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A polyamide-silica composite prepared by the sol-gel process

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Summary

A new kind of organic-inorganic hybrid composite was prepared by means of the sol-gel process. The polymer employed was a mixed-isomer aromatic polyamide having good solubility and thermal stability. The silica constituting the inorganic phase was produced by the hydrolysis and condensation of tetramethoxysilane. The bonding between the phases involved aminophenyl-trimethoxysilane, in which the amino group can react with the phthaloyl chloride end-capped polymer, and the methoxysilane groups undergo hydrolysis. The composition of these composites was varied by changing the linear polymer chain length and relative amount of tetramethoxysilane. The gelation time was found to range from a few minutes to several days. Thermogravimetric analyses showed that decomposition starts at approximately 450 °C. Thin films cast from materials having a relatively high silica content were opaque and rigid, but those with low silica content were flexible and transparent.

Key words: aromatic polyamides, silica, sol-gel process, organic-inorganic hybrid materials, gelation, thermogravimetric analysis.

Introduction

The sol-gel process involves the hydrolysis of metal alkoxides, followed by a condensation reaction to produce metal oxides. It has been extensively studied in the past decade [1-5]. The process has several advantages and unique aspects. For example, by means of it, glass of high purity can be made at processing temperatures well below those required in the conventional techniques of making glass. Another advantage of this process is the possibility of preparing cera-

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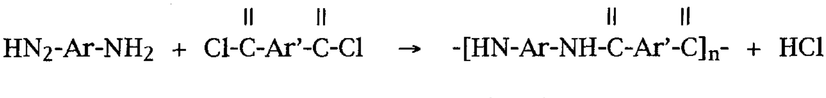
*Permanent address: Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan mic alloys or composites with dispersions at the molecular level. Since the starting metal alkoxides materials are usually liquids, different metal alkoxides are frequently miscible. Thus, the hydrolysis and condensation reactions can form alloys not readily available by other means [6,7]. The metal alkoxides also can be mixed with polymer solutions, or with monomers to be polymerized later, to make organic-inorganic hybrid materials [8,9].

Aromatic polyamides are of importance in basic research as well as for technical applications, because of their superior heat resistance, low density, and high specific strength. An "aramid" is defined as a long-chain synthetic polyamide having at least 85% of the amide-(CO-NH)- linkage attached directly to two aromatic rings [10]. Aramid fibers such as Kevlar® and Nomex® are being widely used to manufacture various objects in the aerospace and automobile industries.

Ceramics and polymers are two major groups in the materials area. Ceramic materials usually have very high thermal stability, good optical properties, and high modulus, but are very brittle. Polymeric materials on the other hand are tougher. The development of new materials containing both organic and inorganic structures is thus of great interest with respect to achievement of new combinations of properties, and the sol-gel process has provided new opportunities for making such materials. Aromatic polyamides, because of their good thermal stability and excellent mechanical properties, are good candidates for this approach. The hybrid materials produced could be useful in high-temperature applications, as coating materials or films.

The present study reports some initial work using this technique to prepare aromatic polyamide-silica hybrid material. The thermal stability of an aromatic polyamides increases with the amount of para-phenylene components [11-13]. Kevlar®, which is prepared from 1,4-phenylene diamines and terephthaloyl chloride, has a higher decomposition temperature than that of Nomex®, which is prepared from 1,3-phenylene diamines and isophthaloyl chloride. However, in order to obtain the solubility required in the sol-gel process, a few meta rings were introduced into the polymer chains. A mixture of 1,3- and 1,4-phenylene diamines and terephthaloyl chloride were thus used to make mixed-isomer aromatic polyamides. The regularity of the chain is thereby distorted, and the possibility of crystallization of polymer has been reduced. The polycondensation is represented as



$$HN_2\text{-Ar-}NH_2 + Cl\text{-}\overset{\overset{O}{\|}}{C}\text{-Ar'-}\overset{\overset{O}{\|}}{C}\text{-}Cl \rightarrow \text{-[HN-Ar-NH-}\overset{\overset{O}{\|}}{C}\text{-Ar'-}\overset{\overset{O}{\|}}{C}]_n\text{-} + HCl$$

Ar: 25% para-phenylene; 75% meta-phenylene
Ar': All para-phenylene

The inorganic part of the hybrid material is silica, which is formed from the hydrolysis and condensation of tetramethoxysilane (TMOS):

$$Si(OCH_3)_4 + H_2O \rightarrow SiO_2 + CH_3OH$$

The bridge between the organic and inorganic components is aminophenyltrimethoxysilane, which can undergo hydrolysis and can react with aromatic polyamides end capped with phthaloyl chloride. The type of composite expected is shown schematically in Figure 1.

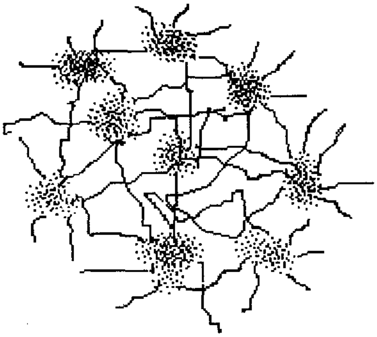


Figure 1. Schematic representation of polymer-silica composite.

By varying the molecular weight of the initial linear chains, or the ratio of polymer to TMOS, the compositions of the organic and inorganic components can be controlled. The properties of these hybrid materials are reported below.

Experimental

The monomers used for the preparation of aromatic polyamide were 1,4- and 1,3-phenylene diamines and terephthaloyl chloride. They were obtained from Aldrich, and were dried under vacuum at 55 °C overnight before use. Anhydrous dimethylacetamide (DMAC), also supplied by Aldrich, was 99^+ % pure and used in this form. Aminophenyltrimethoxysilane and TMOS were supplied by Hüls America Inc., and were also used as received.

In the preparations, 1,3- and 1,4-phenylene diamines in a mole ratio of 75:25 were dissolved in DMAC under nitrogen atmosphere. The solution was cooled to 0 °C, and the required amount of terephthaloyl chloride was added. The mole ratio of phthaloyl chloride to diamine for forming phthaloyl chloride end-capped chains is n + 1 to

n. Values of the ratio and the molecular weight of polymer are listed in the second and third columns of Table I. After complete mixing, the resulting mixture was continuously stirred for additional one hour at room temperature. Aminophenyl-trimethoxysilane was added, and the mixture was then stirred for another hour. Different amounts of TMOS were then mixed into the solutions. Calculated amounts of water (in the DMAC) were added to the samples. All the solutions thus prepared appeared to be homogeneous. The samples were placed into bottles, which were then sealed for the curing at various temperatures. The time required for gelation was taken to be that at which there was no further visible flow. The resulting gels were dried slowly in air, then under vacuum to constant weight. Other samples in the form of thin films (approximately 0.05 mm thickness) were obtained by casting the solutions on glass plates, and curing them at 60 °C for 24 hours.

Small pieces of samples were cut from the dried gels or films and soaked in water to leach out HCl produced during the polymerization. Thermogravimetric analyses on the samples were performed with a Perkin Elmer model TAS-7 system at a heating rate of 20 °C/min, under a nitrogen atmosphere.

Results and Discussion

The gelation time depends on many factors, as been described elsewhere [1]. For example, gelation is much faster at higher temperature than that at lower ones. At room temperature, the gelation was quite slow. It took hours for samples 0-0, 1-0, 2-0, 3-0, and 4-0 to gel, while only minutes at 60 °C. Samples containing TMOS gelled more slowly than those without it. For those samples not gelling after 20 days at 60 °C, the temperature was raised to 80 °C, and the samples were uncovered. By increasing the temperature and removing the volatile methanol produced, gelation did take place. The curling of the samples in film form may therefore be much faster than that of the samples enclosed in the sealed bottles. However, if trimethoxysilane end-capped polyamide with or without additional TMOS is kept under anhydrous conditions, gelation will not take place. Thus, these solutions can be stored for much longer times. Introduction of a small amount of water or exposure to moisture yields networks, giving these precursor materials potential as coatings.

The appearance of the gels and the films are described in the last three columns of Table I. There is apparently a competition between gelation and precipitation. If gelation takes place before precipitation, then the sample is transparent; otherwise, it is not. The silica content also affects the appearance of the sample. All gels and films formed without addition of TMOS are transparent, and light-brown to brown in color. However, with additional TMOS, the gels and films are opaque at

Table I. Preparation and Properties of Aromatic Polyamide-Silica Hybrid Composites

No.	n[a]	M[b]	Silica Content[c]			T_{gel}[d]		Appearance[e]		
			Tri	Tetra	Total	60°C	80°C	Gel	Film	
		(g/mol)		(wt%)		(days, hr, or min)				
0-0	0	467	22.2	0	22.2	10 m		T	T	R
0-1				20	37.8	1 d		T	T	R
0-2				40	53.3	20 d	+2 h	T	T	R
0-3				60	68.9	20 d	+3 h	T	T	R
1-0	2	943	11.0	0	11.0	20 m		T	T	R
1-1				20	28.8	2 d		T	T	R
1-2				40	48.8	20 d	+3 h	T	T	R
1-3				60	64.4	20 d	+4 h	T	T	R
2-0	4	1,419	7.3	0	7.3	30 m		T	T	R
2-1				20	25.8	20 d	+6 h	T	T	R
2-2				40	44.4	20 d	+8 h	T	T	R
2-3				60	62.9	20 d	+5 h	T	T	R
3-0	10	2,848	3.7	0	3.7	40 m		T	T	F
3-1				20	23.0	20 d	+ 1 d	T	T	R
3-2				40	42.2	20 d	+12 h	T	T	R
3-3				60	61.5	20 d	+ 5 h	O	O	R
4-0	30	7,611	1.4	0	1.4	60 m		T	T	F
4-1				20	21.1	20 d	+3 d	O	T	F
4-2				40	40.8	20 d	+2 d	O	O	R
4-3				60	60.6	12 d		O	O	R

[a] In the ratio of phthaloyl to diamine [(n+1)/n]

[b] Calculated molecular weight of the linear polymer chains.

[c] Calculated silica content assuming completed hydrolysis and condensation of methoxysilane.

[d] Gelation times, first at 60 °C covered, then at 80 °C uncovered [represented in days (d), hours (h), or minutes (m)].

[e] Appearance of the gels and films: T for transparent, and O for opaque; R for rigid, and F for flexible.

higher silica contents, but transparent at low contents. The films are flexible when the linear polymer chain is relatively long and the silica content is low, but are rigid if they are not. The flexible films can be used as free-standing materials. The rigid films could possibly be used as high-temperature coatings or adhesives, since they have good adhesion to glass.

The thermal stability of these hybrid materials was measured by means of TGA. Figure 2 shows the curves obtained for gels with various initial linear chain lengths. Figure 3 shows TGA curves of the films with the same polymer chain length but different amounts of silica. These results show that thermal decomposition occurs in a single step starting at approximately 450 °C. The decomposition temperature of poly(1,4-phenylene terephthalamide) has been reported to be around 500 °C [11-13]. The introduction of 25 mol % meta rings into the chains has lowered this temperature. However, as was already pointed out, their presence was necessary to improve the solubility of the aromatic polyamides.

The initial weight loss at lower temperatures increases with silica content. It is probably due to incomplete hydrolysis and condensation reactions between methoxysilane with water. The decomposition temperature is independent of the molecular weight of the initial linear chains (M.W. above 1,000 g/mol), however. The results seem to indicate stable bonding between the organic and inorganic components.

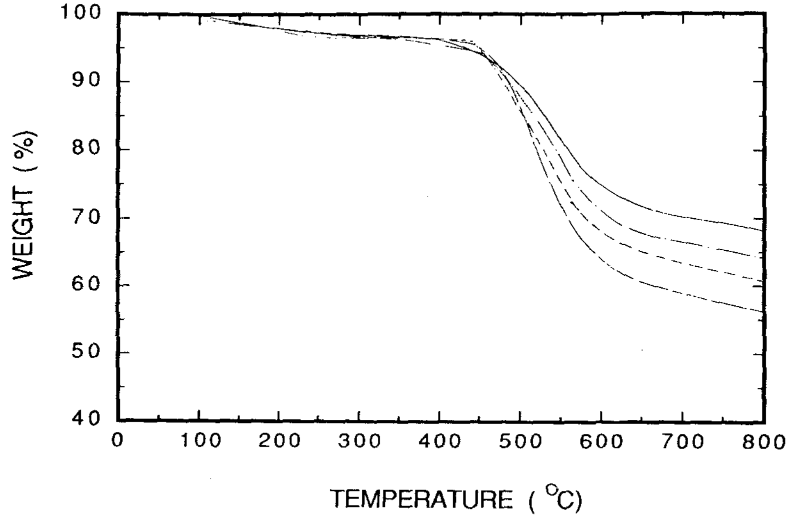


Figure 2. TGA curves for aromatic polyamide-silica hybrid composites with various polymer chain lengths obtained at a heating rate of 20 °C/min in N_2. (The ratio of phthaloyl to diamine was 1:1,— —; 3:2, ———; 5:4, — · —; 11:10; - - -).

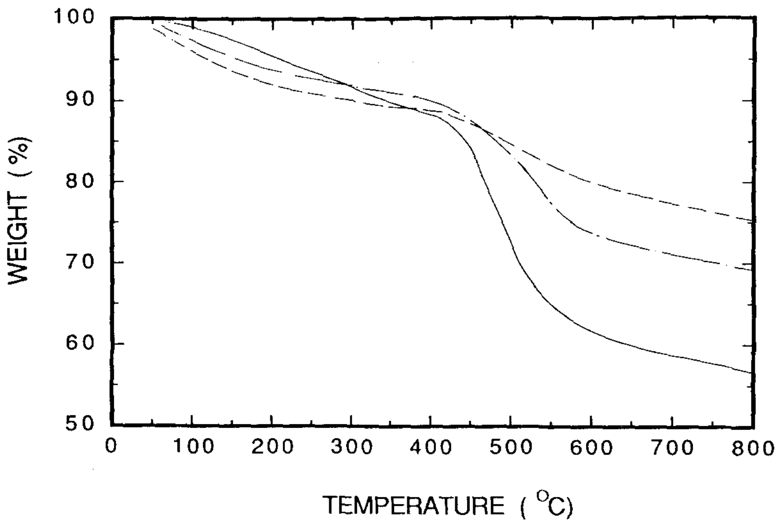


Figure 3. TGA curves for aromatic polyamide-silica hybrid films with various silica contents obtained at a heating rate of 20 °C/min under N_2. (Samples 2-0, — —; 2-1, — · —; 2-2, ——).

The weight of residue at 800 °C was almost proportional to the silica content (the inorganic component) in both cases. The thermal decomposition temperature of the hybrid material prepared was around 440 - 460 °C.

Acknowledgment

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References

1. Brinker CJ, Scherer GW (1990) Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing. Academic Press, Boston
2. Hench LL, West JK (1990) Chem Rev 90: 33
3. Brinker CJ et al (ed) (1986, 1988) Better Ceramics through Chemistry Vol II, III. Materials Research Society, Pittsburgh, PA
4. Klein LC (ed) (1988) Sol-Gel Technology for Thin Films, Preforms, Electronics, and Specialty Shapes. Noyes, Park Ridge, NJ
5. Iler RK (1979) The Chemistry of Silica. Wiley, New York
6. Yamane M, Inous S, Nakazawa K (1982) J Non-Cryst Solids 48: 153
7. Tohge N, Mackenzie JD (1984) J Non-Cryst Solids 68: 411
8. Schmidt H, Wolter H (1990) J Non-Cryst Solids 121: 428

9. Schmidt H (1989) J Non-Cryst Solids 112: 419
10. Preston J (1986) Polyamide, Aromatic. In: Mark HF et al (ed). Encyclopedia of polymer Science and Engineering. Interscience, New York
11. Frazer AH (1968) High Temperature Resistant Polymers. Interscience, New York
12. Conley RT (ed) (1970) Thermal Stability of Polymers. Marcel Dekker, New York, Vol.1
13. Critchley JP, Knight GJ, Wright WW (1983) Heat-Resistant Polymers. Plenum Press, New York

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