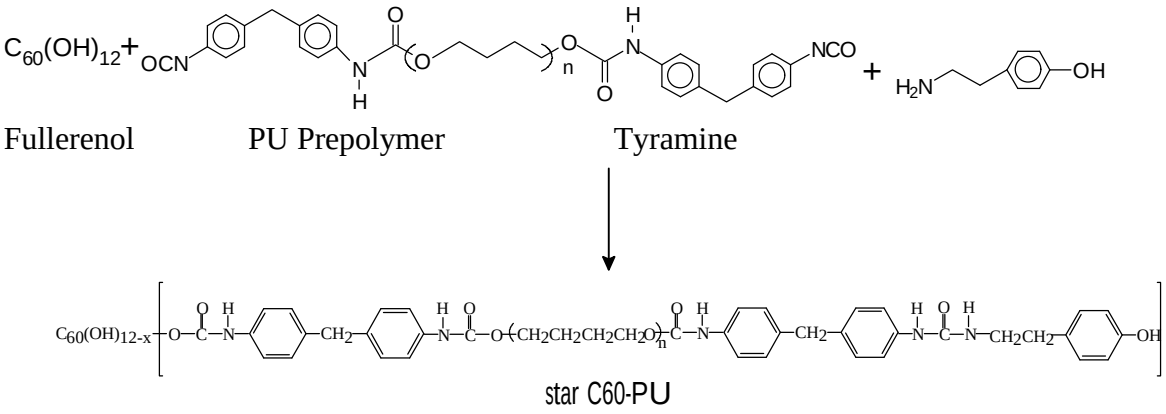


Tyramine



Linear PU

The star C60-PU(SPU) was synthesized by reacting PU prepolymer with fullerenol and tyramine as shown in the following equation.



Curing of phenolic resin with linear PU or C60-PU

Phenolic resin, DGEBA type epoxy resin, linear PU(or C60-PU), and DBU (1 ,8~diazabicyclo[5.4.0]-7-undecene) were dissolved in THF, respectively. Then, the mixture was stirred for 2 days. THF solvent was removed by evacuating at 50 and 100 for 30 minutes, respectively. The modified phenolic resin was heated to 150 at a rate of 3 /min for 1 hour and then cured.

Preparation of carbon/carbon composite

Eight pieces of carbon fiber woven cloth are impregnated with mixed phenolic resin for 1 hour and stacked one by one. To prepare carbon/carbon composite precursor, the stacked woven cloth is compressed by hot press at 150 under 1000 psi for 1 hour. Carbon/carbon composite precursor is carbonized at 1050 in nitrogen gas to form carbon/carbon composite.

RESULTS AND DISCUSSION

Characterization of linear PU(LPU) and star C60-PU(SPU)

The predicted chemical structures of linear PU(LPU) and star C60-PU(SPU) have been studued by H'-NMR spectra and will be presented elsewhere[(1)]. The predicted chemical structures of LPU and SPU were identified.

The molecular weights of linear PU and star C60-PU are 3385 and 18359 obtained from GPC, respectively. The molecular weights of tyramine and $C_{60}(OH)_{12}$ are 137 and 924. The molecular weight of poly(urethane-ether) arms with [-MDI-PTMO-MDI-TYRAMINE] structure is 3248(=3385-137). Consequently, the structure of star C60-PU has been characterized which consists of 5.36(=[1 8359-924]/3248) poly(urethane- ether) arms per C60(OH)12, on average. A novel star polymer utilizing fullerenols ($C_{60}(OH)_{12}$) are obtained.

Table 1 shows the thermal properties of LPU and SPU. The glass transition temperature of LPU is similar to that of SPU. The degradation temperatures of LPU and SPU are also similar. From these results, one can see the thermal properties of LPU or SPU depend on poly(urethane-ether) arms. In addition, LPU and SPU have not only crystal peak but also recrystal peak. The exothermic heat and melting temperature of SPU are smaller than those of LPU. Therefore, SPU is easier to crystallize in cooling process. However the crystalline

amounts of SPU are less than that of LPU.

Table 1 Thermal properties of linear PU and C60-PU

	Linear PU	**C60-PU**
DSC		
Tg( )	-64.5	-65.5
Exothermic		
(J/g)	-42.5	-28.6
( )	-17.7	-27.2
Endothermic		
(J/g)	63.9	54.5
( )	22.0	23.5
TGA		
1st degradation temperature( )	413	419
2nd degradation temperature( )	552	521

Miscibility of phenolic resin and linear PU(LPU) or C60-PU(SPU)

Thermal analysis was used to study the miscibility of polymer blend. In general, a single glass transition temperature(Tg) exited when the polymer blend is miscible. The DSC curves of phenolic resin blends with LPU and SPU show only one Tg for each curve indicating that the miscibility between phenolic resin and LPU or SPU are excellent.

Properties of cured phenolic resin containing LPU

There are two different blending types in polymer blend. If the miscibility of linear PU and phenolic resin is poor, linear PU may entangle with each other in phenolic resin. Then, the mixed resin has multiphase. On the other hand, if the miscibility of linear PU and phenolic resin is acceptable, linear PU can be interpenetrated into phenolic resin. Then, the mixing resin has single phase only. The miscibility of linear PU and phenolic resin is excellent, the mixing resin should be single phase.

Figure 1 shows the TGA curves of cured phenolic resin containing LPU. The trend of degradation temperature was increasing first and then decreased. But the char yield decreases with increasing amounts of LPU.

The main objective of adding linear PU to phenolic resin is to cause stress curve can diffuse along linear PU and form dendritic stress curve. Hence phenolic resin specimen can not be broken when the specimen is subjected to impact. Table 2 shows the impact strength of cured phenolic resin containing linear PU. The impact strength of specimen contains 3phr linear PU is maximum and 27 % higher than that of specimen of neat phenolic resin.

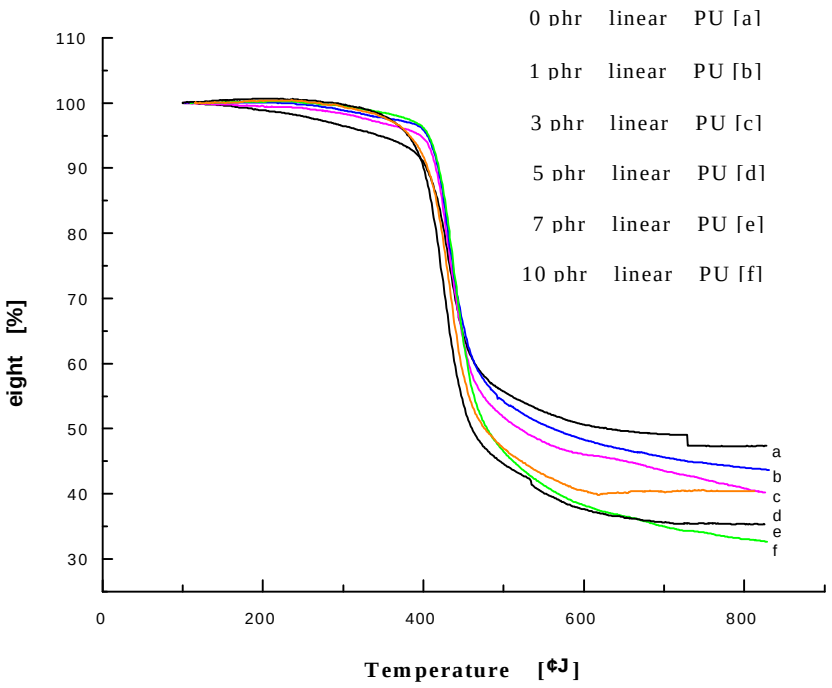


Figure 1 TGA curves of phenolic resin cured with various amounts of Linear PU

Properties of cured phenolic resin containing SPU

The cured mixed resin of SPU and phenolic resin shows its good miscibility with a single phase.Figure 2 shows the TGA curves of cured phenolic resin containing SPU. The trend of degradation temperature is increasing first and then decreasing. But the char yield is decreasing with increasing amounts of SPU.

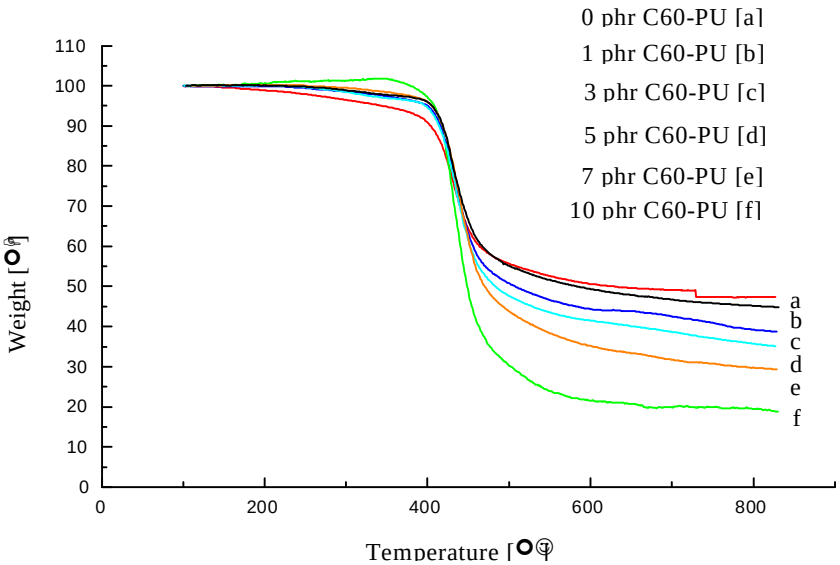


Figure 2 TGA curves of phenolic resin modified with various amounts of C60-PU

The main objective of adding SPU to the phenolic resin is to cause stress curve diffuse along SPU and to form star and circular stress curve. Consequently phenolic resin specimen can not be broken easily when the specimen is subjected to impact. Table 2 shows the impact strength of cured phenolic resin containing SPU.The impact strength of specimen contains 3phr SPU is the maximum and is 57 % higher than that of specimen of neat phenolic resin.

Table 2 Impact strength of cured phenolic resin contains linear PU or C60-PU

Impact strength(J/m)	**Linear PU**	**Star C60-PU**
0phr* PU	25.6	25.6
1phr	31.1	32.7
3phr	32.7	40.3
5phr	311	38.2
7phr	27.7	30.8
10phr	23.0	24.5

*phr: parts per hundred part of resin.

Properties of LPU and SPU modified phenolic resin based Carbon / Carbon composite

Table 3 shows the properties of carbon/carbon composites containing LPU and SPU. When carbon/carbon composite precursor is carbonized at 1050 , resin is changed into char. Then, void content of carbon/carbon composite will be increased. The void content(P) of carbon/carbon composite containing LPU is the maximum. The void content(P) of carbon/carbon composite containing SPU is the minimum. This indicates that carbon/carbon composite precursor containing SPU will have higher char yield and higher density than precursor contains neat phenolic resin. The carbon/carbon composite precursor containing LPU will have lower char yield and lower density than precursor contains neat phenolic resin.

Table 3 Properties of carbon/carbon composite contains linear PU or C60-PU

	Composite contains neat phenolic resin	**Composite contains linear PU**	**Composite contains C60-PU**
Void content P'(%)	22.2	30.6	18.9
Density(g/cm^3)	1.12	1.07	1.15
Flexural strength (Mpa)	34.7	26.0	48.8

CONCLUSIONS

1. The predicted chemical structure of linear PU can be synthesized by reacting the tyramine with PU prepolymer . Chemical structure was identified by H'-NMR spectra.

2. One isocynate group of PU prepolymer can react with tyramine , and then the other isocynate group of PU prepolymer will react with C60(OH)12 . Consequently, the star C60-PU can be synthesized .

3. Both linear PU and star C60-PU can modify phenolic resin. And the impact strength of cured phenolic resin contains linear PU or C60-PU will be higher than that of cured neat phenolic resin.

4. The impact strength of cured resin specimen containing 3phr linear PU is 27 higher than that of specimen of neat phenolic resin. The impact strength of specimen containing 3phr C60-PU is 57 higher than that of specimen of neat phenolic resin.

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