Colloid Polym Sci 278:665–670 (2000)

SHORT COMMUNICATION

Y. W. Park
J. E. Mark

Toughening of polyamides by the in situ generation of elastomeric phases

Received: 30 September 1999
Revised manuscript: 10 January 2000

Y. W. Park · J. E. Mark (✉)
Department of Chemistry and
the Polymer Research Center
The University of Cincinnati,
Cincinnati OH 45221-0172, USA
E-mail: markje@email.uc.edu

Present address:
Y. W. Park,
Department of Polymer Science
and Engineering
Gyeongsang National University
900 Kajwa-Dong
Jinju 660-701, Korea

Abstract Samples of a commercial Trogamid polyamide (an aromatic "nylon") were modified with two silane coupling agents. In the case of the epoxysilyl agent, the silane was incorporated as a side chain by reacting it with the sample at 50–60 °C for 3 days, with triethylenediamine as catalyst. In contrast, an isocyanatosilyl compound was added only to the polyamide end groups (carboxylic acid and amine groups). The polyamide–epoxy composites were linked with a difunctional silane and were then dried into films. They exhibited some improved ultimate properties, including toughness, at the lower epoxysilane contents. In particular, the tensile strengths of the samples that were annealed at 120 °C were greatly improved. Also, the maximum extensibility was increased by increasing the amount of difunctional silane, but at the cost of decreased tensile strengths. The Trogamid isocyanatosilyl materials, on the other hand, showed properties similar to those of polyamides reinforced with silica generated in situ by the hydrolysis of tetraethoxysilane. Specifically, the tensile strengths of these composites increased slightly, but at the cost of decreased toughness. Although it was not possible to improve all the mechanical properties of either type of composite simultaneously, it was possible to identify the conditions for maximizing at least one or two of them at a time. Thus, the results provided guidance on how to optimize the properties of an important class of polyamides for any particular application.

Key words Aromatic polyamides · Nylons · Organic–inorganic composites · Silica · Coupling agents

Introduction

There have now been numerous reports describing the preparation and characterization of organic–inorganic composites. Typically, this involves reinforcing a polymer by the in situ generation of a ceramic-type filler [1–14], for example, by the hydrolysis and condensation of a multifunctional organosilicate. The most important example is the precipitation of silica from tetraethylorthosilicate (TEOS) [$Si(OC_2H_5)_4$].

The degree of homogeneity and the adhesion between the organic (polymer) and inorganic (ceramic) components can be improved by using a bonding agent. This can result in greatly improved mechanical properties and transparency. Such molecules generally have one end which is sufficiently organic to embed into the polymer phase with the other end a trialkoxy silane group which can anchor into the ceramic phase by cohydrolyzing with the TEOS. It is sometimes possible to avoid the necessity for such a bonding agent in the case of polymers which can participate in specific interactions, such as the hydrogen bonding with the reinforcing phase. For example, it has been shown that transparent composites can be obtained by acid catalyzed hydrolysis and condensation of TEOS in poly(vinyl acetate) [11], poly(methyl methacrylate) [12] and a polyphosphazene [13]. Another synthetic approach utilizes organic polymers funtionalized with trialkoxysilane moieties, which facilitate cross-linking between the polymer and the growing ceramic network. A specific example involved bonding polyamide chains into a ceramic matrix by means of such hydrolyzable groups placed at the ends of the chains [15–19]. Because of the limited number of chain ends available in a linear polyamide of reasonably high molecular weight, the improvements in interfacial bonding were limited [10]. This limitation was ameliorated to some extent by dealing with branched chains, but the branching required can interfere with other properties of the composite.

The approach taken in the present investigation relies on the fact that the numerous amide hydrogen atoms of a polyamide can be reacted with functionalized silanes, thus generating coupling groups. It focuses on Trogamid T [poly(trimethylhexamethylene terephthalamide)], which is a commercially available aromatic polyamide with good rigidity, low thermal expansion coefficient, good thermal resistance and insulating properties. More important in the present context is the fact that this polyamide is readily soluble in convenient solvents. This solubility is the result of the design of its repeat unit; it has a mixture of 2,2,4 and 2,4,4 units and this irregularity suppresses some of the crystallinity which would otherwise make the polymer less tractible. Another novel aspect of the present investigation is the use of trifunctional and difunctional organosilicates in the generation of the dispersed phases. The resulting phases should be rubbery because of the generation of siloxane-like structures [-Si*RR′*O-], in addition to the much harder, glassy silica-like phases generated from the tetrafunctional TEOS. This approach is obviously closely related to the now-standard method for toughening polymers in general, by the introduction of a dispersed rubbery phase, and various types of elastomers have now been used in both thermoplastics and thermosets [20–23]. As has been done for many years, however, such phases have been dispersed into a polymer by mechanical blending, but this process is time-consuming and energy-intensive. Moreover, it is very difficult to control the structure of the resulting composite material. There is frequently, for example, inhomogeneous dispersion of the phases, giving less than optimal improvements in mechanical properties. The present in situ technique has the advantage of avoiding these complications.

The composites obtained by this toughening technique are characterized with regard to their mechanical properties in elongation, with the results obtained being interpreted in terms of possible chemical bonding and adhesion between the continuous and dispersed phases.

Experimental

Materials

A sample of Trogamid T was donated by Hüls America, and it was dried in a vacuum oven for 12 h at 50 °C before use. The "isocyanatosilane"chosen was 3-isocyanatopropyltriethoxysilane (95% pure), and it was purchased from Gelest. The "epoxysilane"was 3-glycidoxypropyltrimethoxysilane (98%), the solvent anhydrous dimethylacetamide (DMAc), the catalysts 1,4-diazabicyclo[2,2,2]-octane (triethylenediamine) (98%) and diethyl amine (99%) and the other silanes methyltrimethoxy silane (98%) and diethoxydimethysilane (97%). They were all purchased from Aldrich and were used as received.

Synthesis of polyamide with coupling agent

A mixture of the polyamide (10 g) and one of the catalysts (0.3 g) was placed into a 250-ml Erlenmeyer flask with a magnetic stirrer and dried in a vacuum oven at 50 °C for 24 h. The mixture was then capped with a rubber septum connected to a balloon filled with nitrogen. Anhydrous DMAc was added to the flask and the solution was stirred for 4 h at 50 °C for complete dissolution. The contents of the flask were then cooled to room temperature and the desired amount of 3-isocyanatopropyltriethoxysilane or 3-glycidoxypropyltrimethoxysilane was added. The mixture was reacted for 3 days at 50–60 °C while stirring, and the product was kept in solution for use as described later.

Preparation of amide–silane hybrid films

A known amount of polymer solution was taken and a chosen amount of diethoxydimethylsilane (in DMAc) was added to it. The mixture was stirred for 30 min, and then a stoichiometric amount of water containing 5% of diethylamine as a catalyst in DMAc was added to begin the hydrolysis and condensation. The resulting homogeneous mixture was stirred for an additional 6 h at room temperature and then cast in a Teflon mold, which was held at 50 °C to complete the reaction. The mixture was dried under vacuum at 70–80 °C for 96 h, and the resulting films were kept under vacuum until they had been characterized.

Characterization of composites

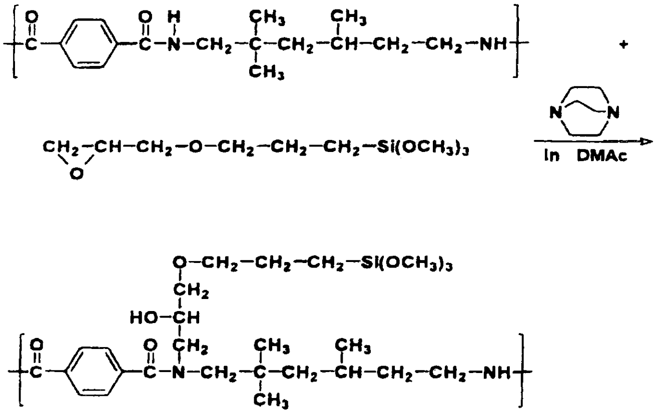
The IR spectra were recorded on a Perkin-Elmer 1600 series Fourier transform IR spectrometer.

The tensile properties of the hybrid films were measured using an Instron universal testing instrument at room temperature. The extension rate was 5 mm/min, the sample dimensions were approximately 40 × 5 × 0.2 mm and the distance between the Instron clamps was 25 mm. Some of the mechanical property measurements were carried out on samples that had been annealed at a carefully chosen temperature for varying amounts of time.

Results and discussion

IR results

(a) *Epoxysilane*: The reaction of the epoxy silane and the Trogamid polyamide is shown in Scheme 1. In this reaction, the catalyst, triethylenediamine, was found to be more active than the 1-methylimidazole frequently used for such work. The IR spectra of the reaction product indicated the presence of a broad OH stretching vibration band at 3300–3600 cm^{-1} and reduction of the sharp N-H stretching band of the amide group at 3300 cm^{-1}. This confirmed that the desired covalent bonding occurred between the amide N-H group and the epoxy group. The stretching vibration band of Si-O-Si at 1000–1100 cm^{-1} was increased sharply upon increasing the amount of bonding agent.



Scheme 1 Synthesis of polyamide with epoxysilane coupling agent

(b) *Isocyanatosilane*: These measurements were carried out to moniter the possible reaction of the isocyanate groups with the amide hydrogens. The relevant regions of the spectrum were the N-H stretching vibration at 3300 cm^{-1}, and the C=O stretching vibration at 1600–1700 cm^{-1}. There were no changes relative to the original polyamide itself, indicating that these reactions did not occur. The isocyanate groups, however, did react with the polyamide COOH and NH$_2$ end groups, producing some coupling groups, as desired.

Effects of epoxysilane content

Figure 1 and Table 1 present the stress-strain results obtained on the reaction products of the polyamide and epoxysilane. Generally, having bulky side chains such as an epoxysilane on a polyamide reduces hydrogen bonding and interferes with the close packing of polymers. Although this can reduce mechanical properties, the subsequent cross linking between chains can enhance the mechanical strength. For the samples with low epoxysilane contents, the tensile strength was greatly reduced due to the lower hydrogen bonding, but the increases in maximum elongation gave substantial increases in toughness.

Effects of isocyanatosilane content

Figure 2 shows the stress–strain isotherms obtained for the polyamide–isocyanatosilane composites, with Table 2 presenting the ultimate properties obtained from these curves. The tensile strength of the polyamide itself was 48.5 MPa and was found generally to increase significantly with an increase in the amount of isocy-

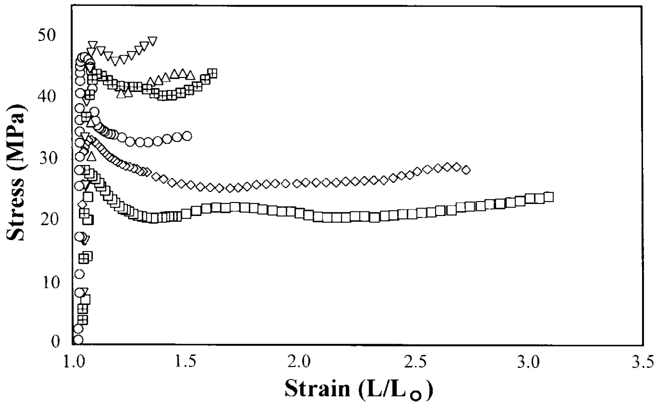


Fig. 1 Stress–strain curves for polyamide with various epoxysilane contents: (○) 0, (□) 20, (◇) 40, (△) 60, (⊞) 80, (▽) 100 mol%/segment

Table 1 Mechanical properties of the polyamide (Trogamid)–epoxysilane composites

Epoxysilane contents (mol%)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
0	48.5	48.5	15.5
20	27.3	207	45.0
40	33.2	175	47.6
60	44.9	52.1	21.4
80	44.4	60.1	24.6
100	49.7	33.4	15.4

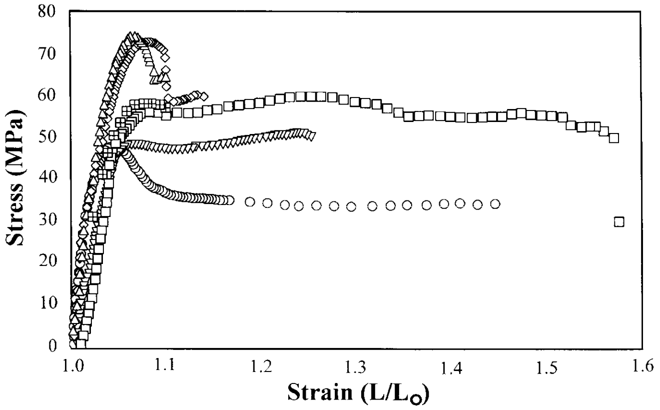


Fig. 2 Stress–strain curves for the polyamide with various isocyanatosilane contents; see legend to Fig. 1

Table 2 Mechanical properties of the polyamide (Trogamid)–isocyanatosilane composites

Isocyanatosilane contents (mol%)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
0	48.5	48.5	15.5
20	59.9	67.5	30.9
40	73.5	15.2	7.9
60	74.9	9.8	5.4
80	58.6	10.4	5.2
100	51.9	22.7	11.3

Table 3 Mechanical properties of the annealed polyamide (Trogamid)–epoxysilane composites

Epoxysilane contents (mol%)	Annealing time (days)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
20	0	27.3	207	45.0
	3	53.1	16.0	6.1
	7	65.0	8.8	3.6
40	0	33.2	175	47.6
	3	59.5	17.0	9.0
	7	69.9	7.2	3.3

anatosilane. It reached a maximum value at 60 mol%, in a way that is reminiscent of the behavior of polyamide hybrid composites containing silica from the hydrolysis of TEOS [16]. The present increase in tensile strength, 55%, is much larger than that observed for the polyamide hybrid composites using TEOS, specifically 25%. The maximum elongation decreased correspondingly, limiting the increase in toughness to that for approximately 20 mol% isocyanatosilane. This increase is quite substantial, however. The coupling agent obtained by reacting the isocyanate with the polymer's COOH and NH_2 end groups was obviously effective at enhancing adhesion between the two phases, with corresponding improvements in mechanical strength. The isocyanate groups can also react with one other and with silanols and form an isocyanatosilane which is tetrafunctional, as is the TEOS.

Effects of aging in the epoxysilane composites

The dependences of mechanical properties on annealing of the epoxysilane hybrid samples are shown in Fig. 3 and Table 3. The samples had been annealed at 120 °C for either 3 or 7 days. The tensile strengths of the annealed samples were greatly improved, presumabaly due to increases in cross-link density and closer molecular packing. Decreases in extensibility, however, caused large decreases in toughness. Annealed samples that had an epoxysilane content above 60 mol%/segment were too brittle for tensile measurements.

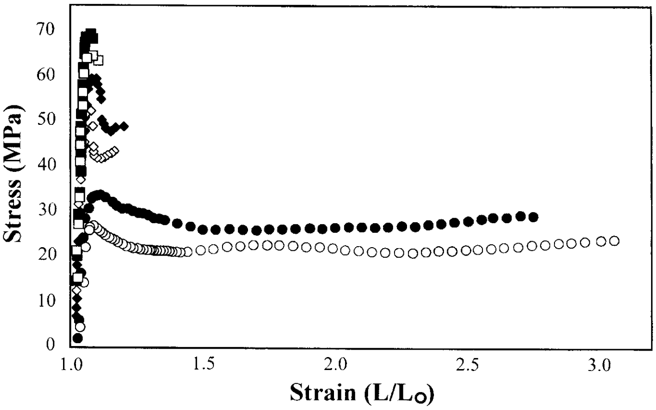


Fig. 3 Stress–strain curves for polyamide–epoxysilane composites with various aging times at 120 °C. For 20 mol%/segment epoxysilane; (○) 0, (◇) 3, (□) 7 days. For 40 mol%/segment epoxysilane; (●) 0, (◆) 3, (■) 7 days

Effects of methyltrimethoxysilane in the isocyanatosilane composites

The stress–strain results obtained by incorporating this trifunctional silane in the 40 mol%/segment polyamide–isocyanatosilane composites gave values of the ultimate strength that were approximately constant around 70 MPa, ultimate elongations that decreased from approximately 47 to 14% and values of the toughness that decreased from approximately 24 to 8 MPa. Samples modified with this silane were therefore not investigated further.

Effects of dimethyldiethoxysilane in the isocyanatosilane composites

The stress–strain results obtained by adding the difunctional silane (diethoxydimethylsilane) to the 40 mol%/segment polyamide–isocyanatosilane composite are presented in Table 4. This silane caused decreases in tensile strength, presumably because of the flexibility intro-

Table 4 Mechanical properties of the polyamide–isocyanatosilane composite (40 mol%) with dimethydiethoxy (difunctional) silane

Difunctional silane contents (wt% basis on SiO_2)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
10	62.1	21.7	11.7
20	46.1	24.2	8.9
30	35.1	117.7	36.5
40	29.5	65.8	17.8
50	23.2	63.1	13.5

duced through its siloxy group. The maximum elongation increased significantly, however, giving at least some substantial increases in toughness.

Effects of dimethyldiethoxysilane in the epoxysilane composites

The stress–strain results obtained upon introducing the difunctional silane (diethoxydimethylsilane) into the 40 mol%/segment polyamide–epoxysilane composite are documented in Fig. 4 and Table 5. The tensile strengths of these samples also decreased with an increase in amount of the silane. Increases in extensibility, however, did give some increases in toughness. The results, in general, indicate that the epoxysilane was a better coupling agent than the isocyanatosilane, at least for this polymer.

Effects of epoxysilane content in the dimethyldiethoxysilane composites

The 20 mol% and 40 mol% polyamide–epoxysilane composites are compared with 20 wt% difunctional silane (SiO_2 basis) in Fig. 5 and Table 5. The former had a lower value of the ultimate strength, but a higher value of the extensibility. This demonstrates the importance of the polymer itself on the types of improvements obtained.

Table 5 Mechanical properties of the polyamide–epoxysilane composite with dimethyldiethoxy (difunctional) silane

Epoxysilane contents (mol%)	Difunctional silane contents (wt% basis on SiO_2)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
40	10	57.1	41.2	22.8
	20	57.3	69.5	35.6
	30	43.2	53.1	22.6
	40	40.7	68.9	24.3
	50	36.6	102	32.6
20	20	40.6	173	61.0

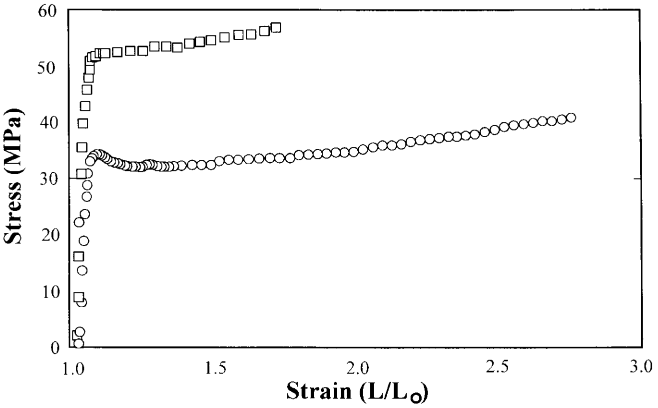


Fig. 5 Stress–strain curves for polyamide and dimethydiethoxysilane (20 wt% based on SiO_2) with various epoxysilane contents: (○) 40 and (□) 20 mol%

Conclusions

Two silane coupling agents were used to modify samples of a polyamide, which was then studied with regard to its mechanical properties. In the case of the epoxysilyl agent, there were some improvements in ultimate properties, including toughness, at the lower epoxysilane contents. For example, the sample with 20 wt% difunctional silane had a tensile strength that was still high and the toughness was greatly improved. For the 20 and 40 mol% polyamide–epoxysilane composites with 20 wt% difunctional silane, the 40 mol% sample had higher tensile strength but lower toughness than the 20 mol% sample. The isocyanatosilyl-treated samples, in contrast, showed properties similar to those of silica-reinforced polyamides. Specifically, the tensile strengths of these composites increased slightly, but at the cost of decreased toughness. The resulting structure–property relationships should be useful in modifying those properties of a polyamid that are of particular importance in a given application.

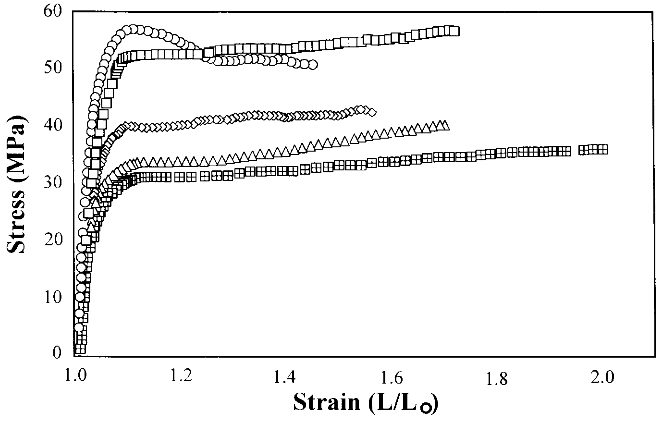


Fig. 4 Stress–strain curves for the polyamide and 40 mol%/segment epoxysilane with various dimethydiethoxysilane contents: (○) 10, (□) 20, (◇) 30, (△) 40, and (⊞) 50 wt%, based on equivalent SiO_2 contents

Acknowledgement It is a pleasure to acknowledge the financial support provided by the US Air Force Office of Scientific Research through grant F49620-96-10052 (Directorate of Chemistry and Materials Science).

References

1. Mark JE (1985) Br Polym J 17:144
2. Huang H-H, Orler B, Wilkes GL (1987) Macromolecules 20:1322
3. Ellsworth MW, Novak BM (1991) J Am Chem Soc 113:2756
4. Novak BM, Davies C (1991) Macromolecules 24:5481
5. Novak BM (1993) Adv Mater 5:422
6. Mark JE (1996) Hetero Chem Rev 3:307
7. Wen J, Wilkes GL (1996) In: Salamone JC (ed) Polymeric materials encyclopedia: synthesis, properties, and applications. CRC, Boca Raton, p 4782
8. Mark JE (1996) Polym Eng Sci 36:2905
9. Mark JE, Premachandra J, Kumudinie C, Zhao W, Dang TD, Chen JP, Arnold FE (1996) In: Coltrain BK, Sanchez C, Schaefer DW, Wilkes GL (eds) Better ceramics through chemistry VII: organic/inorganic hybrid materials. Materials Research Society, Pittsburgh, p 93
10. Erman B, Mark JE (1997) Structures and properties of rubberlike networks. Oxford University Press, New York
11. Landry CJT, Coltrain BK, Landry MR, Fitzgerald JJ, Long VK (1993) Macromolecules 26:3702
12. Landry CJT, Coltrain BK, Brady BK (1992) Polymer 33:1486
13. Coltrain BK, Ferrar WT, Landry CJT, Molaire TR, Zumbulyadis N (1992) Chem Mater 4:358
14. Sur GS, Mark JE (1986) Makromol Chem 187:2861
15. Wang S, Ahmad Z, Mark JE (1994) Chem Mater 6:943
16. Ahmad Z, Wang S, Mark JE (1995) In: Mark JE, Lee C Y-C, Bianconi PA (eds) Hybrid organic-inorganic composites. ACS Symposium Series 585. American Chemical Society, Washington, DC, p 291
17. Ahmad Z, Sarwar MI, Mark JE (1997) J Appl Polym Sci 63:1345
18. Ahmad Z, Sarwar MI, Mark JE (1997) J Mater Chem 7:259
19. Ahmad Z, Sarwar MI, Wang S, Mark JE (1997) Polymer 17:4523
20. Paul DR, Sperling LH (eds) (1986) Multicomponent polymer materials. Advances in Chemistry Series 211. American Chemical Society, Washington, DC
21. Riew CK (ed) (1989) Rubber-toughened plastics. Advances in Chemistry Series 222. American Chemical Society, Washington, DC
22. Brydson JA (1989) Plastic materials, 5th edn. Butterworths, London
23. Collyer AA (ed) (1994) Rubber toughened engineering plastics. Chapman & Hall, New York