Preparation and characterization of hydroxypropyl cellulose/silica micro-hybrids

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Hydroxypropyl cellulose (HPC) was incorporated *in situ* with silica by the sol-gel process involving various amounts of added tetraethoxysilane (TEOS), and hybrids with nanometre-sized silica particles were prepared. To determine the effect of TEOS content on the mechanical properties of the micro-hybrids, the TEOS content in the hybrids was varied from 20 to 60%. The mechanical properties of the micro-hybrids were compared with those of HPC composites mixed with various amounts of glass beads (diameters of 20–40 μm) by solvent blending. The ultimate tensile strength of the micro-hybrid was improved from 6 to 18 MPa when the TEOS content reached 40 wt%. On the other hand, the strength of the blend composite decreased with glass-bead content. The α_1- (molecular motion in a highly ordered amorphous phase), α_2- (molecular motion in a random amorphous phase) and β-relaxations (relating to molecular motion of hydroxypropyl groups) were observed in the temperature dependence of the dynamic viscoelastic properties of HPC. The level of the dynamic modulus, G', of the micro-hybrid increased with initial TEOS content. By hybridization, the α_1-peak in the tan δ curve broadened and its intensity lowered as the initial TEOS content increased. The α_2-peak was observed for the micro-hybrid composed of 20 wt% TEOS, but disappeared when the TEOS content exceeded 40 wt%. The β-peak was not observed in the hybrid. No drastic change was observed in the dynamic viscoelastic behaviour of the blend composite as the glass-bead content was varied. The mechanical properties of the *in situ* micro-hybrid were completely different from those of the blend composite. This difference was caused by the interaction between the filler and matrix. In the micro-hybrid, nanometre-sized ceramic particles may be dispersed in the HPC component, and strong interaction occurs via hydrogen bonding. In contrast, the interaction between the glass beads and HPC in the blend composite is weak.

(Keywords: hydroxypropyl cellulose; silica; hybrid)

INTRODUCTION

In recent years, avid attention has been focused on the sol-gel process as a unique process to produce ceramics under mild conditions. Using the sol-gel process, thermally unstable organic compounds can be incorporated into ceramics. For example, an organic polymer is first dissolved in solvent together with a silicon alkoxide, such as tetraethoxysilane (TEOS). Then after adding a small amount of HCl and H_2O, the mixture is allowed to stand at low temperature ($<200°C$) after removal of the solvent. When hydrolysis and the polycondensation reaction occur, small particles of ceramics are evenly dispersed *in situ* in the polymer matrix. It has been reported that 1–30 nm diameter ceramic particles have been dispersed in an organic polymer matrix according to morphological studies of transmission electron microscopy (TEM)[1–4] and small-angle X-ray scattering (SAXS)[5–7]. Ceramics are brittle but display a number of beneficial properties of surface hardness, strength, modulus, heat resistance and transparency. On the other hand, organic polymers are thermally unstable, but have characteristics of flexibility and low density. Resulting micro-hybrids from organic polymers and ceramics potentially could possess a beneficial combination of properties of both materials.

Recently, various organic polymer/ceramic micro-hybrids have been reported, e.g. poly(ethylene glycol) (PEG)/SiO_2[8], poly(tetramethylene oxide) (PTMO)/TiO_2, ZrO_2[9], PTMO/Al_2O_3[10], PTMO/SiO_2[7,11], poly(n-butyl methacrylate)/TiO_2[12], poly(methyl methacrylate)/SiO_2[13], and perfluoro-sulfonic acid ionomer/SiO_2[14]. In a previous paper[15], we reported that poly(vinyl acetate) (PVAc) and copoly(vinyl acetate-vinyl triethoxysilane) [copoly(VAc-VTES)] had been successfully incorporated with silica using the sol-gel process involving TEOS, and that the mechanical properties of the organic polymers were significantly improved by hybridization. An important point to consider to improve the mechanical properties of composites is a strong interaction between the matrix and filler. PVAc interacts with silica networks through hydrogen bonding, and copoly(VAc-VTES) combines covalently with silica molecules.

In the present study, micro-hybrids of hydroxypropyl cellulose (HPC) and silica were prepared by the sol-gel process involving various initial amounts of TEOS, and are hereafter called micro-hybrids. The physical properties of these hybrids were compared with those of HPC/glass bead ($\sim$20–40 μm in diameter) composites prepared using solution blending with various amounts

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of glass beads. These HPC/glass bead composites are hereafter called blend composites. Because HPC contains hydroxyl groups in its molecular chain, we expect it to have hydrogen bonding with the silica networks in the hybrids prepared from HPC and TEOS. On the other hand, for the blend composite of HPC and glass beads, no interaction is expected between the polymer and filler.

EXPERIMENTAL

Materials

The HPC was purchased from Scientific Polymer Products, and the nominal weight-average molecular weight was 60 000. The degree of substitution was 2.5. The TEOS was purchased from Shin-etsu Chemical Industries and was used without further purification.

The micro-hybrids were prepared as follows. First, a 5 wt% ethyl alcohol solution of HPC was mixed with TEOS, HCl and H_2O, and stirred using an ultrasonic wave homogenizer. The mole fractions of H_2O and HCl to TEOS were 4 and 0.2, respectively. The weight fractions of TEOS in the mixture were varied at 20, 40, 50 and 60 wt%. The mixture was then poured into a Petri dish and was allowed to stand at room temperature for 1 week to evaporate the solvent. An optically transparent film was obtained. This film was heated at 60°C for 1 week to accelerate the curing reaction. The nomenclature used hereafter for these micro-hybrids from HPC mixed with 20, 40, 50 and 60 wt% TEOS is HPC-T20, HPC-T40, HPC-T50 and HPC-T60, respectively.

The blend composites were prepared as follows. First, a 5 wt% solution of HPC in ethyl alcohol was blended with 5, 10, 15 and 20 wt% glass beads. The glass beads of diameter 10–100 μm were sieved to obtain a 20–40 μm sieve fraction. The glass beads used were not chemically modified in order to study the composite system having a weak interaction between polymer matrix and filler. The HPC/glass bead blend was then poured into a Petri dish. Then to evaporate the solvent, the blend was allowed to stand at room temperature for 1 week and then heated at 60°C for 1 week. The nomenclature adopted for the blend composites mixed with 5, 10, 15 and 20 wt% glass beads is HPC-G5, HPC-G10, HPC-G15 and HPC-G20, respectively.

Silica flakes used for thermogravimetry (t.g.) and X-ray diffractometry were prepared under the same conditions as for the micro-hybrid. A 10 wt% ethyl alcohol solution of TEOS was mixed with HCl and H_2O, and the mixture was poured into a Petri dish. The sol-gel reaction was carried out at 60°C for 1 week after evaporating the solvent at room temperature.

Measurements

The t.g. of HPC and of the micro-hybrids was measured using a Seiko TG/DTA 320 (Seiko Instruments Inc.) at a heating rate of 10°C min^{-1} in a nitrogen atmosphere.

The tensile properties were measured using a Tensilon UTM 11 (Orientec Co. Ltd) at 25°C and 50% relative humidity. The crosshead speed was 10 mm min^{-1} and the gauge length was 10 mm. Miniature dumb-bell specimens, JIS K 7113 format, were used for determining the stress–strain behaviour to failure.

The dynamic viscoelastic properties of the hybrids were measured using a DMS 110 (Seiko Instruments Inc.). The heating rate was 2°C min^{-1} and the frequency was 10 Hz. The rectangular specimens used were 5 mm by 0.2 mm and 50 mm long. The dynamic modulus, G', and $\tan\delta$ were measured as a function of temperature using the shear mode.

X-ray diffractometry was measured using a CuKα beam at 30 kV and 30 mA. A Rigaku Geigerflex X-ray diffractometer was used.

RESULTS AND DISCUSSION

Thermogravimetry

Figure 1 shows the t.g. curves of HPC and its micro-hybrids as a function of the mixed amount of TEOS. The weight of HPC markedly dropped at ~350°C due to thermal degradation, and a small amount of char (1.2 wt%) remained at 600°C. For the micro-hybrids, weight loss occurred also at around 350°C, which was caused by thermal degradation of the incorporated HPC. The residual weight of the micro-hybrids at 600°C was dependent on the mixed amounts of TEOS, and involved char from HPC and silica-rich compounds. *Figure 2* shows an enlarged view of the initial stage of the t.g. curves so that the small changes in weight observed below about 300°C can more easily be identified. (The vertical axis has been expanded by a factor of 4 from that of *Figure 1*). The data of HPC-T50 and HPC have been displaced vertically. The first decrease in weight from 30°C to ~100°C was due to water desorption. For HPC no weight loss occurred between 100°C and 300°C. However, silica powder that was prepared by the sol-gel process at 60°C for 1 week showed a two-step weight loss, at 30°C and ~200°C. The first weight loss was due to the water desorption, and the second weight loss possibly to further sol-gel reaction that eliminated water and ethyl alcohol. The sol-gel reaction occurred continuously up to 600°C. For HPC-T50, the sol-gel reaction of mixed TEOS also occurred, indicating a small weight loss at ~200°C. The t.g. data for the micro-hybrids are summarized in *Table 1*. Water content was calculated from weight loss of the specimens at 100°C. Char content

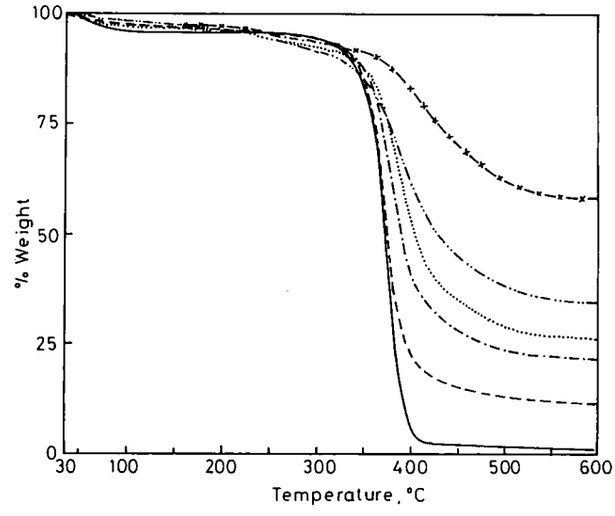

Figure 1 T.g. curves of HPC and its micro-hybrids as a function of initial TEOS content: (——) HPC; (– – –) HPC-T20; (– · –) HPC-T40; (· · · ·) HPC-T50; (– · · –) HPC-T60; (– × –) HPC-T80

was calculated by multiplying the residual weight of HPC by the initial amount of HPC in each micro-hybrid. Calculated values of SiO_2 content were estimated from the initial amount of TEOS, assuming that TEOS was converted completely to silica. However, observed values of SiO_2 were slightly larger than the calculated values because the alkoxysilane groups may not have completely polycondensed to SiO_2, leaving small amounts of silanol groups (SiOH) surrounded by HPC matrix. Furthermore, thermal decomposition of HPC may be affected by the presence of a nanometre-sized interface between silica and HPC resulting in a varied amount of char at 600°C.

Tensile properties

Figure 3 shows the stress–strain curves of HPC and its micro-hybrids as a function of TEOS content. The ultimate strength of HPC was 6 MPa, the elongation 57%, and the yield stress ~5 MPa. The strength of the micro-hybrids increased significantly with increasing amounts of initial TEOS up to 18 MPa for HPC-T40, and then decreased to 12 MPa for HPC-T50. HPC-T20 had a yield stress of 12 MPa. The elongation of the micro-hybrids decreased markedly with increasing amounts of initial TEOS. If the initial amount of TEOS was >60 wt%, the resulting micro-hybrids were very brittle and free-standing films could not be obtained. Small amounts of silica in the micro-hybrids drastically improved the mechanical properties for two reasons: (1) nanometre-sized particles of silica may have been dispersed evenly in the HPC matrix; and (2) the HPC chains strongly interact with silica or silanol through hydrogen bonding and were consequently entrapped in the silica networks. The mechanical behaviour of the micro-hybrids was very different from that of mechanically mixed filler systems.

Figure 4 shows the stress–strain curves of the blend composites. The ultimate tensile strength slightly decreased with filler content. Each blend composite had a yield stress of 5–6 MPa. The elongation decreased with increasing amounts of glass beads, but not as drastically as that seen for the micro-hybrids (*Figure 3*). When loading amounts of filler in a blend system increase, filler

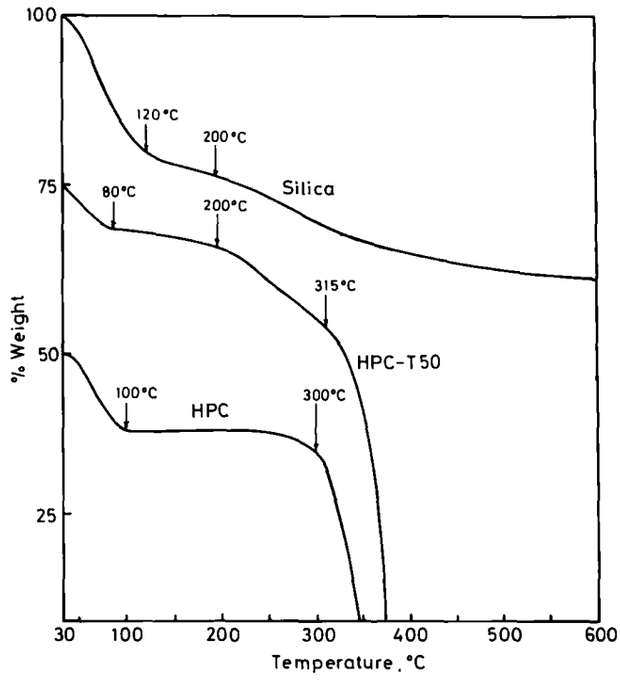

Figure 2 Initial stage of the t.g. curves for silica, HPC-T50 and HPC

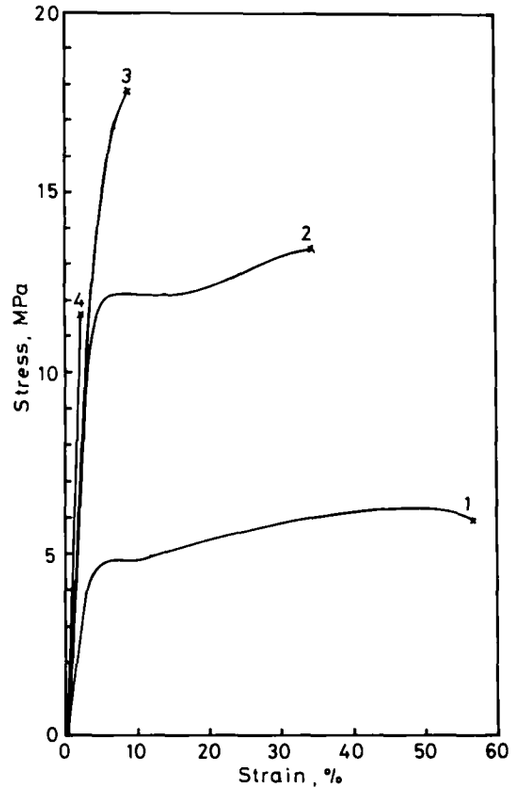

Figure 3 Stress–strain curves of HPC and its micro-hybrids as a function of initial TEOS content: (1) HPC; (2) HPC-T20; (3) HPC-T40; (4) HPC-T50

Table 1 T.g. measurement data for HPC and its micro-hybrids

	Water content (%)	Residual weight (%)	Char content (%)	Ceramic content (%)	SiO_2 calculated (%)
HPC	4.5	1.0	1.0	0	0
HPC-T20	3.1	11.7	0.8	10.9	6.7
HPC-T40	2.8	21.2	0.6	20.6	16.1
HPC-T50	2.7	25.8	0.5	25.3	22.4
HPC-T60	2.2	34.2	0.4	33.8	30.2
HPC-T80	1.9	57.9	0.2	57.7	53.4

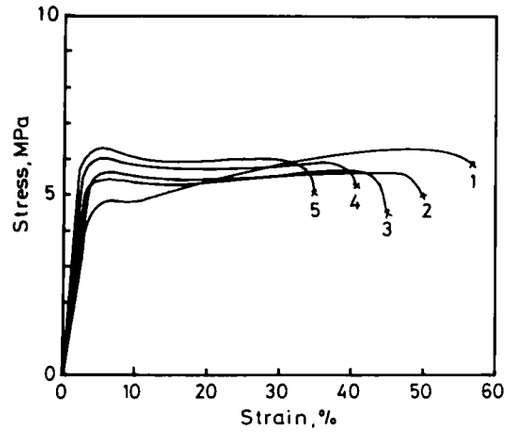

Figure 4 Stress–strain curves of HPC and its blend composites: (1) HPC; (2) HPC-G5; (3) HPC-G10; (4) HPC-G15; (5) HPC-G20

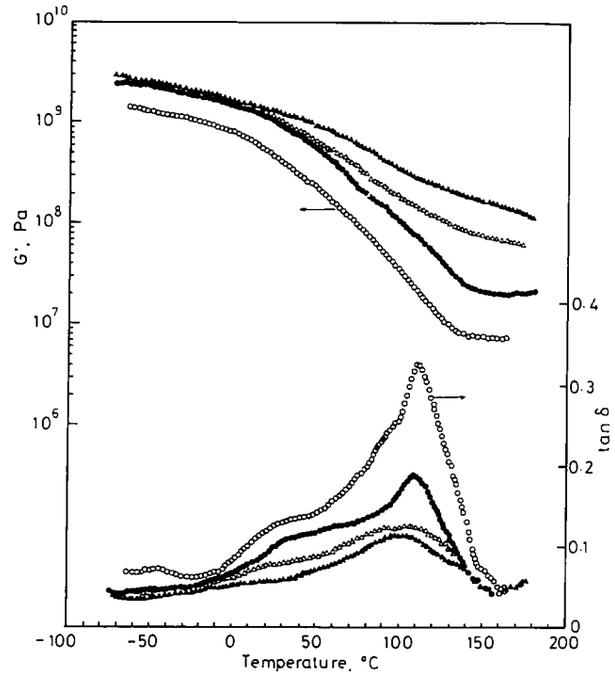

Figure 5 Dynamic viscoelastic properties of HPC and its micro-hybrids: (○) HPC; (●) HPC-T20; (△) HPC-T40; (▲) HPC-T50

particles aggregate and act as a mechanically weak point. The shape of the stress–strain curves is almost the same even when the filler content reached 20 wt%. This indicates that interaction between HPC and the glass beads may be weak, and that molecular motions of HPC are not affected by the glass beads. Landry *et al.*[4] observed aggregation of filler particles in silica/PVAc systems by TEM. However, the micrograph of the *in situ* hybrids made of PVAc and TEOS indicated a much finer texture that was more evenly dispersed than that for silica-filled systems.

Dynamic viscoelastic properties

Molecular motions of polymers are usually characterized by investigating the dynamic viscoelasticity of the polymers. *Figure 5* shows the dynamic viscoelastic properties of HPC and its micro-hybrids at 10 Hz. The dynamic modulus, G', of HPC decreased with temperature from 1.5 GPa at −70°C to 10 MPa at 170°C, and had a plateau at 140°C. By hybridizing HPC with silica, the modulus was improved over the entire temperature range. The G' of the micro-hybrids decreased from 3 GPa at −70°C with increasing temperature and levelled off at temperatures higher than 140°C. The G' level of the micro-hybrids above 25°C increased with the initial TEOS content.

The tan δ curve of HPC shows a high, sharp peak at 110°C (corresponding to the α_1-relaxation) and two small peaks at ~25°C (α_2-relaxation) and −45°C (β-relaxation). The α_1-peak of the micro-hybrids broadened and its height lowered as the initial TEOS content increased. The α_2-peak was observed for HPC-T20, but disappeared when the initial TEOS content increased above 40 wt%. The β-peak was not observed for the micro-hybrids. This behaviour of the tan δ peaks indicates that the molecular motions of HPC entrapped in the silica networks are strongly restricted by silica molecules via hydrogen bonding.

The frequency dependence of the tan δ peak temperature is approximated by the Arrhenius equation:

$$f = f_0 \exp(-E_a/RT)$$

where f is the frequency, f_0 is a constant, E_a is the apparent activation energy, T is the absolute temperature at which the tan δ peak occurs and R is the gas constant. *Figure 6* shows the Arrhenius plot for HPC. From the slope of each line, the activation energies for the three relaxations were derived as 258 kJ mol^{-1} for the α_1-relaxation, 146 kJ mol^{-1} for the α_2-relaxation and 93 kJ mol^{-1} for the β-relaxation. Rials and Glasser[16] have studied the dynamic mechanical properties of HPC and reported that the α_1-relaxation with 232 kJ mol^{-1} occurred at 80°C, the α_2-relaxation with 190 kJ mol^{-1} at 19°C and the β-relaxation with 62 kJ mol^{-1} at −55°C. They also reported that the peak temperatures of the α_1- and α_2-relaxations can be increased by crosslinking. They concluded that the α_1- and α_2-relaxations are similar to glass transitions associated with a more highly ordered

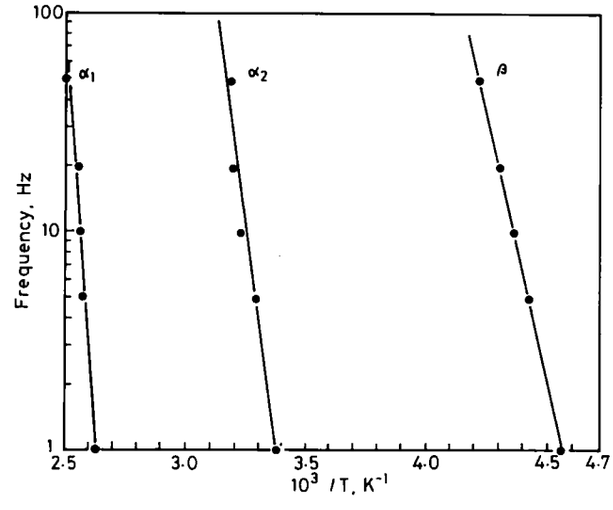

Figure 6 Arrhenius plot of frequencies and reciprocal of the tan δ peak temperature

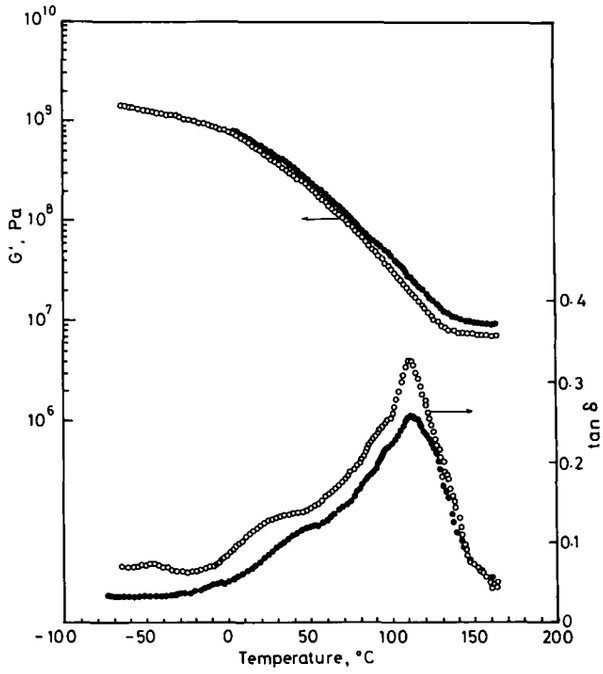

Figure 7 Dynamic viscoelastic properties of HPC and its blend composite: (○) HPC; (●) HPC-G20

phase due to a residual liquid crystal superstructure (for the α_1 case) and an amorphous component (for the α_2 case) in bulk HPC, and that the β-relaxation can be attributed to the interaction between hydroxyl groups of the polymer and residual diluent. Suto *et al.*[17] have also studied the dynamic viscoelastic properties of HPC, and found two tan δ peaks at 25°C and 110°C; the first peak is associated with the glass transition of an anhydroglucose ring in the HPC chain, and the second with the rotation of the ring. However, since HPC is a typical liquid crystalline polymer, a mesophase was observed at ~110°C using d.s.c.[16]. It seems reasonable that the α_1-relaxation is caused by molecular motion in a more highly ordered phase such as the mesophase, and the α_2-relaxation is due to molecular motion in a random amorphous phase. The secondary transition, β-relaxation, which appeared below 0°C, is frequently observed in various cellulose derivatives. For example, in cellulose acetate (−45°C)[18] this transition is caused by the molecular motion of the side chains of acetyl groups, in dialcohol cellulose (−70°C)[19] it is caused by the motion of methylol groups, and in benzylcellulose (−50°C)[20] it is caused by the motion of benzyl groups. For HPC, the β-relaxation may also relate to the molecular motion of the side chain, i.e. the hydroxypropyl group, but further investigation is required for a complete understanding of this secondary relaxation.

As indicated in *Figures 3* and *4*, the tensile properties of the micro-hybrids were considerably different from those of the blend composite because of the strong interaction between HPC and the silica network. In *Figure 7* the dynamic viscoelastic properties of the blend composite HPC-G20 are compared with those of HPC. HPC-G20 contains 20 wt% glass beads, which is almost the same amount of silica as in HPC-T50, namely, 22.4 wt% silica, if 50 wt% TEOS is converted completely. The G' of HPC-G20 in the glassy state below ~25°C is the same level as that of HPC, and above 25°C, the G' level of HPC-G20 is slightly higher than that of HPC. In the tan δ curve, the height of the α_1-peak is lower but sharper than that of HPC-T50 (*Figure 5*). The α_2-peak is still observed at ~40°C as a shoulder, but the β-peak is not detected. Molecular motion of HPC in the blend composite is not restricted by the mixed filler, since the interaction between HPC and the glass beads may be weak.

X-ray diffractometry

Samuels[21] has reported that the crystalline structure of HPC is pseudotetragonal with dimensions $a = b = 11.33$ Å and $c = 15.0$ Å. Also in the X-ray diffraction pattern, he observed a peak from the (1 0 0) spacing at $2\theta = 7.8°$ and an amorphous halo at $2\theta = 20.3°$. He concluded that stiff, rod-like molecules of HPC are packed into microfibrillar crystallites that are 470 Å in length and 34 Å in diameter. *Figure 8* shows the X-ray diffractograms of HPC, HPC-T20, HPC-T40, HPC-T50, HPC-T60 and silica obtained in our study. In the diffraction pattern of HPC, two peaks are observed at $2\theta = 8°$ and 20°. These two peaks are also observed for the micro-hybrids, but the intensity at 8° decreases with increasing amounts of initial TEOS content. It is noteworthy that this peak at 8° is still observed even at 60 wt% initial TEOS. This indicates that when HPC molecules are incorporated and entrapped in the silica network, crystallites of HPC may have formed in the HPC-rich phase of the micro-hybrid. Moreoever in the X-ray diffractograms of the micro-hybrids, the intensity increased with decreasing scattering angle below $2\theta = 7°$. In the case of silica flake prepared by the sol-gel process of TEOS, this scattering at small angles below 7° also occurred. Brinker *et al.*[22] have studied the morphology of sol-gel-derived silica, and

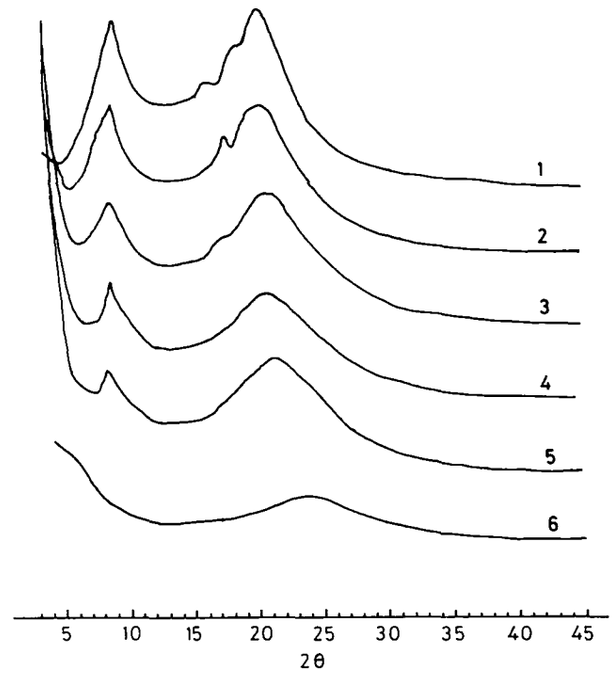

Figure 8 X-ray diffractograms of HPC, its micro-hybrids and silica: (1) HPC; (2) HPC-T20; (3) HPC-T40; (4) HPC-T50; (5) HPC-T60; (6) silica

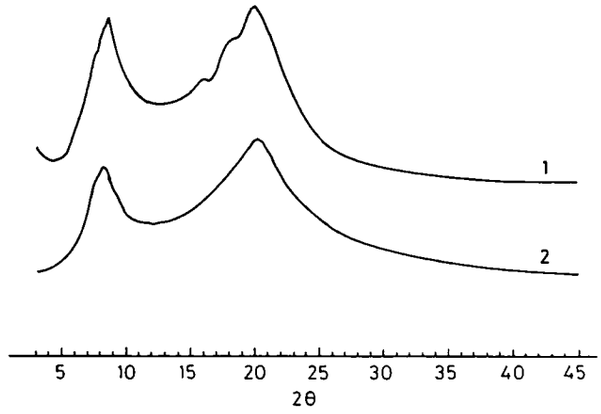

Figure 9 X-ray diffractograms of HPC and HPC-G20: (1) HPC; (2) HPC-G20

reported that acid-catalysed silica has a radius of gyration, $R_g = 15$–17 Å, evaluated using the Guinier relation from the measurement of SAXS. They also observed silicate particles with 50 Å diameters by TEM. Nakanishi *et al.*[23] have studied the SAXS of a sodium polystyrene sulfonate (NaPSS)/SiO_2 micro-hybrid, and reported that a 0.2–50 nm domain was formed during the sol-gel reaction due to micro-phase separation into a silica-rich phase and a polymer-rich phase. The increase in the intensity at small angles below 7° may be caused by an enhanced interface scattering due to the hybridization of HPC with silica. Pore surface scattering of the alkoxide-derived silica flake also appeared at small angles below 7°. However, a further study of SAXS for the micro-hybrids is required for a quantitative understanding.

The X-ray diffractogram of the blend composite HPC-G20 is compared with that of HPC in *Figure 9*. The X-ray diffraction pattern of HPC was not changed by the 20 wt% of glass beads. The crystalline phase in the composite is not affected by the mixed filler, since the interaction between HPC and the glass beads is weak. The scattering (the increase in the intensity) at small angles below 7° cannot be observed in the diffractogram of HPC-G20 because the composite does not have the nanometre-sized domain.

CONCLUSIONS

Micro-hybrids of HPC and silica (i.e. *in situ* micro-hybrids) were prepared by the sol-gel process involving TEOS. The mechanical properties of these hybrids were compared with those of HPC composites blended with 20–40 μm diameter glass beads (i.e. blend composites). The ultimate tensile strength of the *in situ* micro-hybrids increased from 6 MPa with increasing amounts of initial TEOS content, and reached a maximum of ~18 MPa at 40 wt% TEOS content. On the other hand, the strength of the blend composites decreased with glass bead content. The elongation at fracture for the *in situ* hybrids and the blend composites decreased with loading amounts of silica and glass beads.

The dynamic viscoelastic properties of HPC indicated α_1-, α_2- and β-relaxations at 110, 25 and −45°C, respectively. The α_1- and α_2-relaxations were similar to glass transitions associated with a more highly ordered phase and amorphous component, respectively. The β-relaxation may be related to the molecular motion of hydroxypropyl groups. The level of the dynamic modulus, G', of the *in situ* micro-hybrids markedly increased with TEOS content above the glass transition temperature. In the tan δ curve, the α_1-peak broadened and its intensity lowered as the initial TEOS content increased. The α_2-peak could be observed for the *in situ* micro-hybrid with 20 wt% initial TEOS content, but this peak disappeared when the TEOS content exceeded 40 wt%. The β-peak did not appear for the *in situ* hybrid. The dynamic viscoelastic properties of the blend composite mixed with 20 wt% glass bead content were almost the same as those of HPC, demonstrating that the glass beads do not affect the molecular motions of the HPC component of the composite. For the *in situ* micro-hybrids, however, nanometre-sized ceramic particles may be dispersed in the HPC matrix, suggested by the significant increase in the intensity of the X-ray diffractograms at small angles below 7° (as can be seen in *Figure 8*). Therefore, the interaction between the organic polymer and ceramic network is strong due to the hydrogen bonding. This strong interaction improves the mechanical properties of the hybrids such as the ultimate strength and the modulus of elasticity. The molecular motions of the HPC component in the *in situ* micro-hybrids are strongly restricted by the polymer–silica interaction, which then affects the tan δ peaks and the elongation at fracture of the micro-hybrid.

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