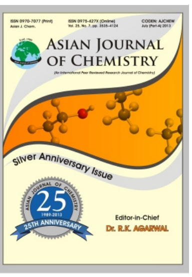
Asian Journal of Chemistry; Vol. 25, No. 12 (2013), 6935-6938

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15268



# Synthesis and Characterization of Macromolecular Coupling Agent Ending with Epoxy Group

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(*Received*: 4 February 2013; *Accepted*: 7 June 2013) AJC-13604

The macromolecular copolymer coupling agent was obtained by free radical solution polymerization using polyalkylene glycol allyl glycidyl ether (AEPH) and vinyl silane coupling agent (A-151) as reacting monomers. The effects of reaction temperature, reaction time and raw material types to the yield of products have been discussed. The structure of the copolymer coupling agent was characterized by Fourier transform infrared spectroscopy and the solubility in water was also investigated. The results show that the copolymer was prepared when the mole radio of AEPH:A-151:BPO was $1:1:1 \times 10^{-3}$, reaction temperature was 80 ºC and reaction time was 2 h. The hydrolyzate of copolymer could form a transparent water solution. Effect of the copolymer on the bend strength of glass fiber/epoxy composite was also investigated. Compared with the sample of A-151, the bend strength of glass fiber/epoxy composite using the copolymer coupling agent was increased 6.5 %.

**Key Words: A-151, AEPH, Free radical solution copolymerization, SEM.**

## INTRODUCTION

It is generally accepted that the response of the fiber-matrix interphase region can contribute to the performance of composite. The effect of interphase can be controlled by appropriate treatment to the surface of fibers[1]. Traditionally, silane coupling agents are used to increase the adhesion between the glass fiber reinforcement and the polymeric matrix, but that can get too high bond strength and poor toughness of composite. Coating rubber polymers to the surface of fiber by polymerization or physical sizing has been studied, but its bond strength with matrix is not enough and the improvement of mechanical property of composite is not obvious[2,3].

Macromolecular coupling agent which combined the silane coupling agent with high molecular polymers by polymerization has aroused many attentions. It has been proved that it can effectively improve the property of interphase of composites[4,5].

The partner of silane coupling agent can react with the glass fiber to form chemical bonds. The other partner of molecular polymer can react with the resin matrix or wind physically through molecular chains. When the failure happened, on the one hand, the high interphase chemical bonding can make high failure energy. On the other hand, long molecular polymer chains can produce large deformations to make more absorption energy[6].

In this paper, a kind of macromolecular coupling agent was prepared by free radical solution polymerization. It kept the siloxane base group of coupling agent which could react with the glass fiber after hydrolysis and the epoxy group which could participate into the curing reaction of resin matrix. The effects of reaction temperature, reaction time and raw material types on the yield of the product and also the solubility of product in water were investigated. At last, the influence of copolymer on the surface morphology of glass fiber and mechanical properties of glass fiber/epoxy composite has been studied.

## EXPERIMENTAL

Vinyl triethoxy silane coupling agent (A-151) was supplied by Mount Tai glass fiber Co., Ltd and distilled under reduced pressure. Polyalkylene glycol allyl glycidyl ether (AEPH, Hangzhou Dilai Trade Co. Ltd.) molecular weight 500/1000 was used after leaching polymerization inhibitor with neutral alumina column and tracing moisture with anhydrous magnesium sulfate by oscillation and at last placing for 8 h after filtering. Benzoyl peroxide and dimethylbenzene (Sinopharm Chemical Reagent Co., Ltd.) analytical grade was used without further purification. Epoxy resin (E-51, Jinan Yicheng Resin Co. Ltd.) and Glass fiber was provided by Mount Tai Glass fiber Co. Ltd, diameter 13 μm, processed by acetone in shaking container and dried in a vacuum oven at 80 ºC overnight.

**Polymerization of macromolecular coupling agent:** Macromolecular coupling agent was synthesized by free radical solution polymerization method. In a three-branched flask, AEPH was firstly dissolved in dimethylbenzene. Then a certain amount of A-151 was added, they were mixed well for 10 min with the speed of 200 rpm. Suitable amounts of BPO dissolved in dimethylbenzene was poured into the three-branched flask and polymerized based on various reaction conditions. After the copolymerization reaction ended, the production was separated by sediment in the methyl alcohol. The crude product was distilled under reduced pressure ($10^{-2}$ Pa) in an all-glass apparatus.

**Characterization of macromolecular coupling agent:** Rate of monomer conversion refers to percentage that polymerization monomer accounts for weight of original monomer. The structure of copolymer was characterized by FTIR in Nicolet Magna-IR 550 and acetone was used as solvent.

**Solubility of macromolecular coupling agent:** After purification quantitative product was dissolved in distilled water to hydrolyze at room temperature. The change of conductivity was recorded by conductivity meter to judge the best time of hydrolysis. The particle size of hydrolysate in water solution was analyzed by LS-1330 laser particle size analyzer (Beckman Coulter, United States).

**Preparation of glass fiber/epoxy composite and its measurement:** The surface treatments of glass fiber with copolymers and A-151 were carried out in aqueous solution at the conditions of same concentration and treatment time. After that, to make glass fiber react with coupling agent fully, they were dried in a vacuum oven at 120 ºC for 1 h. The surface morphology of the glass fibers was observed by SEM (Quanta Feg 250) and the stiffness of glass fiber was measured according to the method[7]. Glass fiber/epoxy composites were prepared through method of cast molding with treated or untreated glass fiber and epoxy solution (100 copies epoxy, 10 copied triethylene tetramine) in silicone rubber mould and cured under 80 ºC for 4 h in a vacuum oven.

## RESULTS AND DISCUSSION

**Synthesis and characterization of macromolecular coupling agent:** The preparation of copolymers is shown in Table-1. The condition of reaction mole rate of AEPH: A-151: BPO is 1:1:1 × $10^{-3}$. From Table-1, it can be seen that the convention rate increases with the time when the temperature is the same, but the conversion rate grows small when reaction time is over 4 h. At the same reaction time, temperature grows from 80 to 90 ºC, the convention rate increases only 2.8 %, but the colour of product becomes deeper. It shows that the effect of temperature to the convention rate of product is not significant. Alternate the molecular weight of AEPH from 500 to 1000, the change of yield per cent is from 75.3 to 74.6 % (as seen sample 7 in Table-1).

Fig. 1 shows the IR spectra of copolymer macromolecular coupling agent, 1250 $cm^{-1}$ is the characteristic absorption peak of epoxy group. The peak at 1100 $cm^{-1}$ is assigned to the characteristic absorption peak of Si-O-Si, which proves the existence of A-151 in the block copolymer. The above analysis shows that the structure of the synthetic product meets the designed block copolymer.

TABLE-1
SYNTHESIS AND CHARACTERIZATION OF MACROMOLECULAR COUPLING AGENT

| Sample | Reaction time (h) | Reaction temperature (ºC) | Yield (%) |
|---|---|---|---|
| 1 | 1.5 | 80 | 66.9 |
| 2 | 2.0 | 80 | 75.3 |
| 3 | 3.0 | 80 | 79.1 |
| 4 | 4.0 | 80 | 84.1 |
| 5 | 7.0 | 80 | 85.5 |
| 6 | 2.0 | 90 | 78.1 |
| 7 | 2.0 | 80 | 74.6 |

In sample 7, the monomer is AEPH1000; the others are all AEPH500.

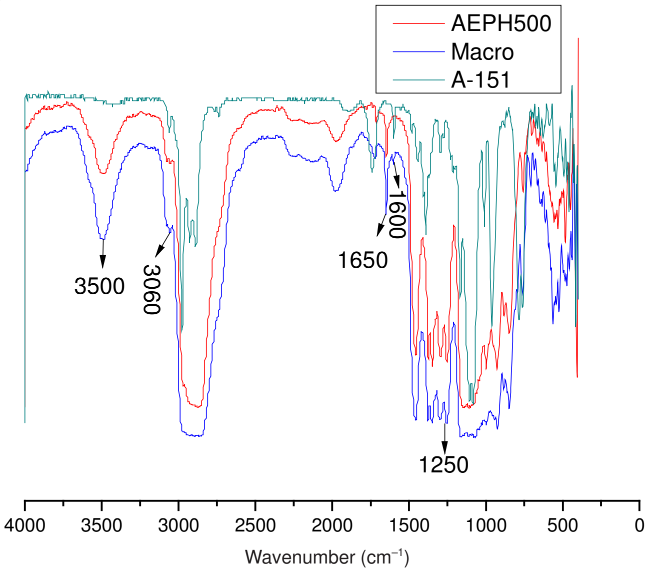
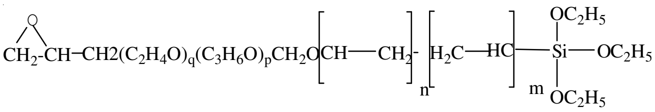


Fig. 1. IR spectra of copolymer macromolecular coupling agent



$$\overset{O}{CH_2-CH}-CH2(C_2H_4O)_q(C_3H_6O)_pCH_2O\left[CH-CH_2\right]_n\left[H_2C-HC\right]_m-\underset{OC_2H_5}{\overset{OC_2H_5}{Si}}-OC_2H_5$$

Fig. 2. Structure of macromolecular coupling agent

**Solubility and hydrolysis of macromolecular coupling agent:** Dissolubility of production and A-151 respectively in different solvents is shown in Table-2. The results show that the product and A-151 can both be dissolved in the four solvents. This provides the possibility and convenience for the later treatment of glass fiber.

TABLE-2
DISSOLUBILITY OF PRODUCTION AND A-151

| Item | Solvent | | | |
|---|---|---|---|---|
| | Deionized water | Ethanol | Tetrahydrofuran | Acetone |
| Production | Dissolved | Dissolved | Dissolved | Dissolved |
| A-151 | Dissolved | Dissolved | Dissolved | Dissolved |

Hydrolysis of macromolecular coupling agent was carried out in deionized water at room temperature. Table-3 shows the trend of conductivity and the change of solution transparency with the time. The conductivity of the monomer of A-151 and AEPH in water solution is zero and 2 μs/cm respectively after hydrolysis for 2 h without adding any acid or alkali. And there is some oil flowing on the surface of A-151 water solution that shows the hydrolysis does not happen. From Table-3, it can be seen that the conductivities of the products after 2 h hydrolysis are all above 8 μs/cm and sample 2 and sample 7 are the biggest. Their hydrolysis solutions show transparency or translucent. Otherwise, after 3 h, there are some flocculates in the bottom of the hydrolysis solution. The high conductivity values of polymer solution show the more strong polarity of the polymer, so the better solubility in the solution and more transparency[7]. As described above, it can be concluded that sample 2 is the best in the water solution. The best reaction temperature is 80 ºC and the best reaction time is 2 h.

TABLE-3
CONDUCTIVITY OF PRODUCT IN WATER SOLUTION

| Item | Sample | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 3 | 5 | 6 | 7 |
| Conductivity (μs/cm) | 9 | 15 | 8 | 10 | 10 | 9 | 15 |
| Degree of transparency | A | B | C | C | C | C | A |

A = Translucent; B = Transparent; C= Flocculation

The particle size distribution of the solution of sample 2 after hydrolysis is shown in Fig. 3. It can be seen that there are two weak peaks and a strong peak. The particle size is mainly distributed among 100 to 150 μm and the mean particle size is 132.3 μm. The reason may be that macromolecular coupling agent in aqueous solution can assemble to form the micelles whose soluble segments is the shell and insoluble segments is for nuclear[8]. The big particle size may be related to the self-assemble of the original micelles and the small particle size may attribute to the dissolved block copolymer in single molecule state or the intermediate form of micelles. Meanwhile the inhomogeneity of the length of the block copolymer is also the reason for the dispersion of the particle size.

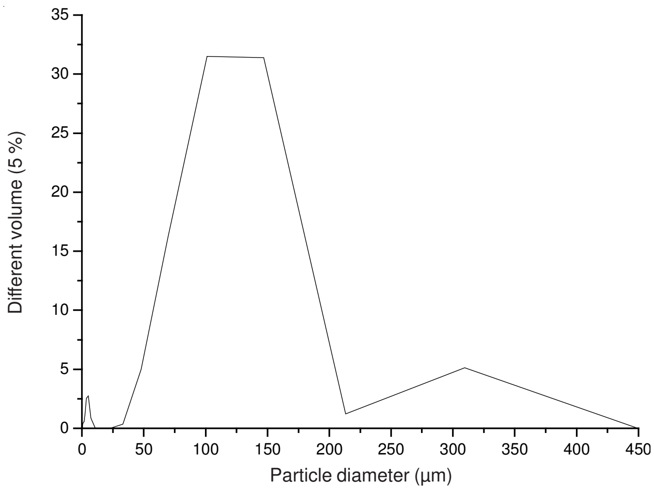


Fig. 3. Particle size of macromolecular coupling agent after hydrolysis in water

**Analysis of glass fiber surface morphology:** Fig. 4 reveals the differences of glass fiber surface morphology after treated with different coupling agent. As seen, the surface of glass fiber treated by A-151 is rough and there are many obvious saliencies and unshaped particles attached to the surface (Fig. 4a). These particles are uniformly scattered, which increase the fiber surface roughness and reaction points thus benefit the adhesion of fibers to the composite matrix. Meanwhile the surface of glass fiber treated by macromolecular coupling agent is not only rough and many obvious thin particles scattered, but also continuous film covered can be seen (Fig. 4b). In addition, compared with the appearance of glass fiber, the appearance of glass fiber treated by A-151 is bright and the stiffness is 50. In the same the appearance treated by macromolecular coupling agent is bright and has good strand integrity. The stiffness is 55, higher than the glass fiber treated by A-151. This is related to the molecular weight of coupling agent. The small molecular weight of coupling agent can be easy to form the dot structure in the surface. Otherwise, the high molecular weight is easier to form film structure in the surface. This is related to the high polymer chain. Meanwhile the thin film structure on the surface of glass fiber can increase not only the hydrophobic of glass fiber, but also the resistance to organic solvent and acid and improve the storage stability of glass fiber.

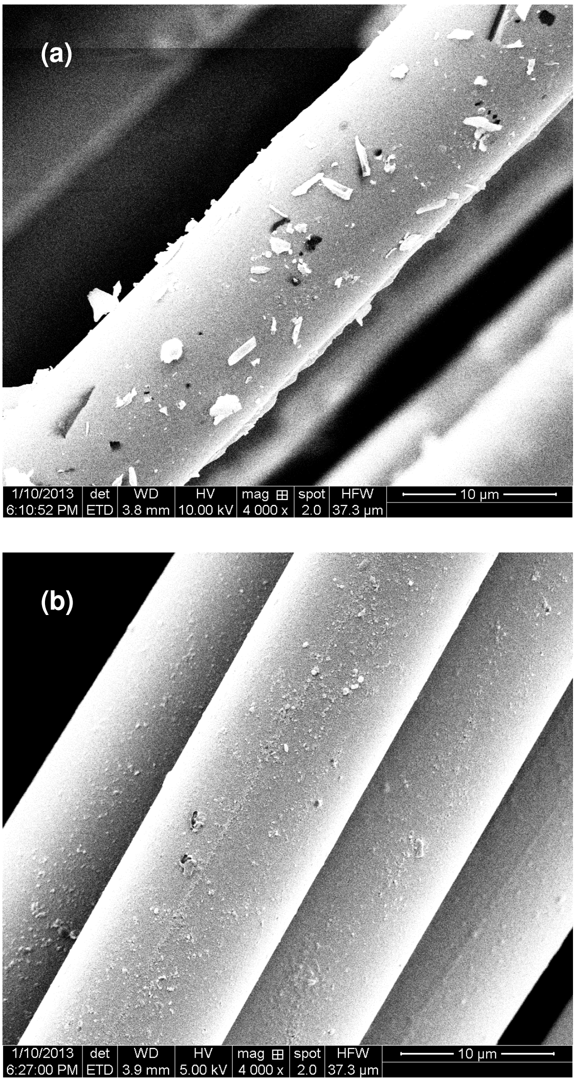


Fig. 4. SEM images of glass fiber surface treated by different coupling agent: (a) A-151 (b) macromolecular coupling agent-sample 2

**Bend strength of glass fiber/epoxy composite:** The glass fiber has been treated with the macromolecular coupling agent and A-151 respectively in the same concentration of water solution. Glass fiber/epoxy composite was prepared through method of casting mold with treated or untreated glass fiber and epoxy solution (100 copies epoxy, 10 copied triethylene tetramine) in silicone rubber mould, then cured under 80 ºC for 4 h in vacuum oven. Mechanical properties of composite are shown in Table-4. As seen, the bend strength of treated glass fiber/epoxy composite treated by A-151(1#) or macromolecular coupling agent (2 and 7) has been both improved compared to the untreated glass fiber (0#). And the bend strength of glass fiber treated by macromolecular coupling agent (2) increased 6.5 % compared to the sample treated by A-151. This is because the silicone group in macromolecular coupling agent can react with the surface of glass fiber after hydrolysis just as A-151 does and also the end epoxy group can react with the resin matrix to form chemical network structure. So the glass fiber treated by macromolecular coupling agent can form a strong interface bonding between glass fiber and resin matrix.

TABLE-4
BEND STRENGTH OF GLASS FIBER/EPOXY COMPOSITE

| Sample | 0# | 1# | 2 | 7 |
|---|---|---|---|---|
| Bend strength (Mpa) | 25.27 | 27.8 | 29.60 | 29.10 |

## Conclusion

(1) End-epoxy group macromolecular coupling agent was successfully prepared by free radical solution polymerization through using functional monomer (polyalkylene glycol allyl glycidyl ether) reacting with vinyl silane coupling agent (A-151).

(2) The block copolymer coupling agent has been prepared when the mole radio of AEPH:A-151:BPO is 1:1:1 × $10^{-3}$, reaction temperature is 80 ºC and the reaction time is 2 h. The hydrolyzate of copolymer product in water can form a transparent solution.

(3) The flexural strength of glass fiber /epoxy composites are increased 6.5 % by using the copolymer coupling agent compared with the A-151.

## ACKNOWLEDGEMENTS

This work is supported by the Natural Science Foundation of Shandong Province of China (ZR2011EL032), Scientific Research Fund of University of Jinan (XKY1001) and Fund of the Science and Technology Program of the Higher Education Institutions of Shandong Province (J13LA06).

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