Synthesis of Macromolecular Coupling Agents and Binders

A. CRESPY,[1,2,*] C. CAZE,[2] and C. LOUCHEUX[2]

[1]Ecole Nationale Supérieure des Arts et Industries Textiles, 2, Place des Martyrs de la résistance, 59070 Roubaix Cedex, France; [2]Laboratoire de Chimie Macromoléculaire U.A.-C.N.R.S. 351, Université des Sciences et Techniques de Lille Flandres Artois, 59655 Villeneuve d'Ascq Cedex, France

SYNOPSIS

Sizes of glass fibers used in composite materials include binders and coupling agents. Usually these types of compounds have a low molecular weight and present two identical reactive groups for binders and two different functions (namely, organic and inorganic groups) for the coupling agents. The aim of this paper was to describe the synthesis of macromolecular binders and coupling agents in order to perform the interphase region. These products appear as difunctional or polyfunctional compounds. Difunctional compounds were obtained by reaction between a telechelic polymer (prepared by anionic polymerization) and alkoxysilane or epoxy groups. Polyfunctional compounds were performed by hydrosilylation reactions between a polysiloxane containing hydrogenosilane functions and vinylsilane, and/or 1-allyloxy-2,3 epoxypropane.

INTRODUCTION

Sizes of glass fibers used as fillers of organic matrix are complex mixtures. Several types of compounds are mixed:

- A binder for strand integrity since the single filaments do not pack well.
- A lubricant, which provides surface lubricity and prevents abrasive damage during handling.
- A coupling agent generally considered to be an adhesion promoter between glass fibers and organic matrix resins.
- Some additives like antistating or emulsifying agents.

Binders are modified epoxy resins and they show good adhesion with glass fibers, good moistening properties, and a small thermal shrinkage that induces a minimum of stresses during cure. Sometimes, some compounds like poly(vinyl acetate) and polyurethane or some acrylate, vinyl acetate, or styrene copolymers are used.

Coupling agents used are generally organofunctional silanes $X — A — Si(B)_3$, where A is an alkyl chain, B is a hydrolyzable group (methoxy or ethoxy) that later will give the link with the filler, and X is a functional group that reacts with the organic matrix.

The nature of adhesion through silane coupling agent and fiberglass has been extensively studied.[1-7] The first step of the reaction is the hydrolysis of the covalent $Si(B)_3$ bonds to silanols by water:

$$X—A—Si (B)_3 + 3H_2O →$$

$$X—A—Si (OH)_3 + 3HB$$
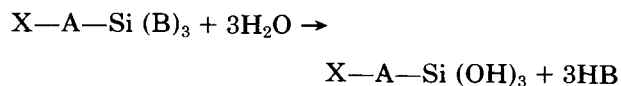
This reaction occurs at acidic pH. The second step is the adsorption on the fiberglass,[8] followed, when the temperature increases, by a condensation between the silanols from the coupling agent and from the surface of the glass[9]:
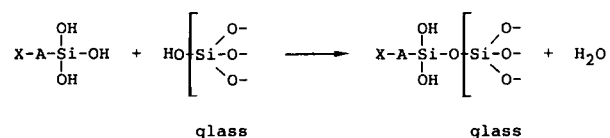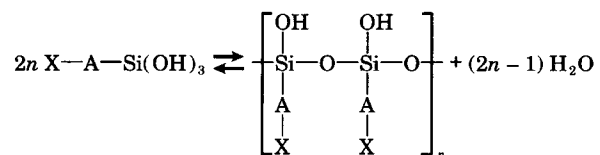

The same author[9] has shown that with methoxysilane 51% of the reacted silanol groups of the glass give a siloxane bond, 35% react with methanol to

form a Si—O—CH_3 bond, and 14% give hydrogen bonds.

A side reaction can occur between the silanols of the hydrolyzed coupling agent[1,3,10,11]:

$$2n \text{ X—A—Si(OH)}_3 \rightleftharpoons \begin{bmatrix} \text{OH} & \text{OH} \\ | & | \\ \text{Si—O—Si—O} \\ | & | \\ \text{A} & \text{A} \\ | & | \\ \text{X} & \text{X} \end{bmatrix}_n + (2n-1)\text{ H}_2\text{O}$$

This reaction must be taken into account when using silane solutions to avoid loss of activity of the coupling agent.

When using a trifunctional coupling agent, the three silanol groups cannot react with the glass surface[10] and the remaining groups may condense with adjacent silanols to form a siloxane layer. This type of reaction could explain how silane forms a multilayer system,[11-14] giving in the composite a complex system called an interphase region.

The reversible nature of siloxane bonding on the fiberglass surface has been demonstrated.[15] This equilibrium bonding may improve total composite performance by allowing a chemical relaxation of stresses across the interface.

The interphase region is composed of different compounds, binders, lubricants, coupling agents, and additives. The aim of this work is to synthesize oligomers or polymers that could act as binders and/ or coupling agents. The oligomeric nature of the products could give flexibility to the interphase. These products were obtained by reacting a silane or an epoxy compound with a living carbanionic or a silicone oligomer. In this way, we can obtain di- and polyfunctional compounds.

EXPERIMENTAL

Materials

Styrene and methylstyrene were dried over calcium hydride and distilled under vacuum prior to use. Tetrahydrofuran (THF) was dried over potassium hydroxide and then over calcium chloride. Enough sodium naphtalene solution was added to produce the characteristic green color and, finally, THF was distilled under nitrogen flux. Sodium was ridden of oxide, washed with THF, and cut in small pieces. 3-Glycidoxypropyltrimethoxysilane was kept with molecular sieve and under nitrogen.

The chemical structure of the epoxy resin (Lopox 200 from Orchem) is shown below:
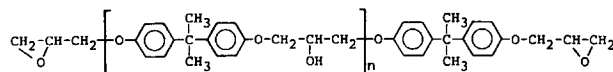
The molecular weight is 380; the n value is weak (0.14), taking into account for the polydispersity; and in the chemical scheme, we made the approximation $n = 0$.

DIFUNCTIONAL COMPOUNDS

Dicarbanionic compounds were obtained starting from α-methylstyrene tetramer (synthesized under nitrogen and in THF).[16] Styrene oligomers are obtained by slowly adding styrene to the tetramer at $-10°C$.[17,18] After that, the addition in two steps of 3-glycidoxypropyltrimethoxysilane and of 2,2-bis [4-(2,3-epoxypropoxy)phenyl]propane (DGEBA) gave the difunctional compound. The first addition was made on the living dicarbanionic oligomer by adding drop by drop a solution of silane to THF. The ratio of silane/carbanion was less than 1, so after the first addition, some living carbanions remained in the solution. This last solution was then added slowly to a solution of DGEBA in THF. At each step, samples were taken to perform analysis (after deactivation with methanol).

Polyfunctional Compounds

The characterization of polysiloxane copolymers used as starting materials and the preparation by acid catalysis of cyclic and linear oligomers has already been described.[19,20] The amount of SiH units was determined by hydrogen volumetry after reaction with alcoholic potassium hydroxide.

Polysiloxane containing pendant trimethoxysilane and/or glycidic groups was obtained by hydrosilylation with vinyltrimethoxysilane and/or 1-allyloxy-2,3-epoxypropane (AEP) in toluene. We used a ratio of SiH/vinyl = 1.05 when the object of hydrosilylation of the initial SiH content is 100%. The reaction was performed at 80°C with a Speier catalyst.[21] Reactions were monitored by IR spectroscopy using the absorption of the SiH group at 2150 cm^{-1} (stretching mode). Titration of epoxy groups was performed according to Jay.[22]

Characterizations

The average number molecular weights were obtained by a vapor pressure osmometer (Knauer

Dampfdruck osmometer) or by gel permeation chromatography with a Waters apparatus. For the last case, three columns were used (10^4, 10^3, and 500 Å), calibrated with polystyrene standards and coupled with a differential refractometer. Elutions were carried out at room temperature with THF (difunctional compounds) or toluene (polyfunctional compounds) as solvents and with a flow rate of 1 mL mn^{-1}. ^{1}H-NMR spectra was recorded on Bruker WP 60 spectrometer, and IR spectra, on a Perkin-Elmer 882 spectrophotometer.

RESULTS AND DISCUSSION

Difunctional Compounds

As for classical coupling agents, we have synthesized difunctional oligomeric products with two chemically different functional groups like Si(B)$_3$ and epoxy or two Si(B)$_3$ groups; the first compound could react as the coupling agent and the second one as the binder.

Starting from a living polystyrene (3000–4000 g mol^{-1}), the chemical modification occurs in two steps: addition of 3-glycidoxypropyltrimethoxysilane in order to functionalize 75% of the original carbanion content, and then the mixture was slowly dropped into DGEBA to give the final products seen in Scheme 1.

Characterization of products **IV** and **V** requires the separation of these two products from the mixture. This separation was made by precipitation in methanol of product **V** from a benzenic solution of the mixture **IV** and **V**. The functionalization of the living polymer by the silane agent was followed by ^{1}H-NMR [Si(OCH3)$_3$ at 3.5 ppm] and the addition of DGEBA by IR (absorption of the epoxy group at 915 and 1250 cm^{-1}) and chemical analysis. The molecular weights of the different products **I**, **II**, **IV**, and **V** determined by vapor pressure osmometry and gel permeation chromatography are reported in Table I.

It is possible to determine the percentage of silane introduced starting from the molecular weight of compound **II** and from ^{1}H-NMR spectra of the mixture of compounds **III** and **IV**. The ratio of the resonance between 2.9 and 3.7 ppm (due to some resonances of the silane agent as we can see in Table II which gives the ^{1}H resonance of 3-glycidoxypropyltrimethoxysilane) and between 6.5 and 7.2 (aromatic ring) allows us to calculate the ratio of silane. The percentage of silane bound was 60%; this cor-

respond to a yield of 80%. As we can see in Table I, the polydispersity increases with the successive chemical modifications and the measured molecular weight is higher than expected theoretically. These observations can be related to side reactions involving epoxy groups (of course, we have worked at low temperature in order to minimize side reactions, but as we can see, some of these occur).

From **II** to **IV**, we have the formation of secondary alcoholate functions. We can envisage the possibility of a reaction between these groups and epoxy groups, but

- their reactivities are smaller than those of the carbanionic species present in the solution, and
- this reaction does not occur with primary alcohol where only a pseudo-network formed by an ion-pair association of the alcoholate was observed during the termination of a living polymer with ethylene oxide.[23]

Functionalization by DGEBA could induce side reactions:

- When the carbanionic solution was added drop by drop to DGEBA, some diadditions could occur, inducing double molecular weight:
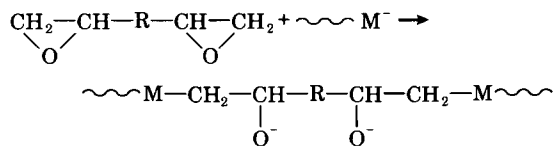
- If some dicarbanionic species remain in the solution, we can have formation of polyalcohol[23]:
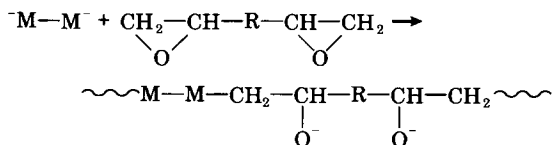
However, this reaction can be excluded because the dicarbanionic species has reacted in a first step with a relative excess of silane compound. Other side reactions between epoxy and hydroxy groups or polymerization of epoxy could be cited, but they are only significant at high temperature.[24,25]

The increases of the molecular weight observed for compound **V**, confirmed by the chemical titrations of epoxy groups (M = 5200 g mol^{-1}), is too high; this observation can be related to the diaddition reaction cited above.

$$Na^+, {}^-\!\underset{\underset{\bigcirc}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{\bigcirc}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-\underset{\underset{\bigcirc}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{\bigcirc}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^-, Na^+$$

Tetramer (I)

Styrene

$$Na^+, {}^-CH\text{-}CH_2\!\!\left[CH\text{-}CH_2\right]_x\!\!\text{-tetramer-}\!\!\left[CH_2\text{-}CH\right]_y\!\!CH_2\text{-}CH^-, Na^+$$

Polystyrene (II)

$$CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$$
(over O)

(75%)

$$A\!\!\left[CH\text{-}CH_2\right]_{x+1}\!\!\text{-tetramer-}\!\!\left[CH_2\text{-}CH\right]_y\!\!B$$

Compound (III)
(≈ 50%)

$$B\!\!\left[CH\text{-}CH_2\right]_x\!\!\text{-tetramer-}\!\!\left[CH_2\text{-}CH\right]_y\!\!B$$

Compound (IV)
(≈ 50%)

DGEBA

$$C\!\!\left[CH\text{-}CH_2\right]_x\!\!\text{-tetramer-}\!\!\left[CH_2\text{-}CH\right]_y\!\!B$$

Compound (V)

$$B\!\!\left[CH\text{-}CH_2\right]_x\!\!\text{-tetramer-}\!\!\left[CH_2\text{-}CH\right]_y\!\!B$$

Compound (IV)

A : $CH_2\text{-}CH^-, Na^+$

B : $CH_2\text{-}CH\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}O(CH_2)_3\text{-}Si(OCH_3)_3$
     O^-, Na^+

C : $CH_2\text{-}CH\text{-}CH_2\text{-}O\text{-}\bigcirc\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}\bigcirc\text{-}O\text{-}CH_2\text{-}CH\text{-}CH_2$
     O^-, Na^+ ... O

Scheme 1

Polyfunctional Compounds

For difunctional compounds, epoxy and trimethoxysilane groups are fixed at the end of the chain; for polyfunctional compounds, they are grafted onto the polymer chain. For this purpose, we start from a poly(dimethylsiloxane) - co - (methylhydrogenosiloxane) and we graft 1-allyloxy-2,3-epoxypropane (AEP)[26] or vinyltrimethoxysilane (both polymers obtained by this way could act as binders). Moreover, AEP and vinyltrimethoxysilane were bound in two successive steps in order to obtain a polymer acting as a binder and as a coupling agent at the same time. In these two cases, the chemical modification is performed by a hydrosilylation reaction (Scheme 2) monitored by ^{1}H-NMR (disappearing of the resonance of SiH and vinyl groups, respectively, at 4.65 and 5.8–6.2 ppm) and IR spectrophotometry (disappearing of SiH absorption at 2150 cm^{-1}). The yield of the hydrosilylation reaction for the two cases is near 100%. The molecular weights and the chemical characteristics of the two initial polysiloxanes (polymer 1a and 1b) used and of the resulting polymers modified by AEP (polymer 2a and 2b) are reported in Table III, and those of polymers modified by vinyltrimethoxysilane (A) or vi-

Table I   Molecular Weights of Difunctional Compounds

Samples	M_n Calculated	$M_n{}^a$	$M_n{}^b$	$M_w{}^b$	$I^b = M_w/M_n$
I	474	500	—	—	—
II	3500	3600	3700	4400	1.19
IV	4072^c	4300	4700	6550	1.39
V	4216^c	5450	5550	8700	1.57

^{a} Obtained by vapor pressure osmometry (g mol^{-1}).

^{b} Obtained by GPC (g mol^{-1} polystyrene equivalent).

^{c} Calculated from the experimental value reached by vapor pressure osmometry for sample II.

nyltriethoxysilane (B), in Table IV. These results confirm that there is no influence of the alkoxy group of the vinylsilane used and that the yield of grafting is near 100%; so it is now possible to adjust different parameters, as, for example:

- the chemical nature of the functions grafted,

- the ratio of these functions, and
- the molecular weight of the polymer.

Now, as seen before, it is also possible to synthesize polymers grafted in the same way but in two steps: (i) reaction with vinyltrimethoxysilane, and (ii) reaction with AEP, resulting in a polyfunctional poly-
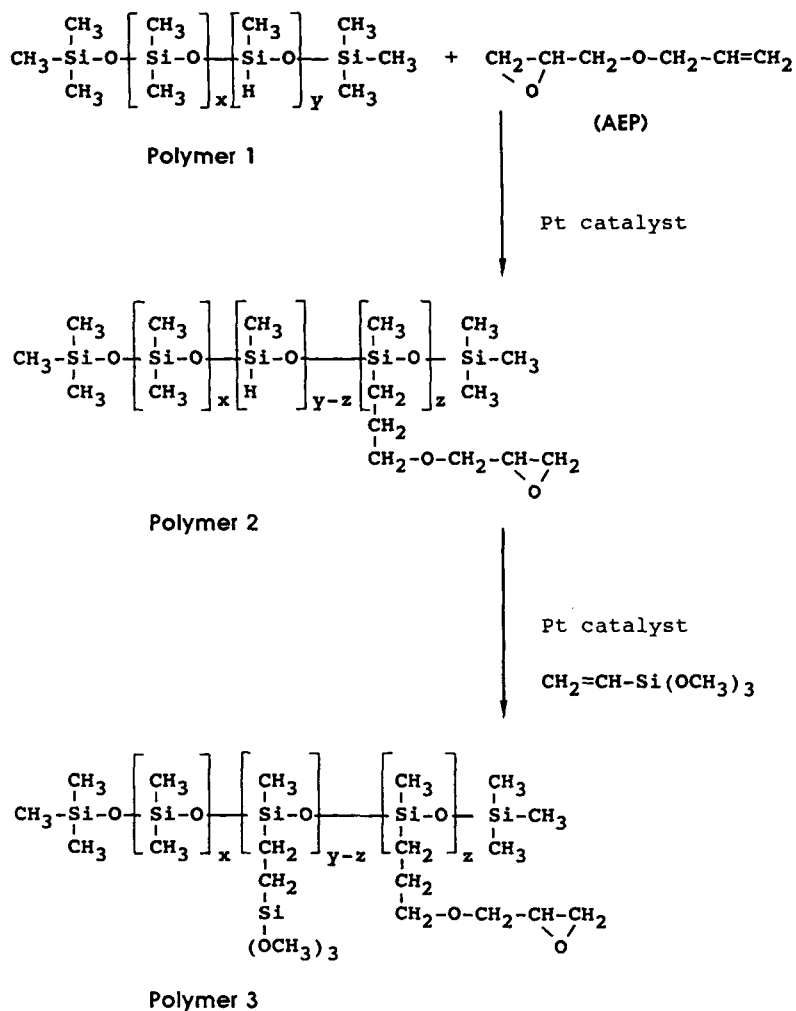
Scheme 2

Table II ¹H-NMR Data for 3-Glycidoxypropyltimethoxysilane:

(g)   (f)   (e)   (d)   (c)   (b)   (a)

CH₂—CH—CH₂—O—CH₂—CH₂—CH₂—Si(OCH₃)₃
      \O/

	Assignment				
	(a)	(b)	(c)	(d), (e), (f)	(g)
Chemical shifts (ppm)	3.5	0.7–0.8	1.7–1.8	2.9–3.7	2.4–2.7

Table III **Characteristics of Polysiloxanes 1a and b and 2a and b**

Polymer	M_n	DPn^c	Si—H^d (mol %)	Epoxy^d (mol %)
1a	2,200^a	31	17	—
1b	2,800^a	31	—	17
2a	9,600^b	130	10	—
2b	11,000^b	130	—	9.2

^{a} Average number molecular weight obtained by vapor pressure osmometry (g mol⁻¹).
^{b} Average number molecular weight obtained by GPC (g mol⁻¹).
^{c} Average number of siloxane units per chain.
^{d} Molar content in reactive siloxane units (chemical titration).

mer containing two different chemical functions. As an example, starting from a liquid polysiloxane (M_n = 2200 g mol⁻¹) containing 17% of hydrogenosilane function (molar ratio), we have made the first modification in order to functionalize 80% of the initial hydrogenosilane by AEP and the remains 20% by trimethoxysilane. Starting from the molecular weight and the chemical analysis of the resulting polymer, we have observed a yield close to 100% for these two modifications.

CONCLUSIONS

We have synthesized some macromolecular binders and coupling agents; these compounds could act as a third component in the interphase region.

Difunctional compounds were obtained by anionic polymerization and modification, so we can

easily control the molecular weight of the compound, and products obtained in this way present a low polydispersity index.

The hydrosilylation reaction was used in order to synthesize polyfunctional compounds, so it is easy to check the ratio of epoxy/silane for the compound used as coupling agent.

The performance of macromolecular coupling agents and binders obtained are now evaluated using a pullout test in order to determine their efficiency and the influence of

- the molecular weight of the polymer chain and
- the percentage of grafting and of the ratio of silane/epoxy for polyfunctional compounds.

REFERENCES

1. E. P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
2. J. L. Koenig and H. Emadipour, *Polym. Composites*, **6**, 142 (1985).
3. H. A. Clark and E. P. Plueddemann, *Mod. Plast.*, **40**(6), 133 (1963).
4. H. Ishida and J. L. Koenig, *J. Colloid Interface Sci.*, **64**, 565 (1978).
5. C. H. Chiang and J. L. Koenig, *Polym. Composites*, **2**, 192 (1981).
6. H. Ishida and J. L. Koenig, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 615 (1979).

Table IV **Average No. Molecular Weights (g mol⁻¹) of Polymer 1a**

Silane	M_n (Polymer 1a)	M_n^a (calc)	M_n^a (exp)
A (M = 148 g)	2200	2980	3000
B (M = 190 g)	2200	3200	3150

^{a} Polymer 1a functionalized by silanes.

7. H. W. C. Yip and J. B. Shortall, *J. Adhesion,* **8,** 155 (1976).

8. F. O. Stark, O. K. Johannson, G. E. Vogel, R. G. Chaffee, and R. M. Lacefield, *J. Phys. Chem.,* **72,** 2750 (1968).

9. W. Hertl, *J. Phys. Chem.,* **72,** 1248 (1968).

10. D. L. Chamberlain, M. V. Christensen, and M. Bertolucci, in *SPI, 24th Ann. Tech. Conf. Reinf. Plast. 19-C,* 1969.

11. B. Chabert, J. Chauchard, M. Escoubes, P. Jeanne, and T. M. Lam, *Bull. Soc. Chim. Fr.,* **1,** 11 (1988).

12. S. Wu, *Polymer Interface and Adhesion,* Marcel Dekker, New York, 1982.

13. H. Ishida and G. Kumar, *Molecular Characterization of Composite Interfaces,* Plenum Press, New York, 1985.

14. H. Ishida and J. L. Koenig, *J. Polym. Sci. Polym. Phys. Ed.,* **17,** 1807 (1979).

15. H. Ishida and J. L. Koenig, *J. Polym. Sci. Polym. Phys. Ed.,* **18,** 233 (1980).

16. D. H. Richards and R. L. Williams, *J. Polym. Sci. Polym. Chem. Ed.,* **11,** 89, (1973).

17. A. Crespy and M. J. M. Abadie, *Eur. Polym. J.,* **17,** 213 (1981).

18. A. Crespy and M. J. M. Abadie, *Eur. Polym. J.,* **17,** 221 (1981).

19. E. Lemaître, X. Coqueret, R. Mercier, A. Lablache-Combier, and C. Loucheux, *J. Appl. Polym. Sci.,* **33,** 2189 (1987).

20. R. Mercier, X. Coqueret, A. Lablache-Combier, and C. Loucheux, *Eur. Polym. J.,* **24,** 639 (1988).

21. J. L. Speier, J. A. Webster, and G. H. Bernes, *J. Am. Chem. Soc.,* **79,** 974 (1957).

22. R. R. Jay, *Anal. Chem.,* **36,** 667 (1964).

23. D. H. Richards, in *Developments in Polymerization,* R. N. Haward, Ed., Applied Science, Barking, Essex, UK, 1978.

24. M. F. Grenier-Loustalot, F. Cazaux, and P. Grenier, *Makromol. Chem.,* **187,** 1855 (1986).

25. J. Ancelle, A. J. Attias, B. Bloch, F. Laupretre, and L. Monnerie, *Makromol. Chem. Macromol. Symp.,* **9,** 123 (1987).

26. X. Coqueret, A. Lablache-Combier, and C. Loucheux, *Eur. Polym. J.,* **24,** 713 (1988).