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A study on composites of Nylon-6 with hollow glass microspheres

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SUMMARY:

The preparation of nylon-6/hollow glass microspheres composites by the RIM procedure, leading to a new material with reduced density and increased stiffness, is described. The shear moduli of these composites show a linear dependency on the filler concentration. By means of a modified Kerner equation the shear moduli of the various glass spheres were calculated. A linear dependency between the shear modulus of a glass sphere and its wall thickness is demonstrated. A direct method for the determination of the shear moduli of those glass spheres having a density lower than the matrix material is presented.

INTRODUCTION

The application of light weight fillers, in the form of hollow glass spheres, in plastics has become more and more important in the last few years [1]. The main reason of this is weight reduction without loss of stiffness and strength. As a consequence of their relatively low compressive strength they cannot be blended with thermoplastic materials in the usual blending equipment (e.g. extruders, banbury mixers etc.). So applications have been restricted to thermoset materials only.

We felt however, that the use of the glass spheres in thermoplastic materials would become possible if these spheres are added to an in situ polymerising system, if at least measures are taken to prevent segregation of the glass spheres during polymerisation. The fast activated anionic polymerisation of caprolactam [2], a technique also used in reaction injection moulding (RIM), seemed ideally suited for this purpose.

In order to be able to predict mechanical properties like the modulus of elasticity or the shear modulus of a composite material, the knowledge of those moduli of the filler materials is of primary importance. For hollow glass spheres these data are not known, however.

In this paper we describe the preparation of a series of nylon-6-hollow glass spheres composites. A study was made on the relationship between some mechanical properties and the volume fraction and kind of microspheres.

EXPERIMENTAL

Materials: The catalyst and the activator, supplied as masterbatches in caprolactam, were gifts from DSM, The Netherlands. The catalyst contains 1.39 moles sodium salt of caprolactam per kg of material; the accelerator contains 2.0 moles of the reaction product of 1 mole hexamethylenediisocyanate with 2 moles of caprolactam per kg of material. The caprolactam, a special anionic polymerisation quality, was purchased from DSM, The Netherlands. The hollow glass microspheres were a gift of 3M Company. Their properties are summarized in Table 1. The glass bubbles,

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Table 1. Properties of 3M glass spheres with diameter ≈ 60μm (10-160 μm).

coated[a]			uncoated		
type of[b] sphere	wall thickness[c] (μm)	density[d] (kg/m^3)	type of[b] sphere	wall thickness[c] (μm)	density[d] (kg/m^3)
A32/2500	1.01	280	C15/250	0.49	140
A38/4000	1.41	390	B23/500	0.8	230[f]
			B28/750	0.74	210
			B38/4000	1.41	390
			S60/10000	2.13	575
			massive[e]		2900

a) coated with Volan, a chrome methacroyl compound [3]. b) data given by 3M e.g. A32/2500: density 32 g/dl, compressive strength 2500 psi. c) wall thickness calculated from density and diameter = 60μm. d) data obtained by helium pyknometer determinations. e) glass spheres (diameter 45-70μm) purchased from Tamson N.V., Zoetermeer, The Netherlands. f) value from 3M.

dried for 24 h at 120 °C, and the caprolactam were stored slightly above roomtemperature. Catalyst and activator were stored in a dessiccator

<u>Preparation of nylon-6 [4]</u>: Caprolactam (37.5 g, 0.33 mol) was equally divided into two separate glass tubes (A and B) and was heated in a silicone oil bath held at a temperature of ca 135 °C. When the caprolactam was molten, the catalyst (1.5 g, 2.1 mmole) was added to tube A and the accelerator (1.05 g, 2.1 mmole) was added to tube B. When these additions were molten, heating was continued for another 5-10 min. Then the contents of tube B were added to tube A and the mixture was stirred with a glass rod for about 10 s (total polymerisation time is about 100 s). Then the contents of the tube were poured as fast as possible into an upright stainless steel mould, which was preheated for at least 30 min in an oven at ca 145 °C. The oven was closed again and after 5 min the nylon plate was removed from the mould and allowed to cool in a dessiccator.

The mould consists of two highly polished stainless steel plates (20*8.5 cm) kept apart by an aluminium spacer of 5 mm thickness. The parts are clamped together by nuts and bolts. The mould is open at one end; in this way 5 mm thick nylon plates with a width of 6.5 cm and a maximal length of 19 cm are produced.

<u>Preparation of glass filled nylon-6</u>: The same procedure as outlined above was followed. After all organic additions were molten, the desired amount of glass bubbles was added to tube A. The amount of catalyst was increased gradually, with increasing amount of glass bubbles, to 120% of the prescribed amount at 50 vol % of glass bubbles. In this manner we prepared nylon plates filled with glass bubbles of the types given in Table 1. The volume fraction of glass was increased in steps of 0.05.

<u>Determination of shear modulus</u>: The composite plates, dry as made, were cut into strips of about 63*12*5 mm. The shear modulus was determined with a torsion pendulum [5] at room temperature. (In fact, with a torsion pendulum the storage modulus is determined, so where shear modulus is written, one should read storage modulus). In this way a curve of the shear modulus versus composition was obtained (Fig.1). In a second series the shear modulus was measured as a function of temperature (Fig.3).

Determination of impact strength: Izod notched impact strengths were determined according to ASTM D256. The strips had the same dimensions as those used for the determination of the storage modulus. A notch of 0.1 inch was cut in the narrowest side.

RESULTS AND DISCUSSION

In preparing the nylon/glass composites the polymerisation sometimes failed at higher filler volume fractions. These problems were solved by increasing the amount of catalyst slightly. Apparently some water adhering to the glass bubbles caused this problem. In this manner we prepared composites with a range of densities, varying from 1130 kg/m^3 (nylon-6) up to 1750 kg/m^3 (nylon with 35% massive glass spheres) and down to 780 kg/m^3 (nylon with 35% C15 glass bubbles). Measurements of the density of the composites over the plates from top to bottom showed that no segregation of the hollow glass spheres had taken place.

As stated above we would like to be able to predict the flexural and shear moduli of the composite. These will be dependent on the volume fraction of filler and on the moduli of the matrix and the filler. If both these moduli are known, those of the composite can be predicted with the aid of Kerner's equation which for materials filled with spherical particles reads [6]:

$$\frac{M}{M_0} = \frac{1+A*B*\phi}{1-B*\phi} \qquad (1)$$

in which M=modulus of composite; M_0=modulus of matrix; ϕ=volume fraction of filler; $A=(7-5\nu)/(8-10\nu)$; ν=Poisson ratio (i.e. 0.38 for nylon-6); $B=(\alpha-1)/(\alpha+A)$; $\alpha=M_1/M_0$; M_1=modulus of the filler.

Although the moduli of the hollow glass spheres are not known, it should be possible to determine them via Kerner's equation by measuring the moduli of the matrix material and of the composite. For that case we simplified Kerner's equation into a linear form, eq(2), from which B and hence α can be determined by a simple linear regression analysis of the measurements (Fig.1 and Table 2).

$$\ln (M/M_0) = B\phi(1+A) \qquad (2)$$

Control calculations showed that the use of this simplified equation is allowed for all values of α and for filler volume fractions ϕ=0 to ϕ=0.50. No significant deviations are observed from Kerner's equation itself.

Fig.1 shows that the linear relation holds for all composites, hence it is not necessary to use the modified Kerner equation, which takes account of a correction for the maximum filler volume fraction [7].

Although coated and uncoated glass bubbles have been used, a difference in adhesion between matrix and filler, if there is any, will have no influence on the shear modulus as only small deformations were applied. In accordance with this expectation, the materials filled with A38 or B38 glass bubbles show the same result.

As can be seen also from fig.1 the slope of the curve of the composite filled with glass bubbles B28 is more negative than expected on account of its suggested density. The only way to explain this curious result was to assume that the density of the B28 glass bubbles was lower than 280 kg/m^3. Helium pyknometer measurements confirmed this assumption (Table 1).

Another conclusion that can be drawn from these measurements is that a linear relationship exists between the shear modulus of the glass bubbles

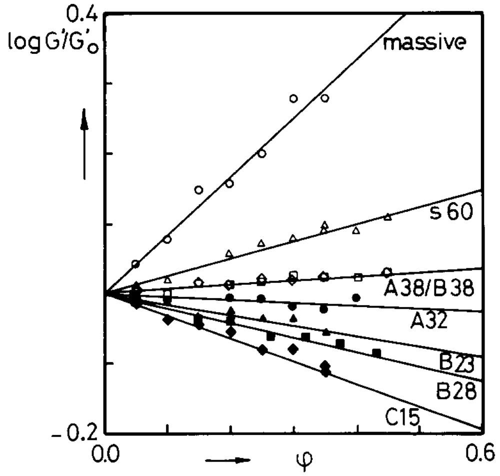

Fig.1. Experimental reduced storage modulus plotted against filler volume fraction of various nylon-6-hollow glass spheres composites (every point represents the mean value obtained from 4 to 8 samples). Full lines: results of regression analysis according to Eq.(2).

and their density (Fig.2). And although the relationship between the wall thickness (d) and the density (ρ) is not a strict linear one:

$$d = r[1- \sqrt[3]{(1-\rho/2900)}] \approx \rho/290 \ \mu m \qquad (3)$$

(for $r = 30\ \mu m$, mean radius; 2900 = density (in kg/m^3) of pure glass)

the deviations in the range ρ=100 to ρ=600 kg/m^3 are so small that for practical purposes a linear relationship between shear modulus and wall thickness of the glass bubbles can be assumed.

This linear relationship is in agreement with theoretical considerations based on Kerner's equation. For that purpose we consider a glass matrix filled with air bubbles and one filled with hollow glass spheres with the same amount of air. This finally leads to the conclusion that α is linearly dependent on d (see Appendix):

$$\alpha = \frac{3d}{r} * \frac{A}{A+1} \qquad (4)$$

By means of this equation we now can calculate the overall shear modulus of the hollow glass spheres, using the values for the shear modulus and the Poisson ratio of glass (1.9*10^4 N/mm^2 and 0.22 respectively) and the wall thicknesses of the spheres as given in Table 1. As can be seen

Table 2. Storage moduli calculated from experiments according to eq.(2).

type of sphere	α	$G'_{glassbubble}$ (N/mm^2)	G'_{nylon}[a] (N/mm^2)
C15	0.45	507	1128
B28	0.62	719	1170
B23	0.70	824	1172
A32	0.91	1052	1157
B38	1.16	1384	1193
A38	1.16	1360	1172
S60	1.84	2002	1088
Massive	15.7	18870	1200

a) G'nylon was found by extrapolation to ϕ=0; pure nylon-6: G'=1090 N/mm^2.

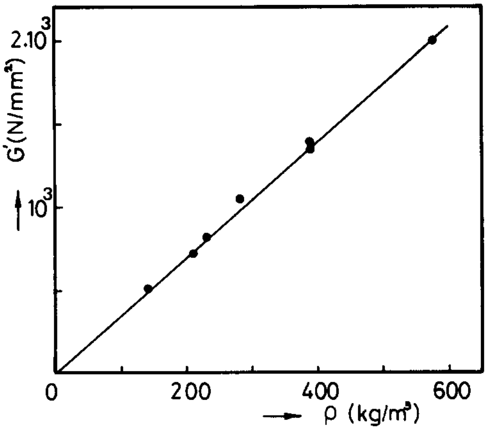

Fig.2. Relationship between storage modulus and density of the hollow glass spheres.

from Table 3 a very good agreement with the measured values is obtained.

For those glass bubbles having a modulus lower than that of the matrix an alternative method for the determination of this modulus seemed possible by its measurement as a function of the temperature. In these particular cases the modulus of the composite at temperatures below Tg will be the lower the more filler is present ($\alpha<1$), whereas at higher temperatures the modulus will be the higher the more filler is present ($\alpha>1$). The result is that the curves of the modulus versus temperature of a particular composite at different filler volume fractions will intersect at a point corresponding to the modulus of the filler (Fig.3; Table 4).

Comparison of the moduli estimated by this method with those presented in Table 2 shows that a reasonable agreement exists in the order of magnitude of the various values. It is clear that this method has a limited applicability, as it is only usable for those filler materials having a lower modulus below Tg than the matrix. Moreover, the accuracy decreases strongly when the storage modulus of the filler approaches that of the matrix. However, in principle this is a direct method to measure the modulus of filler particles, independent of any theory.

From Fig.1 it is clear that blending nylon-6 with hollow glass spheres can result in an increase as well as a decrease of the stiffness with respect to the stiffness of the pure polymer. Of course a decrease in the stiffness is a disadvantage but, on the other hand, the decrease of the density is an advantage. In Table 5 some reduced moduli, compared with pure nylon-6, are shown for composites containing 40% (v/v) of glass spheres.

Table 3. Experimental and calculated shear moduli of the glass spheres.

type of sphere	α(calc)	α(exp)	G' calc.(N/mm²)	G' exp.(N/mm²)
C15	0.025	0.027	475	507
B23	0.041	0.043	779	824
B28	0.037	0.038	703	719
A32	0.050	0.055	950	1052
B38	0.071	0.073	1349	1384
A38	0.071	0.072	1349	1360
S60	0.107	0.105	2033	2002

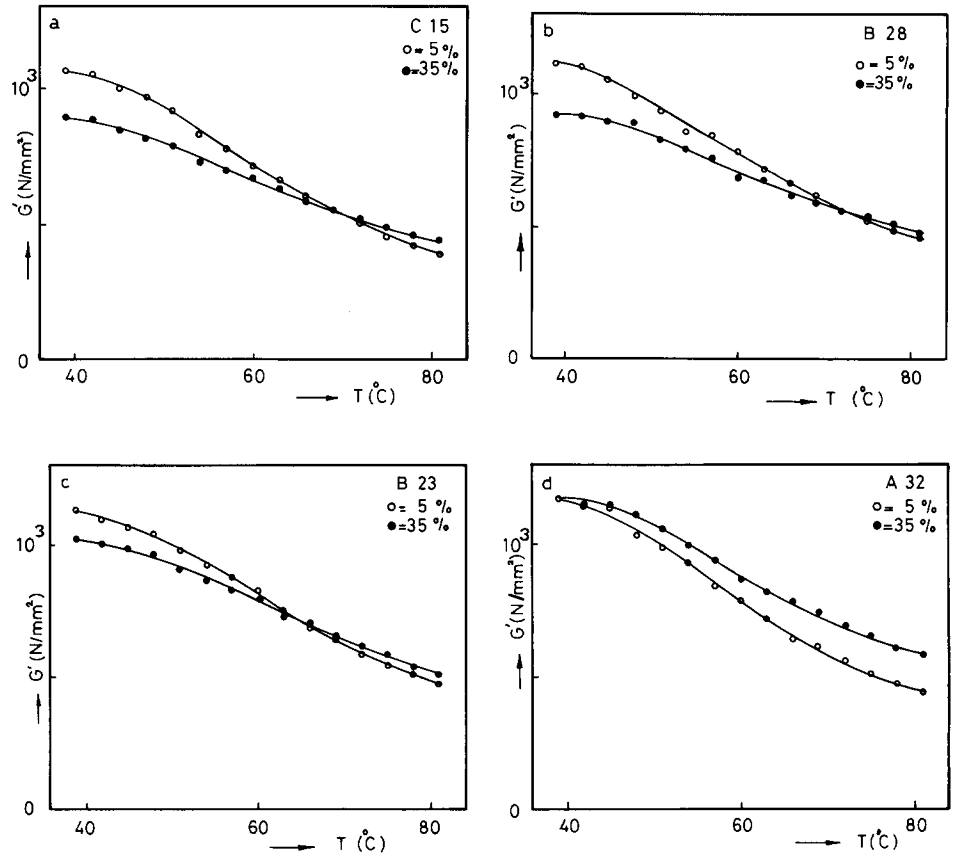

Fig.3a-d. Storage modulus of various composites versus temperature.

Although a decrease in the modulus can occur ($G'/G'_0 < 1$), the value of the reduced modulus (G'/ρ) is always larger than that of the pure polymer.

No relationship between the data of the Izod notched impact strength determinations and the type of filler could be found. The only general conclusion is that the impact strength even at a small filler volume fraction of 0.05 is lowered, in some cases even to 45% of the value of the unfilled polymer, and that at higher filler fractions the impact strength is going down, for all composites to about 25% of the value of nylon-6.

The fracture surface of the samples was studied by scanning electron microscopy. The observations we made, were the following:

Table 4. Shear modulus of glass spheres in N/mm^2

type of sphere	point of intersection	Kerner
C15	550	507
B23	720	824
B28	560	719
A32	1170	1052

Table 5. Properties of composites containing 40% (v/v) glass spheres.

type of filler	ρ (kg/m^3)	G'/G_0'	$(G'/\rho)/(G_0'/\rho_0)$
None	1130	1	1
C15	734	0.75	1.16
B28	762	0.83	1.24
B23	770	0.87	1.28
A32	790	0.96	1.39
A38/B38	834	1.06	1.45
S60	908	1.28	1.59
Massive	1838	2.16	1.33

G_0', ρ_0: modulus and density of pure nylon-6.

a) In the composite filled with C15 glass bubbles nearly all bubbles were broken, in the composite filled with S60 bubbles only about 10% was broken. The other composites showed an intermediate picture, dependent on the density of the bubbles.

b) In the composites filled with A38 and B38 bubbles a distinct difference was observed. In the A38 composite 60-70% of the bubbles was broken, while in the B38 composite only 30-40% was broken. Apparently the A38 bubbles, coated with Volan, adhere much better to the matrix than the B38 bubbles. If the adhesion strength is larger than the ultimate strength of the filler particles, these filler particles will fail; in the reverse case the adhesion will fail and the filler particles will remain unbroken. This behaviour is not reflected in the impact strength, however. This might mean that the impact strength of the hollow glass sphere itself is smaller than that of the matrix. The fact that at high filler fractions the impact strength of all composites, with exception of the one filled with massive glass, is the same, supports this view.

CONCLUSIONS

The RIM procedure is ideally suited for the preparation of nylon-6 hollow glass sphere composites. The shear moduli of these materials show a linear dependency on the filler concentration. By means of Kerner's equation the shear moduli of the various glass bubbles were calculated and the correctness of these data was confirmed by means of torsion pendulum measurements. As a consequence it is possible to predict, with the aid of Kerner's equation, the modulus of any composite with hollow glass spheres as long as the properties of the matrix material are known.

For composites containing glass bubbles with a modulus below Tg lower than that of the matrix material, curves of the shear modulus versus temperature show a point of intersection at the shear modulus of the filler material. For a limited number of filler materials this is an alternative method for the determination of this quantity and moreover, it is an absolute method, independent of any theory.

Determination of the impact strength did not show a relationship between this quantity and the nature of the filler material. On the one hand the impact strength is lowered considerably upon filling with hollow glass spheres, apparently this filler being the weakest link in the composite, on the other hand an appreciable weight reduction up to 35% can be achieved, while the reduced stiffness of the composite is always increased. The choice of material will be dependent on its applications, especially the reduction in density to values far below that of water will make it usefull for buoyancy applications.

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APPENDIX

An air bubble of diameter 2r embedded in a matrix, can be represented by a hollow sphere embedded in that matrix, with a thin wall consisting of the same material as that of the matrix. The diameter of the sphere being 2r+2d, where d is the wall thickness (Fig.4).

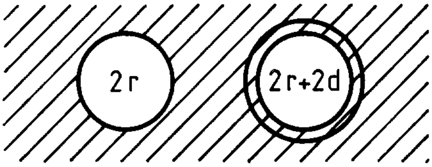

Fig.4. Hollow glass bubbles in a glass matrix

The volume fraction of the air bubbles $V(a) = N*4/3*\pi*r^3$ and that of the hollow spheres $V(h) = N*4/3*\pi*(r+d)^3$, where N is the number of spheres per unit of volume. Substitution of $\alpha=0$ (i.e. $B=-1/A$) in Kerner's equation (eq.1) for the air bubble composite yields:

$$M = M_1 * \frac{1-N*4/3*\pi*r^3}{1+N/A*4/3*\pi*r^3}$$

whereas for the thin walled spheres composite ($\alpha>0$) is found:

$$M = M_1 * \frac{1+N*4/3*\pi*(r+d)^3*A*B}{1-N*4/3*(r+d)^3*B}$$

Equating both expressions yields:

$$A*B = [r/(r+d)]^3 \approx -1/(1+3d/r) = -1/C$$

where $C = 1+3d/r \approx 1$

so that: $B = (\alpha-1)/(\alpha+A) = -1/(A*C)$

or $\alpha = (3d/r)*A/(1+A*C) \approx (3d/r)*A/(1+A)$.

The conclusion is that α is proportional to the ratio of the wall thickness and the radius of the hollow spheres. The overall modulus now reads:

$$M = M_1*(3d/r)*A/(1+A).$$

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