Organic–Inorganic Hybrid Networks

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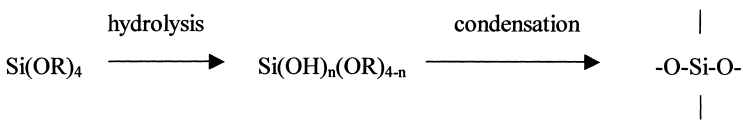
SUMMARY: Two types of organic–inorganic (O-I) networks with nanosized silica structures formed in situ by the sol-gel process were studied: (a) interpenetrating epoxy-silica networks and (b) hybrid networks with silica domains as crosslinks prepared from O-I precursors (alkoxysilyl end-capped polymers, organofunctional silsesquioxane clusters, functional microgels and polyhedral silsesquioxane "cages"). The effects of the type of the O-I precursor and interphase interaction on the formation, structure and mechanical properties of the hybrid network were determined. The formation of compact domain-like crosslinks from rigid precursors was shown to affect the critical behaviour in the system's gelation and resulted in a decrease in the dynamic critical exponent. Considerable reinforcement of the epoxide network by a small volume fraction of the in-situ formed silica was achieved. Dynamic mechanical analysis and comparison with bicontinuous theoretical models proved the co-continuous morphology of the hybrid silica-epoxy network.

Introduction

Organic–inorganic (O-I) hybrids are attractive materials studied with increasing interest in the last decade. The inorganic phase is formed in situ in a polymer matrix by the sol-gel process and, due to this procedure, the growing inorganic structures are homogeneously distributed within the polymer on a molecular scale. A microphase-separated structure with nanosized inorganic domains is formed. Both linear and crosslinked organic polymers were modified and reinforced by the in-situ formed silica filler.[1)] These nanocomposites offer a possibility of controlling the structure and morphology by modification of the reaction conditions of the sol-gel process, consisting of hydrolysis and condensation of alkoxysilanes to form an inorganic network. The most common monomer is tetraethoxysilane (TEOS).



An important part of the O-I hybrids are the hybrid networks.

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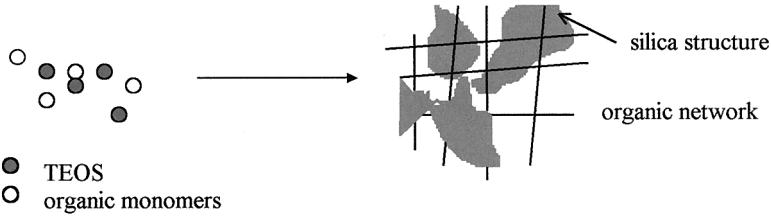
Types of Hybrid Networks

Two main types of the hybrid networks can be classified according to the precursors for crosslinking and the interaction between the organic and inorganic phases.

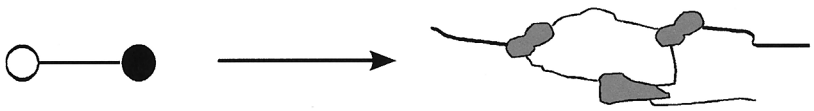
A. Interpenetrating (IPNs) Networks (or Semi-Interpenetrating Networks) from O and I Monomers

The organic and inorganic networks are formed by independent reaction mechanisms; the polymerization of organic monomers and the sol-gel polymerization of alkoxysilanes. Generally, there is no chemical bonding between network phases, however, the occurrence of interphase interaction, including the formation of covalent bonds, depends on the particular system.



B. Networks from O-I Precursors

The hybrid networks are built from O-I (macro)monomers as precursors of both the polymer and the Si-rich phases. The network junctions are formed by silsesquioxane domains connected by polymer chains. Covalent bonding exists between phases increasing compatiblity.



○ organic functionality or polymer chain

● alkoxysilyl group or silsesquioxane(Si)-domain

A. Epoxy-Silica Network

The hybrid epoxy-silica network DGEBA-D2000–TEOS is composed of the rubbery epoxy-amine network DGEBA (diglycidylether of Bisphenol A) - D2000 (poly(oxypropylene)di-

amine, M=2000) and the silica network formed by the sol-gel polymerization of TEOS.[2)] Both simultaneous and sequential polymerization procedures were used for the synthesis. The evolution of the structure and morphology as well as the mechanical properties of the hybrid networks were studied. The question addressed was whether the hybrid morphology is consistent with the Wilkes model[1c)] of silica-rich domains dispersed in an organic matrix or if a co-continuous phase morphology is formed.

Structure Evolution of Silica Domains and Morphology of the Hybrid

a. Simultaneous IPNs

The simultaneous formation of both networks was affected by the sol-gel catalysis and the method of polymerization. The one-stage process was base-catalyzed with polymeric amine D2000. The two-stage acid/base-catalyzed polymerization was carried out by prehydrolysis of TEOS under acidic conditions followed by base-catalyzed polycondensation.

One-Step Polymerization

The evolution of the silica structures was followed by small-angle X-ray scattering (SAXS).[3)] The scattered intensity of the monotonically decaying SAXS profiles increases as the structures grow and the silica clusters overlap in the early stage of the reaction. Analysis of the "dilute" system characterizing the inner structure of a single cluster shows non-homogeneous branching under base catalysis and the formation of gradually growing heterogeneous domains with a higher branching density within a cluster. Linearity of the intensity curves reveals a fractal behaviour of the formed system. The fractal dimension, D_m, increases during the reaction, due to a change in the inner structure, and the final value, D_m=2.7, corresponds to a quite compact structure formed by monomer–cluster aggregation. SEM micrographs show large silica aggregates of the size ~100–300 nm.

Two-Step Polymerization

The acid pre-hydrolysis of TEOS results in acceleration of the polymerization. During the acid-catalyzed step, the growth of small particles of the size ~2 nm occurs followed by a fast base-catalyzed aggregation of primary particles and gelation in the second step.[3)] The fractal dimension is constant during the polymerization implying the growth of the polymer chain without any change of inner structure. Two sizes of fractal structure were determined in the cured hybrid network: small compact particles (D_m=2.7) and large loose clusters with the low

fractal dimension D_m=1.7. The open structure of the clusters is consistent with the model of diffusion-limited cluster–cluster aggregation as fast gelation results in chemical quenching of the system and a slowing down of the diffusion. The silica domains detected by SEM are smaller compared to the one-stage system, d~50–100 nm, and seem to span continuously throughout the organic matrix.

b. Sequential IPN

The sequential IPN was prepared by swelling the epoxide network in TEOS and subsequent TEOS polymerization, with silica structures growing within the preformed organic network. SEM revealed a very fine morphology, showing a rather small size of silica domains, ~10 nm, the result of steric restrictions for cluster growth in the epoxide network. SAXS analysis established an open silica structure with D_m=1.9–2.2.

Dynamic Mechanical Properties

The in situ formed, hard glassy silica domains reinforce the rubbery epoxide network. An increase in modulus of the hybrid networks by two orders of magnitudes compared to the neat epoxide network was observed (Fig. 1a).[4] Such a high increase at a low content of silica (<15 vol%) is not consistent with the Kerner-Nielsen model of particulate composites of a matrix with a dispersed hard filler (Fig. 2). Hence, an effect of morphology and interphase interaction has to be taken into account. Figure 1b shows a drop in the loss factor, tan δ, corresponding to the relaxation of chains of the epoxide network and the appearance of a new relaxation peak at a higher temperature in the hybrid systems. This new peak was assigned to the glass transition of the network chains immobilized by interaction with the glassy silica domains. The most efficient reinforcing is shown by the sequential and the two-stage simultaneous hybrid networks (Fig. 1a). These systems also exhibit the strongest interphase interaction (Fig. 1b) as a result of the network grafting through the reaction between C-OH and Si-OH of the epoxide and silica networks, respectively. The interaction is promoted by the large surface area of the silica domains (small size and open structure) and a high content of SiOH in the acid-catalyzed system.

Analysis of dynamic mechanical properties proved: (a) an increase in the effective fraction, v_{eff}, of a reinforcing hard phase by the immobilized glassy interphase, the volume fraction of which could be determined, and (b) co-continuous morphology of the epoxy-silica phase domains in the hybrid networks. The experimental data are in agreement with the theoretical predictions[4] of the bicontinuous model – equivalent box model (EBM) (Fig. 2b)

and Davies' equation – for two continuous phases in IPNs (Fig. 2a). The interaction strength, characterized by parameter K, and the extent of Si-phase continuity, characterized by percolation critical volume fraction, v_{cr}, were determined and taken into account in the EBM model.[4)]

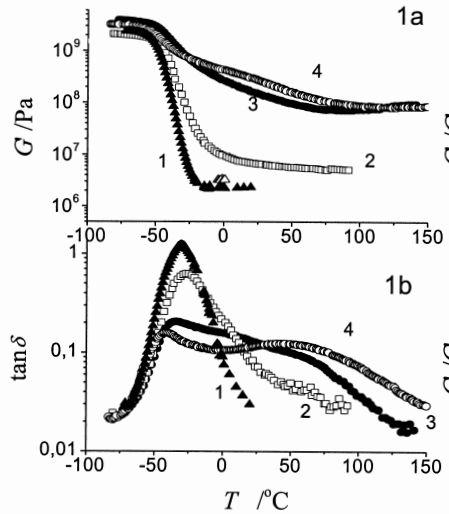


Fig. 1: (a) Dynamic shear modulus and (b) loss factor tan δ of the hybrid networks as a function of temperature. 1: DGEBA-D2000, 2-4: DGEBA-D2000–TEOS; 2: simultaneous one-stage, 3: simultaneous two-stage, 4: sequential network.

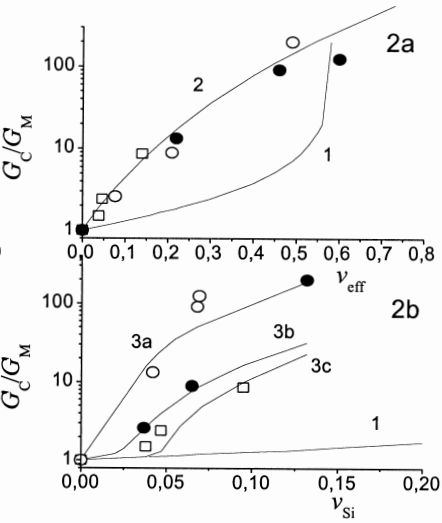


Fig. 2: Relative modulus of the DGEBA-D2000–TEOS composite as a function of (a) effective fraction of a filler and (b) fraction of the in-situ formed silica. (G_C, G_M – modulus of the composite and matrix, respectively) Theoretical curves: 1: Kerner-Nielsen model, 2: Davies equation, 3: EBM model, a) K=10, b) K=1, c) v_{cr}=0.02□ simultaneous one-stage, • simultaneous two-stage, ○ sequential network.

B. Networks from O-I Precursors

Precursors and their Formation

● alkoxysilyl group, ○ organic functionality

The following O-I crosslinking precursors of various size, shape and functionality (as illustrated) were used:

a. Alkoxysilyl end-capped polymer (SiP)

b. Silsesquioxane clusters with organic functionalities (OC)

c. Functional microgels

d. Functional polyhedral oligomeric silsesquioxanes (POSS)

a. Alkoxysilyl End-Capped Oligomers

Alkoxysilyl end-capped oligomers were prepared from poly(oxypropylene)diols of various molecular weights (M=400–4000) by modification with (3-isocyanatopropyl)-triethoxysilane.

b. Organofunctional Silsesquioxane Clusters

Silsesquioxane clusters with organic functionalities (F) were synthesized by the sol-gel process from organofunctional trialkoxysilanes F-Si(OR_3). Polymerization of (3-glycidyl-oxypropyl)trimethoxysilane led to a bimodal distribution of molecular weight of products including a stable oligomer identified as the polyhedral octamer "cage" with pendant epoxy groups.[5] The cage formation was the result of extensive cyclization preventing gelation of the trifunctional monomer under specific conditions. Functional clusters with a broad distribution of branched and cage-like structures of molecular weight M=1000-6000 and functionality f=5–30 were used for crosslinking.

c. Functional Microgels

Functional microgels were synthesized by microemulsion copolymerization of methyltrimethoxysilane and organofunctional trialkoxysilanes.[6] Vinyl- and methacryloyl-functionalized spherical particles of a narrow size distribution with molecular weight M_w=4x10^5–2x10^6, hydrodynamic radius R_H=10–30 nm and functionality f~500–1000 served as large crosslink domains of extremely high functionality.

d. POSS

The functional POSS cages (received from Aldrich and Hybrid Plastics) were used as well-defined rigid molecular building blocks[7] of size ≈ 10–15 Å.

Crosslinking of Precursors

The alkoxysilyl end-capped oligomers (SiP) were crosslinked by the sol-gel process and the other functional precursors by a reaction with functional oligomers of various sizes. The effect of the precursor type on network formation and structure was investgated.

Gelation

Gelation of the hybrid systems was followed using chemorheology experiments and the gel point was identified from the power-law behaviour[8] at the critical state; $G'(\omega) \sim G''(\omega) \sim \omega^n$ (G',G'', and ω are dynamic storage and loss moduli, and frequency of measurement, respectively). A close correlation was found between the critical exponent n and the structure of the critical gel. Crosslinking of the compact precursors to form networks with compact domain-like junctions results in low values of the critical exponent. This is the case of crosslinking of the POSS cages (n=0.32), microgels (n=0.45) and TEOS under acid/base catalysis where the compact primary particles are formed (n=0.45). On the contrary, a point-like junction in the flexible epoxide network (n=0.72) or crosslinking of loose clusters or SiP (n=0.75–0.85) leads to critical gels with a high value of the critical exponent.

Structure Evolution

During the sol-gel polymerization of the SiP, the Si-domains grow at the extremities of a chain forming a network junction and causing microphase separation and gelation to occur. In contrast to the monotonic decay of SAXS profiles in the DGEBA-D2000—TEOS networks, appearance of an interference maximum just around the gel point reveals the formation of a regular arrangement of the growing domains. Also, during crosslinking of the epoxy-functionalized silsesquioxane clusters with oligomeric diamine, the structurale organization of clusters occurs. The structure is gradually fixed by gelation and an increasing crosslinking density.

In spite of different network synthesis procedures, a similar structure in both OC- and SiP-based networks was built, the former being less organized. The correlation distance between clusters characterized by the position of the SAXS maximum corresponds to the length of the connecting oligomer for both networks and is affected by the reaction mechanism of the sol-gel process. The acid-catalysis promoted hydrolysis results in an increasing H-bond interphase interaction of SiOH in clusters with the oxygen atoms in the polyether chain and

leads to a shortening of the distance between the clusters compared to those formed in the base-catalyzed polymerization.

Mechanical Properties

The reduction in polymer chain mobility due to H-bond interactions in the interphase results in the appearance of a new DMA relaxation peak and an increase in T_g in both the OC- and SiP-based networks polymerized under acid catalysis. The interaction, however, is weaker and the increase in T_g, as well as the reinforcement, are smaller compared to these for grafted epoxy-silica IPNs of the same silica content.

Introducing POSS cages as dangling blocks or in the backbone of a linear polymer was reported[7] to appreciably increase T_g and modulus due to POSS–POSS interactions and reductions in chain mobility. However, in the DGEBA-D2000 epoxide network with dangling POSS (6 wt%), we have observed no change in T_g and only a mild increase in modulus, not exceeding that of the Kerner-Nielsen theoretical prediction. The POSS–POSS interactions obviously were not developed because of a fixed network structure.

Acknowledgments

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References

1. (a) J.E. Mark, S.J. Pan, *Makromol. Chem. Rapid Commun.* **3**, 681 (1982), (b) G.L.Wilkes, B. Orler, H.H. Huang, *Polym. Prepr.* **26**(2), 300 (1985), (c) H.H. Huang, G.L. Wilkes, *Polym. Prepr.* **28**(2), 244 (1987), (d) J.E .Mark, *Polym. Eng. Sci.* **36** 2905 (1996)
2. L. Matějka, K. Dušek, J. Pleštil, J. Kříž, F. Lednický, *Polymer* **40**, 171 (1998)
3. L. Matějka, J. Pleštil, K. Dušek, *J. Non-Cryst. Solids* **226**, 114 (1998)
4. L. Matějka, O. Dukh, J. Kolařík, *Polymer* **41**, 1449 (2000)
5. L. Matějka, O. Dukh, J.Brus, W.J. Simonsick, B. Meissner, *J. Non-Cryst Solids* **270**, 34 (2000)
6. F. Baumann, B. Deubzer, M. Geck, J. Dauth, S. Sheiko, M. Schmidt, *Adv. Mater.* **9**, 955 (1997)
7. J.D. Lichtenhan, T.S. Haddad, J.J. Schwab, M.J. Carr, K.P. Chaffee, P.T. Mather, *Polym. Prepr.* **39**(1), 489 (1998) , A. Lee, J.D. Lichtenhan, *Macromolecules* **31**, 4970 (1998)
8. H.H. Winter, *Polym. Eng. Sci.* **27**, 1698 (1987)