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Dynamic mechanical characterization of hydroxyapatite reinforced polyethylene: effect of particle size

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Dynamic mechanical analysis (DMA) was used to characterize biomedical composites consisting of synthetic hydroxyapatite (HA) particulate reinforced polyethylene (PE). The effects of the HA volume fraction, temperature and HA particle on the storage modulus (E^I) and damping (tan δ) were investigated.

Increasing HA volume fractions increased E^I and decreased tan δ. E^I was found to be linearly related to the Young's modulus values obtained from quasi-static tensile tests. Relative modulus and damping studies showed that the viscoelastic behavior of unfilled PE was different to that of the filled matrix due to the presence of thermally induced tensile stresses in the matrix at the filler-matrix interface.

1. Introduction

Bone, at an ultra-structural level, can be considered as a composite material consisting mainly of a mineral phase, hydroxyapatite, and a protein phase, collagen [1]. Bone is viscoelastic within the range of physiological loading, providing an important energy dissipating mechanism during deformation. Bonfield [2] stated "that the existence of viscoelasticity should be recognized as an essential feature of an optimized prosthetic material for bone".

Over the past decade, there has been considerable interest in the development of polymer-based composites as biomaterials for bone and joint replacement. HA reinforced polyethylene (PE) composites (HA/PE) have been designed as bone analog materials [3] and have established successful clinical uses in ophthalmic [4] and otologic applications [5].

Dynamic mechanical analysis (DMA) measures the response of a material to a sinusoidal stress over a range of temperature and frequencies and is sensitive to chemical and physical structure of polymers and their composites. The main variables obtained from DMA are the storage modulus (E^I), which represents the elastic component of a system and is equivalent to the energy stored through deformation, the loss modulus (E^{II}), which represents the viscous component and is equivalent to the energy dissipated through deformation, and tan δ, which is the ratio of E^{II}/E^I and provides a measurement of the damping of the material. However, limited work has been performed previously relating the viscoelastic properties of particulate-filled polyethylenes to those of the unfilled polymer.

A particular HA/PE composite, at the 0.4 volume fraction of HA level (HAPEX^{TM}) has been shown to be mechanically compatible to bone, with a modulus approaching the lower bound of that for cortical bone [6]. However, composites based on thermoplastic polymers are viscoelastic and the mechanical properties are temperature and strain-rate dependent. As the response to dynamic loading can not be predicted by quasi-static loading alone, evaluation of the viscoelastic properties using DMA is required for the overall mechanical characterization. The objective of this work was to stimulate physiological loading by applying small strain cyclic deformations by DMA on HA/PE composites, so as to determine the associated viscoelastic variables.

2. Materials

The matrix investigated was high-density PE (Rigidex HM4560XP, BP Chemicals Ltd, UK) (Table I). Two forms of morphologically similar synthetic HA particles – HA P88 and HA P81B (Plasma Biotal Ltd, UK) –were used as reinforcing agents in PE (Table II).

Compression molded HA/PE composites were manufactured with 0.1, 0.2, 0.3, 0.4 and 0.45 HA volume fractions of each HA type and unfilled PE [6]. Synthetic HA particles were mixed with PE and subsequently processed in a twin screw compounder-extruder (Betol BTS40L). The compounded material was extruded into distilled water at room temperature, so as to produce rapid cooling of the extrudate to prevent oxidation and degradation of the polymer matrix. After cooling, the extrudate was dried by compressed air, pelletized and powderized. The HA/PE powder was compression molded into plates from which specimens were machined.

3. Methods

3.1. Density

The density of the composites was determined by Archimedes' Principle, based upon ASTM D792–86, with an Ohaus® Analytical Plus Balance and Density Detection Kit. The specimens were weighed in air, to an accuracy 0.0001 g, followed by weighing in distilled water at 25 °C. The density of the PE samples was measured by the same method, but using absolute alcohol at 25 °C.

3.2. Determination of the HA content

The ash content of the various compression molded composites was measured to quantify the amount of HA in the composites. Ashing was carried out for all the HA/PE volume fractions for the two different particle sizes. As a control, ashing was carried out for specimens of molded 100% PE and 100% HA powder of both particle sizes. The ashing process was undertaken at 900 °C for 24 h. The specimens in flake form were cut from blocks taken from random parts of molded plates and kept in dried ceramic cups. After ashing, the specimens were placed in a desiccator over silica gel to cool. All weight measurements were carried out at room temperature in an Ohaus® Analytical Plus Balance accurate to four decimal places. Ash contents were calculated as a percentage of the original specimen weight, from which values the HA volume fraction was calculated.

3.3. Dynamic mechanical analysis

The HA/PE samples were prepared from molded plates, which were sectioned into rectangular beams ($1 \times 3 \times 24$ mm) using a Struers Accutom-2 (Struers Tech A/S, Denmark) rotating band saw. Water cooling was maintained throughout the cutting process. The specimens were lightly dry polished, using 1000 grade silicon paper, followed by 4000 grade paper to improve the surface finish and to remove cutting marks. Five specimens were prepared for each variable. Prior to analysis the specimens were stored in sealed plastic bags and kept at room temperature.

TABLE I Properties of PE (Rigidex HM 4560 XP, BP Chemicals Ltd, UK)

Density/ $\mathrm{Mg\,m^{-3}}$	Melt flow rate/g/10 min	Tensile modulus/GPa	Yield strength /MPa	Elongation to fracture/%
0.945	6	0.68	23.5	> 300

TABLE II Characteristics of HA P88 and HAP81B

Parameter	HA P88	HA P81B
Median particle size $d_{50}/\mu\mathrm{m}$	4.53	7.43
Measured surface area/$\mathrm{m^2 g^{-1}}$	8.27	7.61
Particle density/$\mathrm{Mg\,m^{-3}}$	3.151	3.151
Bulk density/$\mathrm{Mg\,m^{-3}}$	0.58	0.77

Analyses were carried out using a Perkin-Elmer DMA-7 (Perkin-Elmer Corp., USA) in conjunction with a DEC-personal computer. A three-point bend system was employed where the beam rests on two supports and is loaded by means of a loading nose (probe tip) midway between the supports 20 mm apart.

Dynamic mechanical tests were performed using the temperature scan mode conditions as shown in Table III. Temperature was measured with a thermocouple positioned approximately 1 mm away from the specimen. Helium gas was used as purge in the furnace and a water circulator was used to maintain an isothermal environment outside the furnace.

The DMA results are presented in terms of two main variables: storage modulus (E') and mechanical loss tangent ($\tan \delta$). The mean and standard deviation were calculated for the repeat specimens and unpaired Student's *t*-tests were used to compare different groups of samples.

4. Results

4.1. Density

Table IV shows the theoretical and pre-testing measured densities for HA(P88)/PE and HA(P81B)/PE composites. The theoretical densities were calculated using values of density of 0.945 $\mathrm{Mg\,m^{-3}}$ polyethylene and 3.151 $\mathrm{Mg\,m^{-3}}$ for HA [7] with their respective volume fractions. The measured densities were consistently below the theoretical values. The HA(P81B)/PE composites appeared to have a lower density than the HA(P88)/PE composites, at the equivalent volume fraction. Student's *t*-test confirmed that the differences were statistically significant at the 5% significance level.

4.2. HA content

Ash content determinations on molded plates gave the volume fractions of HA shown in Table V. Again the densities of both composites were consistently lower than the theoretical values. As with the density measurements, the measured HA volume fractions for HA(P81B)/PE were lower than for HA(P88)/PE,

TABLE III Conditions applied in DMA analysis

Parameter	Conditions
Temperature range	20–100 °C
Heating rate	4 °C $\mathrm{min^{-1}}$
Static control – tension	120%*
Dynamic control – strain	0.02%
Frequency	1 Hz

*The static stress applied was maintained at 120% the value of dynamic stress.

TABLE IV Calculated and experimentally measured densities of HA/PE composites

HA volume fraction	Calculated density/Mg m^{-3}	Measured density ($n = 5$)/Mg m^{-3}	
		HA(P88)/PE	HA(P81B)/PE
0	0.945	0.943 ± 0.001	0.943 ± 0.001
0.10	1.166	1.124 ± 0.012	1.109 ± 0.001
0.20	1.386	1.348 ± 0.008	–
0.30	1.607	1.553 ± 0.004	1.498 ± 0.001
0.40	1.827	1.731 ± 0.010	–
0.45	1.938	1.839 ± 0.008	1.815 ± 0.005

TABLE V Theoretical and measured HA volume fractions

HA volume fraction	Theoretical HA Wt %	HA(P88)/PE			HA(P81B)/PE		
		Measured density	Wt % of inorganic matter	Measured volume fraction	Measured density	Wt % of inorganic matter	Measured volume fraction
PE	0	0.943	0	–	0.943	0	–
0.10	27.03	1.129	24.11	0.089	1.108	21.65	0.080
0.20	45.46	1.344	43.04	0.189	–	–	–
0.30	58.11	1.556	56.65	0.293	1.493	53.05	0.274
0.40	68.97	1.733	65.55	0.380	–	–	–
0.45	73.18	1.836	69.96	0.430	1.814	69.27	0.426
HA	100	–	97.21	–	–	97.05	–

suggesting that the DMA data were obtained for lower HA volume fractions than predicted.

4.3. Dynamic mechanical analysis

Tables VI and VII give the mean (x) and standard deviation (s) for the storage modulus (E^I) and damping ratio (tan δ) at various temperatures from 20 to 100 °C. It can be seen that E^I decreases with an increase in temperature and increases with an increase in HA volume fraction. Tan δ, in contrast, decreased with increasing HA volume fraction and increased with increasing temperature.

The two fillers were compared at three volume fractions, 0.1, 0.3 and 0.45. As seen in Table VI, for the lower volume fractions, (0.1 and 0.3), the smaller P88 particles gave higher moduli at an equivalent volume fraction than P81B particles. Student's *t*-tests showed that the differences between the mean storage modulus values of the 0.1 and 0.3 volume fractions for the two fillers were significant at all temperatures chosen at the 5% significance level. This trend was not reflected with the 0.45 volume fraction where the difference was not significant and above 60 °C there was a cross-over between the two composites, when the larger particles (P81B) gave higher values than the smaller (P88) particle reinforced composite.

TABLE VI Mean (x) and standard deviation (s) of storage modulus values of HA(P88)/PE and HA(P81B)/PE composites

Material		E^I (GPa) at temperature (°C)						
		20	30	37	45	60	80	100
PE	x	1.444	1.262	1.122	0.959	0.676	0.422	0.250
	s	± 0.065	± 0.057	± 0.049	± 0.041	± 0.029	± 0.020	± 0.013
0.1 (P88)	x	1.973	1.726	1.534	1.308	0.929	0.578	0.336
	s	± 0.063	± 0.063	± 0.055	± 0.050	± 0.041	± 0.025	± 0.010
0.2 (P88)	x	2.570	2.313	2.066	1.760	1.272	0.811	0.504
	s	± 0.063	± 0.050	± 0.050	± 0.045	± 0.040	± 0.033	± 0.024
0.3 (P88)	x	3.784	3.390	3.050	2.645	1.943	1.246	0.742
	s	± 0.193	± 0.195	± 0.184	± 0.160	± 0.119	± 0.069	± 0.034
0.4 (P88)	x	5.011	4.496	4.070	3.552	2.657	1.759	1.070
	s	± 0.195	± 0.175	± 0.165	± 0.155	± 0.111	± 0.092	± 0.072
0.45 (P88)	x	6.427	5.776	5.257	4.612	3.497	2.397	1.499
	s	± 0.079	± 0.073	± 0.063	± 0.059	± 0.058	± 0.043	± 0.061
0.1 (P81B)	x	1.732	1.527	1.342	1.127	0.797	0.492	0.282
	s	± 0.055	± 0.049	± 0.042	± 0.034	± 0.024	± 0.014	± 0.008
0.3 (P81B)	x	3.441	3.089	2.749	2.348	1.713	1.087	0.624
	s	± 0.064	± 0.060	± 0.052	± 0.050	± 0.032	± 0.021	± 0.010
0.45 (P81B)	x	6.264	5.735	5.209	4.592	3.567	2.509	1.574
	s	± 0.222	± 0.205	± 0.194	± 0.174	± 0.143	± 0.116	± 0.084

TABLE VII Mean (x) and standard deviation (s) of damping values of HA(P88)/PE and HA(P81B)/PE composites

Material		Tan $\delta(\times 10^2)$ at temperature (°C)						
		20	30	37	45	60	80	100
PE	x	10.365	12.537	14.921	17.659	24.709	32.165	44.441
	s	± 0.822	± 0.422	± 0.606	± 0.594	± 2.601	± 2.771	± 6.073
0.1 (P88)	x	8.345	10.878	13.307	16.445	22.487	29.820	43.203
	s	± 0.688	± 1.052	± 1.483	± 1.904	± 3.055	± 2.917	± 2.754
0.2 (P88)	x	6.832	9.046	10.985	13.413	17.422	21.498	28.028
	s	± 0.341	± 0.258	± 0.372	± 0.417	± 0.555	± 0.879	± 1.777
0.3 (P88)	x	5.836	8.127	9.996	12.381	16.571	20.898	28.306
	s	± 0.217	± 0.192	± 0.441	± 0.528	± 0.917	± 1.243	± 1.811
0.4 (P88)	x	4.927	6.941	8.618	10.738	14.383	18.787	26.259
	s	± 0.292	± 0.216	± 0.234	± 0.310	± 0.388	± 1.401	± 3.223
0.45 (P88)	x	4.629	6.651	8.217	10.338	13.858	18.550	26.639
	s	± 0.224	± 0.396	± 0.503	± 0.687	± 0.755	± 2.110	± 4.931
0.1 (P81B)	x	8.321	11.024	13.451	16.184	20.828	26.323	34.177
	s	± 0.342	± 0.392	± 0.289	± 0.536	± 1.295	± 2.377	± 3.598
0.3 (P81B)	x	6.246	8.555	10.536	12.890	16.408	19.790	25.681
	s	± 0.249	± 0.240	± 0.235	± 0.264	± 0.469	± 1.028	± 1.764
0.45 (P81B)	x	4.456	6.278	7.841	9.727	12.665	15.749	23.053
	s	± 0.156	± 0.095	± 0.071	± 0.154	± 0.364	± 0.618	± 1.455

In terms of damping, no clear differences were observed between the two particle sizes and in most cases the differences were not significant (Table VII). The standard deviations for the two variables indicate the repeatability and in general, the standard deviation for E^I was lower than for tan δ.

Fig. 1 shows E^I measured at 20 °C versus E measured at room temperature for both composites. It can be seen that the two are linearly related with a gradient within 2% of unity but with an offset.

5. Discussion

The properties of polymeric composites depend primarily on the relative amounts and properties of the filler and matrix. HA is a ceramic material which is much stiffer, with a Young's modulus of 80 GPa [8], than PE, at 0.65 GPa [6] as measured by quasi-static tensile tests at room temperature. Therefore incorporating particles of HA into the PE matrix stiffens the PE by an amount depending on the HA content. The shape of the particles and the efficiency of dispersion and packing of the filler also influence the magnitude of the enhancement [9]. In Fig. 1 the observed increase in E^I with increasing HA volume fraction is comparable to E values observed in quasi-static tensile testing and indicates the stiffening effect of the particles on the matrix. The higher storage modulus values are expected due to the higher strain rate and lower strain levels used in DMA compared to quasi-static testing. Polyethylene is a non-linear viscoelastic

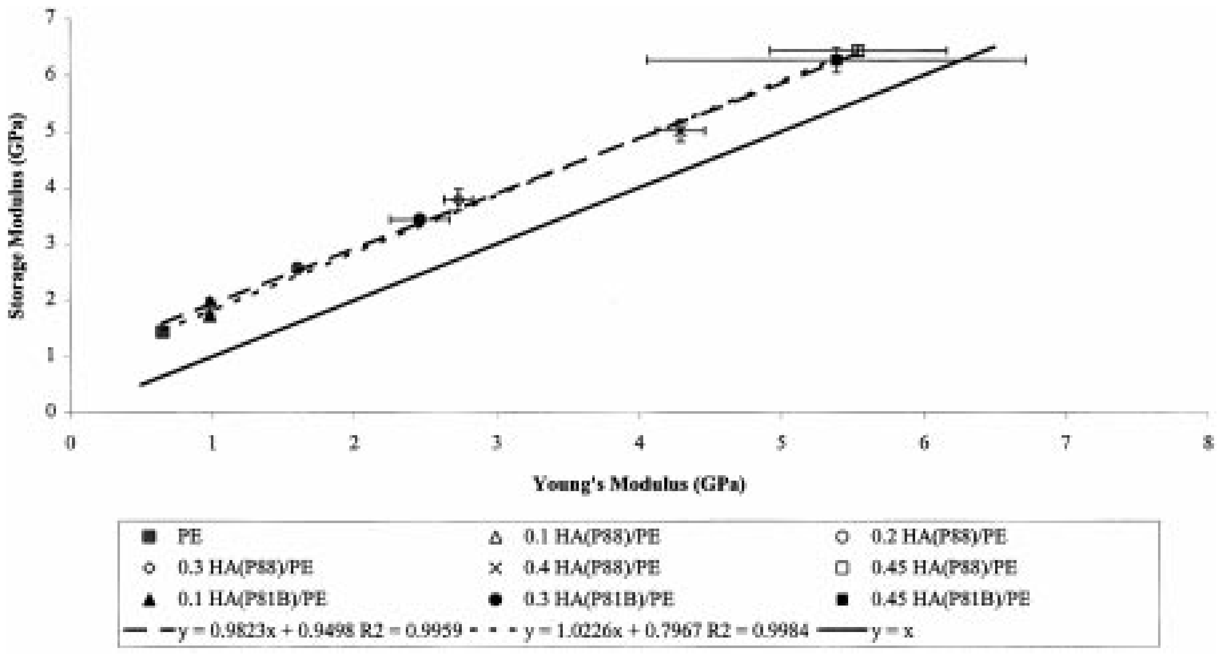

Figure 1 Storage modulus versus Young's modulus for HA(P88)/PE and HA(P81B)/PE composites.

material and the modulus increases as the strain rate increases, or the strain decreases.

To analyze the efficiency of the HA filler, relative modulus values were calculated according to Equation 1

$$E_r^I = \frac{E_c^I}{E_m^I} \tag{1}$$

where E_r^I, E_c^I and E_m^I are the relative modulus, storage modulus of the composite and storage modulus of the unfilled matrix, respectively, at the same temperature [10]. Fig. 2 shows the relative modulus values for the composites as a function of temperature. It can be seen that E_r^I is always > 1, confirming the reinforcing effect of HA, namely as the HA volume fraction increases, so does the relative modulus. It can also be seen that for HA(P88)/PE the values of relative modulus for 0.1 and 0.2 volume fractions do not appear to vary significantly with temperature, whereas those obtained at 0.3, 0.4 and 0.45 volume fractions increase with increasing temperature. The slope of relative modulus versus temperature increased with higher HA volume fraction, indicating that the decrease in storage modulus was dependent on the amount of HA in the composites. The increase in relative modulus with temperature suggests that HA at higher volume fractions tends to control the values of E^I, which reinforces previous conclusions [6]. Nielsen and Lewis [10] stated that the changes in relative modulus with temperature for particulate reinforced composites are primarily due to thermally induced tensile stresses in the polymer. These thermal stresses result from differences in thermal coefficients as the composite cools from the molding temperature. Polymers have non-linear stress-strain curves, with the elastic modulus decreasing with increasing stress. Thus, the stressed polymer surrounding the filler particles will have a lower modulus than the bulk polymer. Therefore the increase in relative modulus in the higher volume fraction composites at higher temperatures was due to the reduction in thermal stresses, combined with the modulus of the filler, since the rate increase was dependent on the amount of filler in the composite.

For both particle sizes, the increase in relative modulus with temperature was dependent on the amount of HA in the composite where 0.1 was constant, 0.3 showed a slight increase and 0.45 gave the greatest increase with temperature.

Some theories indicate that the modulus of a material should be independent of the size of the filler particles [12]. However, other authors [13–15] have reported an increase in modulus with a decrease in particle size. Various theories have been suggested, including that as the particle size decreases, the increase in surface area and surface energy provides more efficient interfacial bonds [15]. In this study the smaller particles were generally the more efficient reinforcing agents.

Tan δ is given by the ratio E^{II}/E^{I} and is an indication of the fractional energy lost in a system due to deformation. Thus, the increase observed with increasing temperature is due to the increase in thermal energy given to the polyethylene chains, which become more mobile and hence more able to dissipate energy. The effect of the filler can also be seen by the reduction in the energy loss with increasing amounts of HA. In addition to modulus changes, damping can also vary with temperature. Fig. 3 shows a graph of relative damping ($\tan\delta_r$), given by Equation 2

$$\tan\delta_r = \frac{\tan\delta_c}{\tan\delta_m} \tag{2}$$

where $\tan\,\delta_c$ and $\tan\,\delta_m$ are the loss tangents of the composite and polymer respectively at the temperature of interest. Tan δ_r less than 1 indicates less damping in

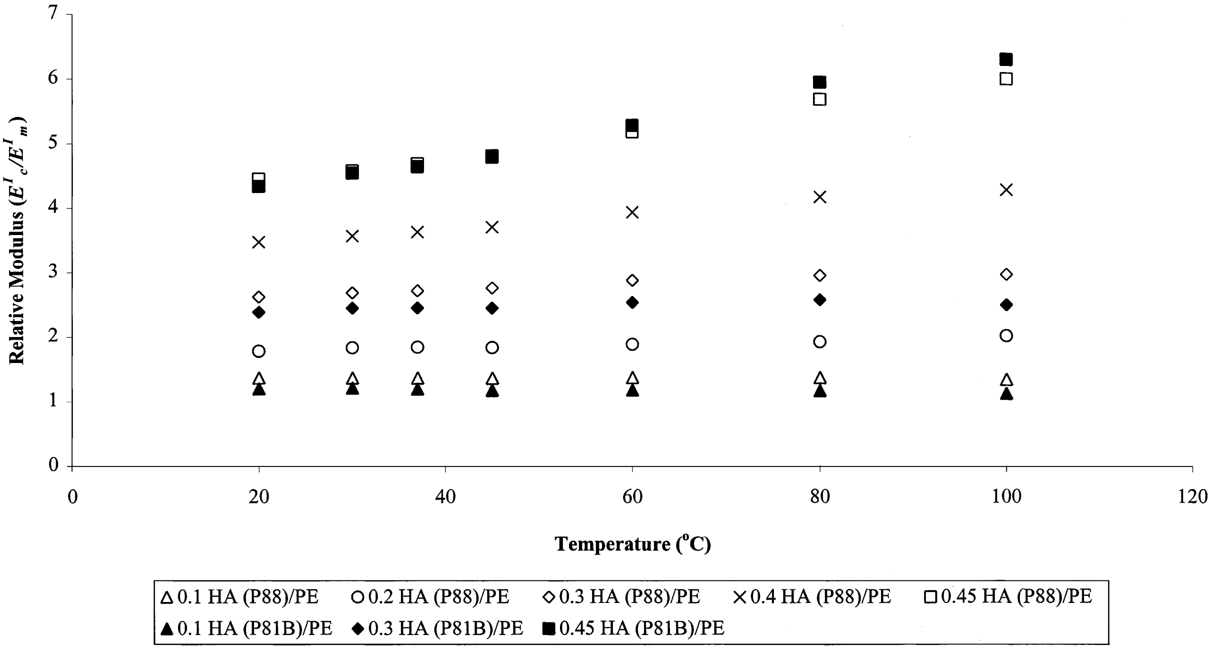

Figure 2 Relative modulus versus temperature for HA/PE composites (Equation 1).

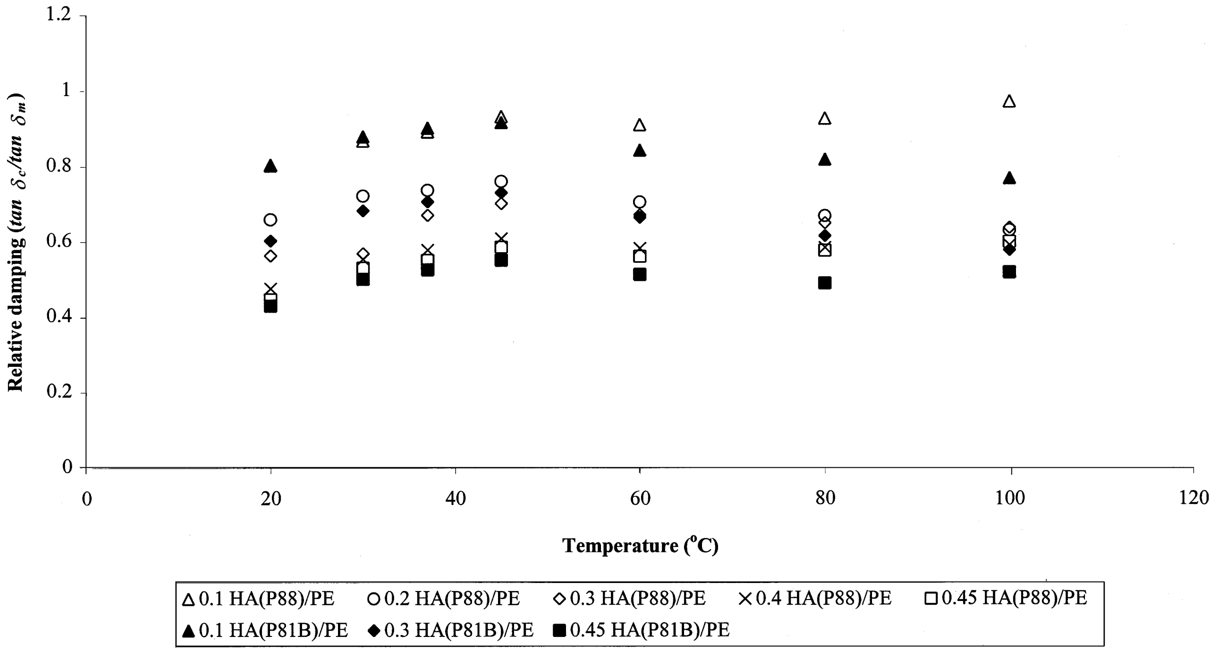

Figure 3 Relative damping versus temperature for HA/PE composites (Equation 2).

the composite than in the unfilled polymer. Similar to the relative modulus study, the values tended to decrease with increasing HA volume fraction. All compositions followed similar trends where, after an initial increase in $\tan\delta_r$ between 20 and 45 °C, the curves leveled off up to 100 °C. This trend suggests that $\tan\delta_c$ increased at a greater rate than for polyethylene alone, within the initial temperature range, which could be explained by the composites having lower values for damping at lower temperatures due to the presence of the particles, restricting movement of polymer chains. As the temperature increases, the thermal energy given to the chains also increases allowing greater energy loss due to movement in a similar fashion to the unfilled polymer. However, the energy loss mechanism is complex within particulate composites, with the possibility of additional losses occurring at the filler-matrix interface. In filled systems, there is evidence that a filler surface can change the properties of the polymer in contact with it, but also in HA/PE composites any changes in the interfacial region will be largely swamped by the bulk of the matrix away from the interface.

If damping is only dependent on the volume fraction of the matrix, then the experimental results would match the theoretical relative damping given by Equation 3

$$V_m = \frac{\tan\delta_c}{\tan\delta_m} \tag{3}$$

where V_m is the volume fraction of the matrix in a composite, $\tan\delta_c$ is the damping of that composite and $\tan\delta_m$ is the damping of the unfilled polymer [12]. If the damping in a filled polymer results only from the same mechanism which produces the damping in the unfilled matrix then the ratio holds.

Fig. 4 compares the theoretical prediction of relative damping and the experimental relative damping as a function of HA volume fraction at 20, 37 and 60 °C for HA(P88)/PE. While the experimental relative damping also tends to decrease with increasing HA volume fraction, the non-linear experimental results show lower values than the theoretical at 20 °C. The trends at 37 and 60 °C are similar to the theoretical with a linear reduction with increasing volume fraction. Thus, as the temperature increases the experimental values approach the theoretical values. This suggests that at 20 °C HA reduces the damping by more than just reducing the polymer volume. The additional factor may be the presence of thermally induced stresses, which to some extent reduced the damping behavior of the polymer near the particles by restricting polymer chain movement.

It is therefore possible to predict the effect of the thermal stresses in HA/PE composites and four damping regions can be identified (Fig. 5):

1. The filler, as HA does not contribute to damping.
2. The HA/PE interface.
3. The interphase, that is the matrix region near the interface which is under thermally induced stresses.
4. The bulk PE matrix away from the filler.

The regional variations in the matrix would suggest that the damping mechanisms for the filled and unfilled PEs were dissimilar at low temperatures, but similar at higher temperatures. The reduction in the thermal stresses in the polyethylene around the HA particles allows the damping behavior of the filled polymers to be closer to that of the unfilled polymer.

The density and inorganic content for the volume fractions with the two types of particles were investigated to see if they accounted for some of the differences in the dynamic mechanical properties. As shown in Table IV, all measured densities and ash contents were less than the theoretical values and those for HA(P81B)/PE were

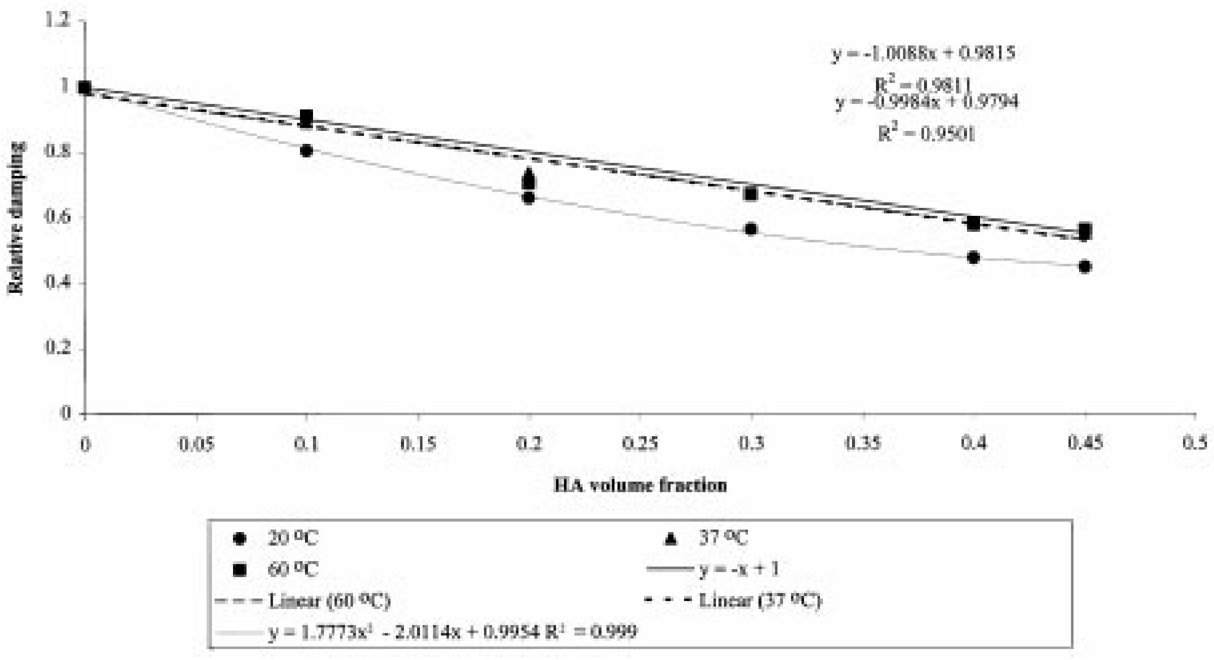

Figure 4 Theoretical and experimental relative damping as a function of HA volume fraction for HA(P88)/PE composites (Equation 3).

lower than those for HA(P88)/PE composites, suggested that HA P88 was more easily incorporated into PE than HA P81B. All of the above factors could account for differences in the dynamic mechanical behavior observed between the two types of composites.

6. Conclusions

1. An increase in HA volume fraction in the composites increased the storage modulus at all temperatures. An increase in temperature reduced the storage modulus values for all volume fractions.

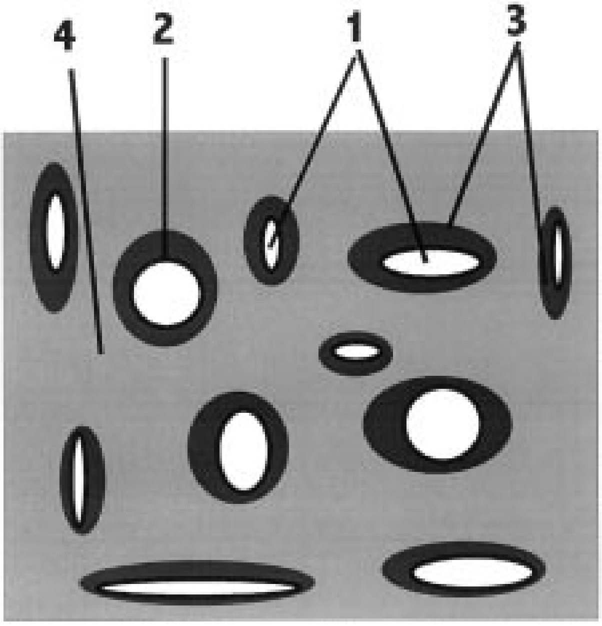

Figure 5 Schematic diagram showing the thermally stressed polyethylene around the HA particles.

2. The smaller particle sized HA (P88) reinforced PE more efficiently.

3. An increase in relative modulus was observed for composites of higher HA volume fraction with increasing temperature. The rate of increase was dependent on the HA content. This implies the existence of a thermally stressed region in the filled polyethylene matrix near the HA particles. These thermally induced stresses reduced the modulus and restricted the damping behavior of the matrix near the HA particles, hence reducing the damping at lower temperatures.

4. Storage moduli obtained by DMA were consistently higher than, but linearly related to, Young's moduli obtained by quasi-static tensile tests.

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