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Synthesis and thermomechanical characterization of polyimides reinforced with the sol–gel derived nanoparticles

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Abstract

Polyimide-based nanocomposites prepared by the in situ generation of inorganic nanoparticles (silica) through the sol–gel process were characterized by kinetics of water uptake, thermogravimetry and dynamic mechanical analysis.

Silica particles turned out to possess a rather loose inner structure characterized by enhanced water diffusivities and by dynamic elasticity moduli comparable to that of the pristine, glassy PI. Thermal stability and thermomechanical properties of nanocomposites in the glassy state remained nearly the same as those of the pristine PI, while a significant reinforcement effect was observed for the rubbery PI matrix.

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Keywords: Sol–gel derived nanoparticles; Thermomechanical characterization; Polyimides

1. Introduction

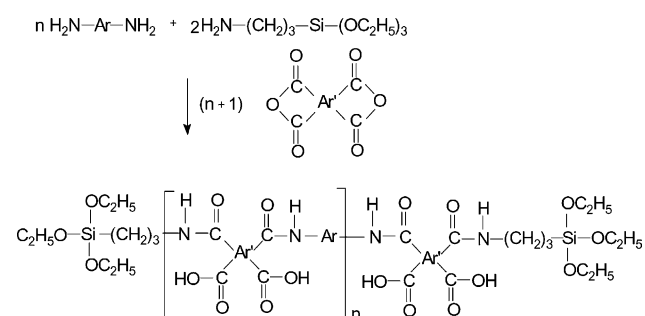
Structural implications of unusually high gain in mechanical properties of inorganic nanoparticles-filled polymers at relatively low filler (mostly, clay) contents remain one of the key problems for polymer nanocomposites. The dramatic improvement of performance of polymer–clay nanocomposites can be achieved, however, through a special time/energy-consuming technology, ensuring the initial penetration of polymer molecules into the interlayer space (*galleries*) of clay tactoids (*intercalation*) and subsequent forcing the layers apart up to the complete dispersal (*exfoliation*) of clay nanolayers throughout a polymer matrix [1]. In this communication, we report on the alternative approach to prepare polyimide-based nanocomposites involving the in situ generation of inorganic nanoparticles through the sol–gel process [2,3]. This approach is assumed both to ensure the homogeneous dispersion of sol–gel derived nanoparticles within a continuous polymer matrix, and to make advantage of

the autocatalytic effect of acidic groups of a precursor (polyamic acid) in the polycondensation reaction.

2. Experimental

2.1. Materials

Polyamic acid of molar mass 5000 with ethoxysilane end-groups (PAAS) was prepared by dissolution of 0.01044 mol of 4,4'-diaminodiphenyl ether and 0.025 mol of 3-aminopropyl triethoxysilane in 17.4 g of *N,N*-dimethyl acetamide, step-wise addition of 0.01169 mol of pyromellitic dianhydride to the solution and stirring at room temperature (r.t.) during 2 h (see the reaction scheme below).



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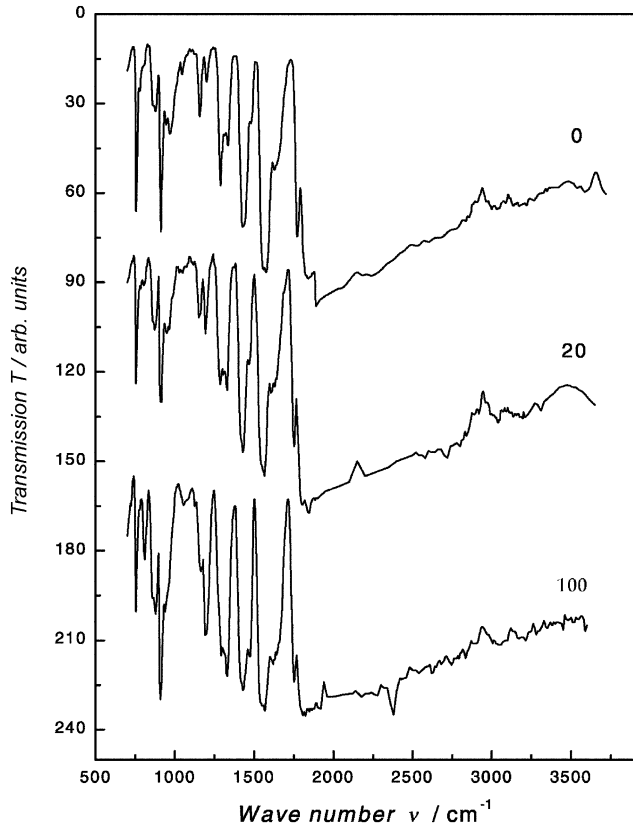


Fig. 1. IR transmission spectra for selected samples. Numbers refer to the MTS content S.

the first 3 h increased linearly with $t^{1/2}$ up to the breakpoint with the coordinates w^* and t^* , above which the w continued to increase at a significantly lower, composition-invariant rate to the final value (corresponding to $t_{\text{inf}} = 28$ h) w_{inf} (Fig. 2). Formally, the apparent two-stage pattern of w vs. $t^{1/2}$ plots is consistent with the dual-sorption model for glassy polymers [5,6] which assumes the initial fast filling by water molecules of the pre-existing microcavities (i.e. loosely packed regions),

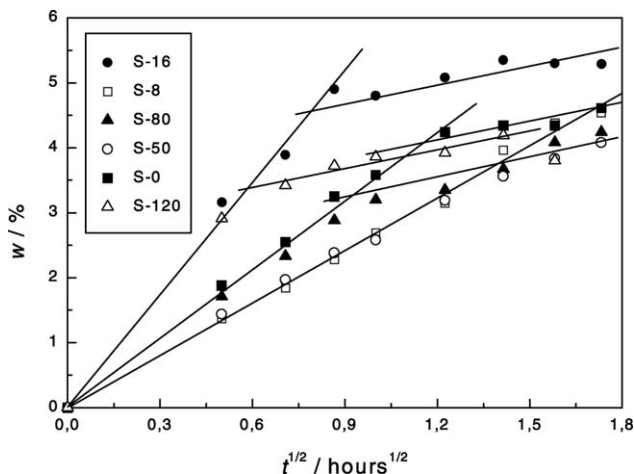


Fig. 2. w vs. $t^{1/2}$ plots for selected samples.

Table 1
Selected properties of nanocomposites

Sample	ρ (g cm ⁻³)	t^* (h)	w^* (%)	w_{inf} (%)	$10^{12}D$ (m ² s ⁻¹)	T_{α} (°C)
S-0	1.3782	1.35	4.1	4.2	0.65	405
S-8	1.3771	2.95	4.6	5.8	1.6	420
S-16	1.3965	0.65	4.5	5.3	2.0	–
S-20	1.3899	–	–	–	–	395
S-40	1.3461	–	–	–	–	–
S-50	1.3614	2.0	3.7	4.7	2.2	400
S-60	1.3748	–	–	–	–	–
S-80	1.3823	0.85	3.3	4.8	2.5	400
S-100	1.3722	–	–	–	–	–
S-120	–	0.35	3.3	4.5	2.9	390

and subsequent slow mechanism of water penetration into defect-free (i.e. densely packed), continuous matrix. The experimental data at $t < t^*$ were treated according to the standard relationship [5],

$$w/w_{\text{inf}} = 4(Dt/\pi d^2)^{1/2},$$

where D is the apparent diffusion coefficient, and d is the film thickness. As can be seen from Table 1, the apparent water diffusivities D (estimated with the relative error $\sim 25\%$) are smaller by about an order of magnitude than those for the soft phase of segmented polyurethanes [7] and tend to increase, the higher the MTS content S; the values of w_{inf} for nanocomposites are also systematically higher than that for the pristine PI. These results combined with the low (compared to the additive values estimated assuming $\rho_2 \approx 2$ g/cm³ for bulk silica [8]) densities of nanocomposites (Table 1) imply a rather loose inner structure of silica particles formed during the sol-gel procedure.

The normalized TGA traces for all studied samples exhibited the initial slight (a few%) deflections in the temperature interval up to about 180 °C (presumably, associated with evaporation of the traces of water and/or solvents) followed by plateaus extending over the broad (~ 300 °C) temperature intervals (Fig. 3). The final accelerated weight losses set on around $T_{\text{deg}} \approx 580$ °C for the pristine PI and at $T_{\text{deg}} \approx 550$ °C for all nanocomposites (except S-8 and S-20 for which $T_{\text{deg}} \approx 520$ °C was observed); as expected, the char residues tended to increase, the higher the MTS content. Judging by these data, thermal stability of nanocomposites remains nearly the same as that of the pristine PI.

As can be seen from the E^* vs. T plots (Fig. 4a), the complex moduli in the glassy state smoothly decreased from ~ 2.6 GPa at r.t. for all samples (except S-8, for which $E^* \approx 3.1$ GPa was observed) to ~ 1 GPa at ~ 300 °C. Nearly composition-invariant moduli in the glassy state imply similar values of E^* for both the pristine PI and for sol-gel derived silica particles. As usual, the onset of the main (α -) relaxation at T_{α} manifested itself as an accelerated decrease of E^* ; however, the rubbery plateau moduli above

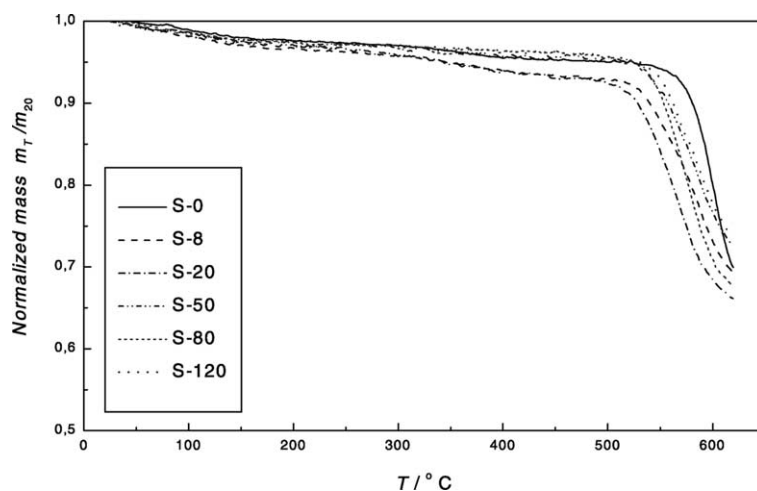


Fig. 3. Normalized TGA traces for selected samples.

T_α sharply increased, the higher the MTS content S . In view of nearly composition-independent moduli below T_α , the latter result suggests a significant reinforcement of PI matrix in the rubbery state by silica particles. Plots of $\tan \delta$ vs. T

(Fig. 4b) exhibited weak relaxations in the glassy state around $T_\beta \approx 90^\circ\text{C}$ and prominent main relaxation maxima around $T_\alpha \approx 400^\circ\text{C}$ for all samples except S-8, for which $T_\alpha \approx 420^\circ\text{C}$ was observed (Table 1).

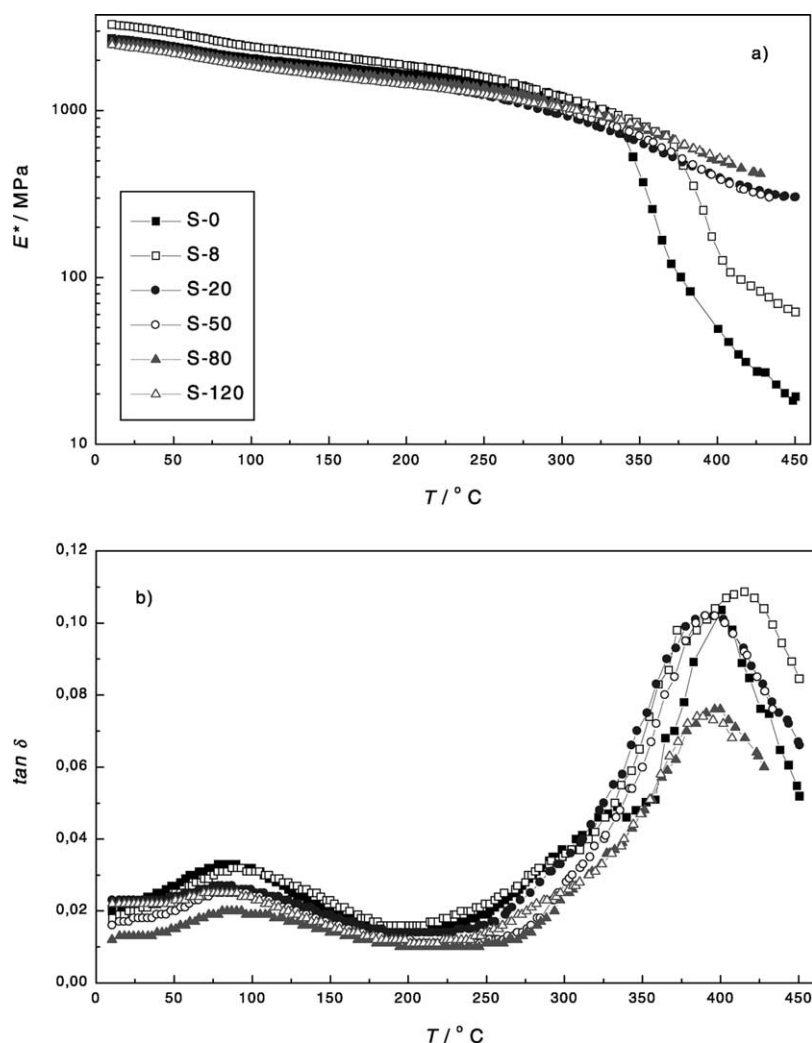


Fig. 4. Complex Young's moduli (a) and mechanical loss tangents (b) for selected samples.

4. Conclusions

1. Silica particles formed by the sol–gel procedure possess a rather loose inner structure characterized by enhanced water diffusivities and by dynamic elasticity moduli comparable to that of the pristine, glassy PI.
2. Thermal stability and thermomechanical properties of nanocomposites in the glassy state remain nearly the same as those of the pristine PI, while a significant reinforcement effect is observed in the rubbery state above the main relaxation at T_{α} .

Acknowledgements

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