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# Hybrids of $SiO_2$ and poly(amide 6-*b*-ethylene oxide)

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Hybrids of poly(amide-6-*b*-ethylene oxide), Pebax®, and silica were prepared by using a sol–gel process. The inorganic phase was grown by hydrolysis-condensation of tetraethoxysilane, TEOS, by acid catalysis, in presence of Pebax/*n*-butanol or Pebax/formic acid:tetrahydrofuran (1:1 w/w). Pebax/silica hybrids, with different compositions, were obtained and characterized by stress–strain tests, dynamic-mechanical analysis, X-ray diffraction, transmission electron and scanning electron microscopy. The effect of the preparation conditions on the hybrid properties is discussed. © 1997 Elsevier Science Ltd.

**(Keywords: sol–gel process; poly(amide-6-*b*-ethylene oxide)/silica; organic–inorganic composite; hybrid materials)**

## INTRODUCTION

Polymer composites have been widely investigated[1]. The introduction of inorganic fillers in a polymer matrix increases its strength and stiffness. The particle size of the inorganic compound influences the final properties, which are also controlled by the interfacial interactions between matrix and inorganic filler. A new class of inorganic–organic composites is now being investigated, using a sol–gel process to grow the inorganic phase *in situ*. In most of the cases of sol–gel hybrid preparation, the inorganic phase is grown from hydrolysis-condensation reactions of alkoxysilanes, mainly tetramethoxy- or tetraethoxysilanes. The mechanism of hydrolysis-condensation of alkoxysilanes is also well described[2]. The most simple procedure is to form an inorganic network in a solution containing organic polymers. Hybrid preparation in this way has also been described, using poly(vinyl alcohol)[3], poly(acrylic acid)[4], poly(methyl methacrylate)[5], poly(vinyl pyrrolidone)[6], poly(ethylene oxide)[7] and Nafion®[8,9].

The sol–gel process allows the preparation of inorganic–organic hybrids with a fine dispersion even at the molecular level[10]. The advantages lie not only in the physical and chemical properties, but also in the wide versatility in processing offered by the colloidal state. The low viscosity of sols allows the preparation of films by dip-coating, spraying or spin-coating[11]. The various characteristics of the sol–gel process, such as low processing temperatures, allow the introduction of organic molecules into an inorganic network, improving the matrix characteristics. For instance, the mechanical properties[12] can be modified, porosity can be controlled and the hydrophilic/hydrophobic balance[13] can be adjusted. The inorganic component contributes to the mechanical and thermal stability and may lead to interesting electrochemical or electrical properties[14]. The nanocomposites synthesized by sol–gel exhibit novel properties and have a potential application for biomaterials[15,16], membranes[17], non-linear optics[18], coatings[19], catalysis[20], optics and electrooptics[21], and solid electrolytes[7]. Recently, reviews on this new family of inorganic–organic hybrids have been published[22,23].

In this work, hybrids of poly(amide-6-*b*-ethylene oxide) and silica were prepared. The copolymer is an elastomer and its combination with silica results in a large diversity of mechanical properties. It is also quite hydrophilic, dissolving in polar solvents and favouring dispersion of the inorganic polymer. Also, because of its high hydrophilicity, poly(amide-6-*b*-ethylene oxide) has been used for membrane preparation[24], and the hybrid formation may give new permselectivity properties, as already verified for other elastomers such as silicone[25]. Another possible application for poly(amide-6-*b*-ethylene oxide)/silica hybrids is in the preparation of solid electrolytes with improved mechanical properties. The characteristics of the copolymer itself (without silica) have recently been reported[26]. The application of these hybrids for membranes and solid electrolytes is the subject of current work in this laboratory. Here, in this paper, the influence of different preparation conditions on the morphology and mechanical properties is reported.

## EXPERIMENTAL

### *Hybrid preparation*

The copolymer with polyamide-6 and poly(ethylene oxide) blocks was kindly supplied by Elf Acquitaine with the trade name PEBAX® MX1657. The chemical composition of Pebax was confirmed in a 2400 Perkin Elmer CHN elemental analyser. It contains 40 wt% polyamide-6 blocks and 60 wt% poly(ethylene oxide) blocks.

Since one of the copolymer blocks is a polyamide, it can dissolve in only very few solvents. In this paper experiments were performed in formic acid and

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**Table 1** Young's modulus, stress at break, strain at break and energy at break of Pebax/silica hybrids, prepared in *n*-butanol

| Pebax/TEOS | Young's modulus (MPa) | Stress at break (MPa) | Strain at break (%) | Energy at break (J) |
|---|---|---|---|---|
| 100:0[a] | 37 ± 5 | 34 ± 6 | 330 ± 35 | 0.52 ± 0.09 |
| 78:22[a] | 55 ± 5 | 43 ± 16 | 309 ± 39 | 0.8 ± 0.2 |
| 75:25[a] | 56 ± 8 | 40 ± 11 | 304 ± 34 | 0.7 ± 0.1 |
| 71:29[a] | 50 ± 5 | 41 ± 7 | 300 ± 31 | 1.0 ± 0.1 |
| 67:33[a] | 50 ± 7 | 39 ± 10 | 287 ± 33 | 1.0 ± 0.2 |
| 60:40[a] | 62 ± 6 | 23 ± 7 | 168 ± 28 | 0.4 ± 0.1 |
| 100:0[b] | 49 ± 9 | 0.8 ± 0.2 | 1.8 ± 0.5 | $(2.6 \pm 0.8) \times 10^{-4}$ |

[a] pH = 7
[b] pH = 1

**Table 2** Young's modulus, stress at break, strain at break and energy at break of Pebax/silica hybrids prepared in 1/1 HCOOH : THF

| Pebax/TEOS | Young's modulus (MPa) | Stress at break (MPa) | Strain at break (%) | Energy at break (J) |
|---|---|---|---|---|
| 100:0 | 12 ± 1 | 40 ± 12 | 469 ± 97 | 1.9 ± 0.3 |
| 78:22 | 15 ± 2 | 77 ± 6 | 679 ± 92 | 1.9 ± 0.3 |
| 75:25 | 16 ± 1 | 151 ± 42 | 904 ± 178 | 3.0 ± 0.6 |
| 71:29 | 18 ± 2 | 53 ± 7 | 434 ± 80 | 1.6 ± 0.2 |
| 67:33 | 21 ± 6 | 41 ± 8 | 352 ± 62 | 1.8 ± 0.5 |
| 60:40 | 28 ± 5 | 33 ± 13 | 267 ± 78 | 1.3 ± 0.5 |
| 100:0[a] | 28 ± 4 | 20 ± 1 | 137 ± 12 | 0.9 ± 0.1 |

[a] Films obtained from solutions in HCOOH : THF which were previously heated for 6.5 h at 60°C

*n*-butanol. The former is a known solvent for polyamides. As previously shown, butanol is also one of the few solvents for the copolymer. When compared to formic acid, it is more volatile and allows work at a higher pH.

Different volumes of tetraethoxysilane (TEOS) (Aldrich) were carefully added to a 10 wt% Pebax solution in 1 : 1 (w/w) HCOOH : THF under stirring, with pH around 1. Water was dropped into the Pebax solution, always keeping a 2 : 1 molar water/TEOS stoichiometric proportion. The solution (*ca.* 30 ml) was further stirred for 8 h at room temperature and transferred to a closed glass Petri dish of 11 cm diameter. The reaction was allowed to continue for 16 h. The dish was opened, the solvent was evaporated at 50°C and the films were further dried under vacuum for one week.

The same procedure was used with a 3 wt% *n*-butanol/Pebax solution. Solutions with higher polymer contents easily gel and could not be obtained with this solvent. In this case, a 0.15 M HCl aqueous solution was added instead of pure water for keeping the 2 : 1 molar water/TEOS stoichiometric proportion. The pH of these solutions was near 7. Solutions with pH = 1 were also prepared by adding concentrated HCl in order to compare the results with those obtained for systems prepared in 1 : 1 HCOOH : 1 : 1 THF. The solution was stirred for 6.5 h at 60°C and transferred to a closed Teflon dish. Hybrids prepared from solutions in butanol on glass dishes were quite adherent and could not be conveniently handled. The reaction was allowed to continue for 16 h. The dish was opened, the solvent was evaporated at 50°C, and the films were further dried under vacuum for one week.

### *Stress–strain tests*

Stress–strain measurements were performed using an Emic Mem 200 equipment with crosshead speed of 500 mm min$^{-1}$ and a 500 N cell. Specimens measuring 10 × 0.70 × 50 mm were used. The results presented in *Tables 1* and *2* are averages of more than ten measurements.

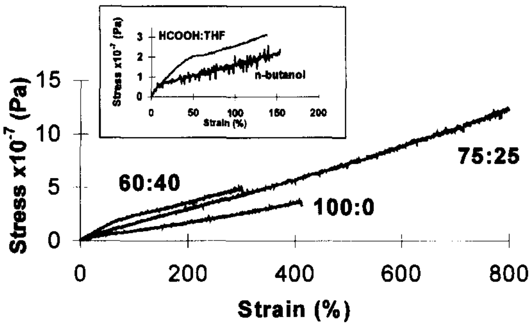


**Figure 1** Stress–strain curves for Pebax hybrids prepared in HCOOH : THF. Insert: Detail of the yield point on the stress–strain curve for 60 : 40 Pebax/TEOS prepared in HCOOH : THF or *n*-butanol

### *Dynamic-mechanical analysis*

Dynamic-mechanical analysis was performed with a DMA 983 TA Instruments thermal analyser from −150 to 200°C, at a frequency of 1 Hz and an amplitude of 0.20 mm.

### *Scanning electron microscopy*

The samples were fractured in liquid nitrogen and coated with gold by sputtering. Images were obtained in a JEOL T-300 scanning electron microscope.

### *Transmission electron microscopy*

Samples were cut at −80°C with a diamond knife in an FC4E Ultracut Leitz–Reichert–Jung microtome and observed in a Zeiss CEM-902 transmission electron microscope.

### *Infrared spectroscopy*

Infrared spectroscopy was performed with a 1600 Perkin Elmer *FT*i.r. spectrometer. Samples were analysed as films, using a reflectance accessory.

### *X-ray diffraction*

X-ray diffraction measurements were performed with an XD-3A Shimadzu X-ray diffractometer, using Cu $K_\alpha$ radiation.

## RESULTS AND DISCUSSION

### *Physical characteristics of Pebax/silica hybrids*

Pebax films (without silica) were obtained by casting the copolymer solution. HCOOH : THF/Pebax solutions gave translucent films and *n*-butanol/Pebax solutions (pH = 7) formed completely transparent films. Both were very flexible, non-adherent on a glass Petri dish and easy to handle.

The incorporation of silica (via the sol–gel process) into Pebax matrices produced films with different optical characteristics. Hybrids obtained from solution in HCOOH : THF were translucent when the TEOS content was no higher than 67 wt% and were opaque above this limit. All hybrids prepared from solution in butanol (TEOS content up to 78 wt%) were transparent.

With regard to their mechanical properties, all hybrids prepared from solution in butanol (pH = 1) were very brittle. Hybrids prepared from solution in HCOOH : THF, as well as in butanol (pH = 7), were flexible when the TEOS contents were lower than 50 wt%.

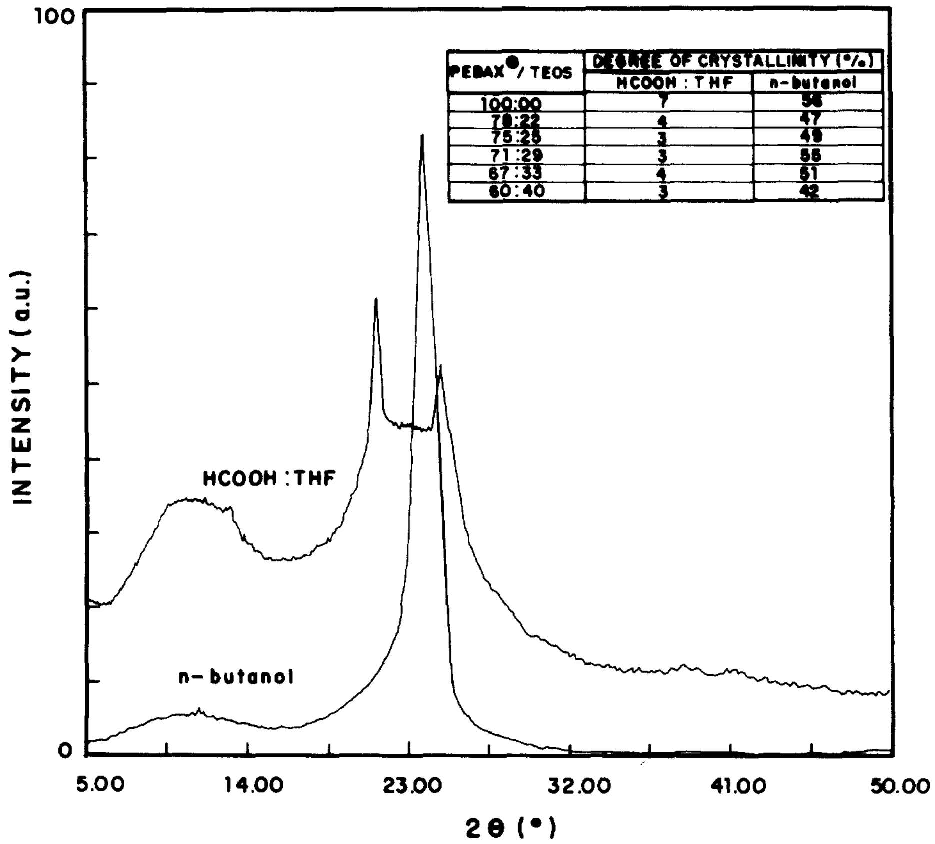
### *Stress–strain tests*

*Figure 1* shows stress–strain curves for films of 100 : 0, 75 : 25 and 60 : 40 Pebax/TEOS ratios. Hybrids with other compositions were also tested and *Tables 1* and *2* show their Young's modulus, stress at break, strain at break and energy at break.

A considerable increase of the elasticity modulus was observed when 22 wt% TEOS was incorporated in films prepared from solutions in *n*-butanol (*Table 1*). A further increase was observed when the TEOS content changed from 33 to 40 wt%. With the incorporation of 22% TEOS, the stress and energy at break also increased. On the other hand, the strain at break always decreased as a function of TEOS concentration. Similar behaviour has been described also for polyimide–silica hybrids[27] and for poly(dimethyl siloxane) filled with $TiO_2$[28]. When the TEOS content was higher than 33 wt% in Pebax/TEOS hybrids (also obtained in *n*-butanol, pH = 7), a decrease of both stress and energy at break was observed, and the hybrids became more rigid and brittle, as expected.

With regard to the behaviour of hybrids obtained in HCOOH : THF, shown in *Table 2*, the elasticity modulus gradually increased with TEOS concentration. The stress at break and the energy at break were maximum for 75 : 25 Pebax/TEOS. This behaviour, although more accentuated, is similar to that observed for hybrids prepared in *n*-butanol. A clear difference was detected for the strain at break, which had a maximum for samples obtained in HCOOH : THF instead of always decreasing as in the case of butanol.

The mechanical behaviour of hybrids can be explained in analogy to the effect of rigid fillers on the stress–strain properties of polymers. Rigid particulate fillers increase



| PEBAX®/ TEOS | DEGREE OF CRYSTALLINITY (%) | |
|---|---|---|
| | HCOOH : THF | n-butanol |
| 100:00 | 7 | 56 |
| 78:22 | 4 | 47 |
| 75:25 | 3 | 49 |
| 71:29 | 3 | 56 |
| 67:33 | 4 | 51 |
| 60:40 | 3 | 42 |

**Figure 2** X-ray diffractograms of 75 : 25 Pebax/TEOS prepared in HCOOH : THF or in *n*-butanol. Insert: crystallinity degree as a function of composition

the modulus, at least when the matrix–filler adhesion is good. Generally, fillers cause a decrease in elongation at break as in the case of hybrids obtained in butanol. Fillers also often decrease the tensile strength, but there are numerous exceptions (for instance, carbon black in rubber). With rigid fillers, the actual elongation experienced by the polymer matrix is much greater than the measured net elongation of the specimen as a whole. Although the specimen is part filler and part matrix, all the elongation comes from the polymer if the filler is rigid. The theory is complex and still incomplete at present, and the expected results depend upon the exact fracture mechanism. However, simple models give a qualitative and often a semi-quantitative understanding of experimental results. If there is good adhesion between matrix and filler, and if the fracture path tends to go from particle to particle rather than giving a perfectly smooth fracture surface, the following equation is expected to be approximately correct[29,30]:

$$\epsilon_B = \epsilon_B^0(1 - \varphi_2^{1/3}) \qquad (1)$$

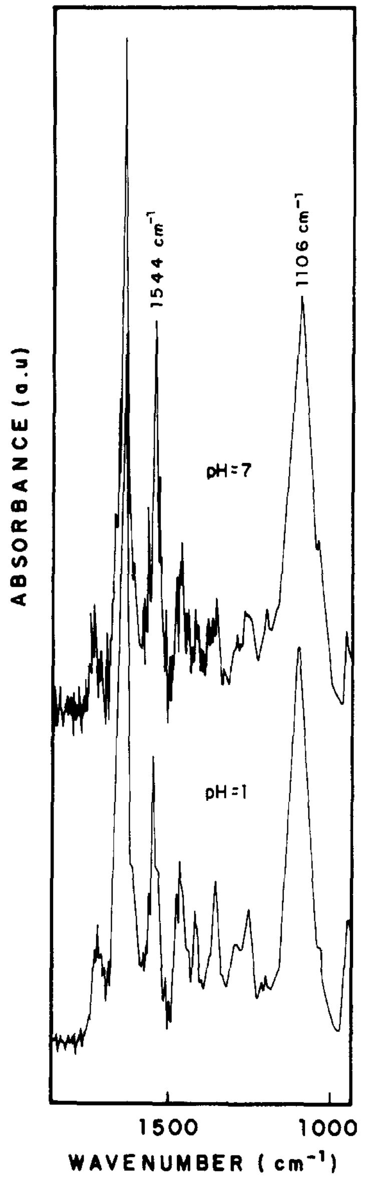


**Figure 3** Infrared spectra of pure Pebax films prepared in *n*-butanol with solution pH = 7 or 1

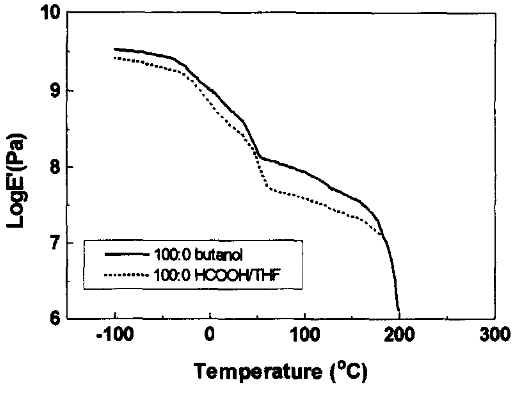


**Figure 4** Dynamic-mechanical analysis (storage modulus as a function of temperature) for pure Pebax films prepared in HCOOH : THF or *n*-butanol

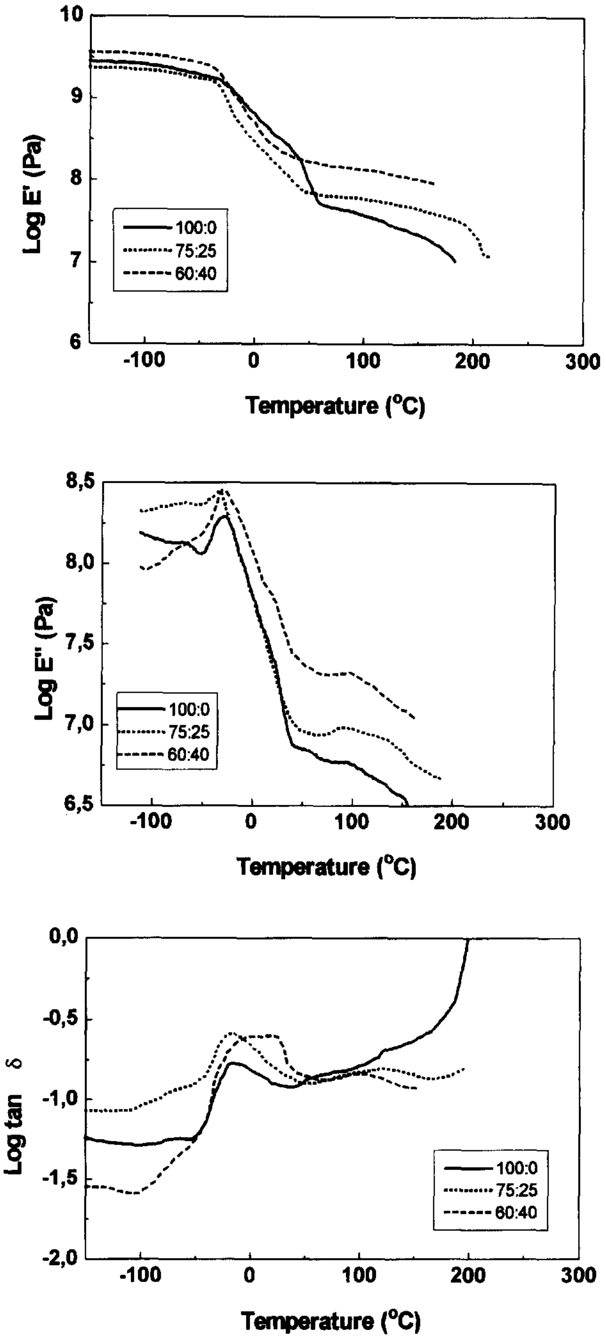


**Figure 5** Dynamic-mechanical analysis of Pebax/TEOS hybrids prepared in HCOOH : THF

where $\epsilon_B$ is the elongation at break of the filled polymer, $\epsilon_B^0$ is the elongation at break of the unfilled polymer and $\varphi_2$ is the volume fraction of the filler. This equation determines a very dramatic decrease in elongation that can be brought about by even small amounts of fillers. It can be noted that the decrease in elongation at break for hybrids prepared in *n*-butanol (or even for hybrids prepared in HCOOH : THF with 29–40% TEOS) is not so dramatic as predicted by equation (1). Only in rare instances where fillers introduce additional crazing, and perhaps at the same time act as stoppers to crack growth, do polymers filled with rigid fillers have elongations at break which are equal to or greater than that of the unfilled polymer[31], as in the case of hybrids prepared in HCOOH : THF.

Fillers often induce yield points in the stress–strain curves of rubbers and ductile polymers. The yielding phenomenon is due to crazing or to a dewetting effect, in which the adhesion between filler and matrix is destroyed and, as a consequence, the modulus decreases. At the same time, voids are created and the specimen dilates[32–37]. A tendency to develop a yield point was clearly seen for 60 : 40 Pebax/TEOS hybrids prepared in HCOOH : THF. For hybrids prepared in *n*-butanol ($pH = 7$), this trend was not observed. As will be shown below, the films prepared in *n*-butanol are more crystalline than those prepared in HCOOH : THF (practically amorphous), which are much more rubbery and, therefore, more susceptible to yield.

Novak[10] has reported that hybrids prepared by simultaneous formation of an inorganic network into a polymerizing monomer, such as 2-hydroxyethyl methacrylate, act fundamentally differently from the organic polymer alone. Under specific sol–gel conditions, hybrids can be obtained with much better mechanical properties than the pure polymer (higher yield strength, elastic modulus and toughness).

The increase in the elasticity modulus with the introduction of particles of the disperse filler can be described in different ways. The equation that describes the experimental data more precisely is[38]:

$$E_{fp} = E_p(1 + 2.5\varphi_2 + 1.4\varphi_2^2) \tag{2}$$

where $E_{fp}$ and $E_p$ are the moduli of elasticity of the filled and unfilled polymers, respectively. In the case of hybrids obtained in this investigation it was verified that the increase in elasticity modulus is higher than that predicted in equation (2). In hybrids, the inorganic phase (and therefore the 'filler') is usually formed as a silica network[2,6,39] and not as an ordinary particulated filler, specially at low pH. This could explain the deviation from equation (2).

Comparing stress–strain data obtained for hybrids prepared in HCOOH : THF ($pH = 1$) and in *n*-butanol ($pH = 7$), it was verified that, independently of composition, those prepared in *n*-butanol had higher elasticity modulus and lower stress, strain and energy at break than hybrids synthesized in HCOOH : THF. Even pure Pebax films obtained from solutions in different solvents had distinct properties. *Figure 2* shows that Pebax films obtained from solutions in different solvents have quite different degrees of crystallinity. Films obtained from solutions in butanol are much more crystalline. If the hybrids are taken into account, other additional aspects should be considered beside crystallinity. During the preparation in HCOOH : THF and butanol, other conditions—pH and temperature—have been changed.

In order to analyse the importance of acidity, Pebax/TEOS hybrids were prepared from *n*-butanol/Pebax solutions, adjusting $pH = 7$ or $pH = 1$. Both pure polymer films and hybrids obtained at $pH = 1$ produced very brittle and fragile materials. Since low pH could

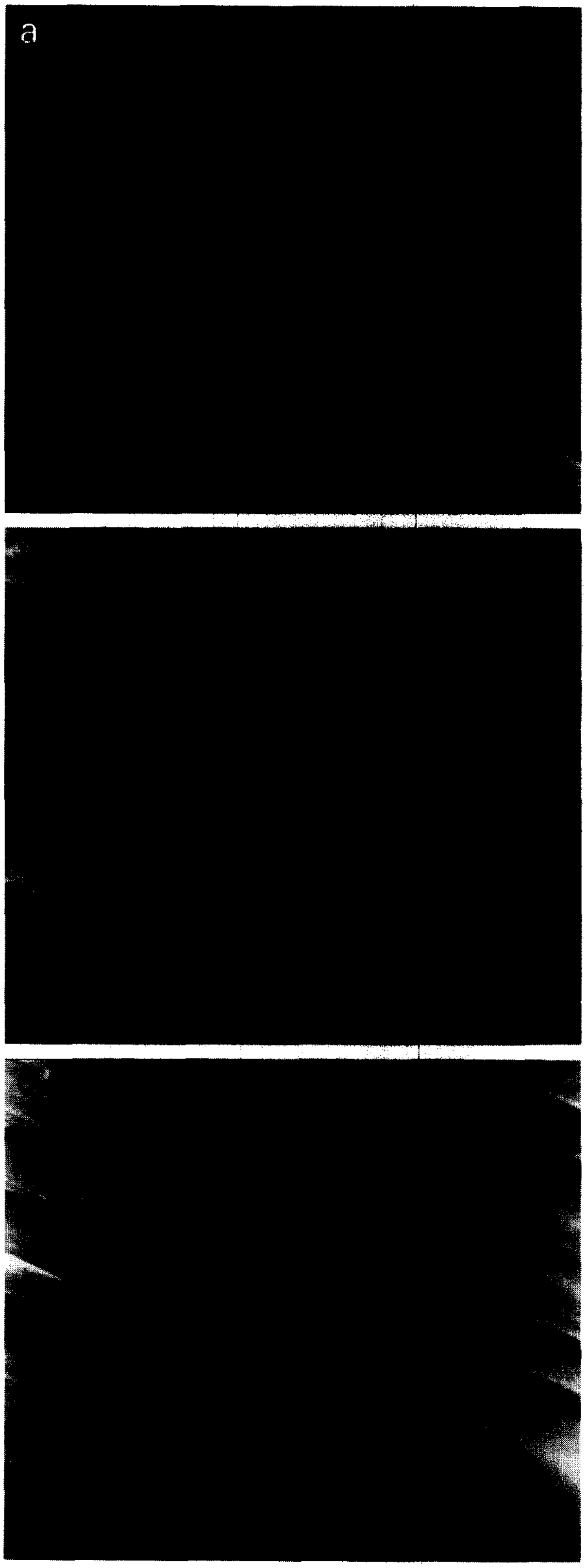


**Figure 6** Scanning electron microscopy of (a) 78 : 22, (b) 22 : 78 Pebax/TEOS hybrids prepared in 1 : 1 HCOOH : THF or (c) 22 : 78 in *n*-butanol

have promoted polymer degradation, pure Pebax films obtained in different pHs were analysed by infrared spectroscopy, as shown in *Figure 3*. The intensity ratio between bands in 1106 $cm^{-1}$ (characteristic of C–O–C stretching in poly(ethylene oxide)) and 1544 $cm^{-1}$ (characteristic of amide N–H deformation and C–N stretching in polyamide-6) changed from 1.00 at pH = 7 to 1.13 at pH = 1. This confirms that in acid solutions the amide groups hydrolyse, forming amine and carboxylic acid[24].

In order to analyse the influence of temperature, pure Pebax films were prepared in HCOOH : THF at room temperature or at 60°C (*Table 2*). When prepared at 60°C, the films were more rigid and fragile. However, the effect is much less accentuated than the pH effect.

*Dynamic-mechanical analysis*

Pebax films obtained from solution in different solvents were subjected to dynamic-mechanical analysis. Curves of log $E'$ as a function of temperature are shown in *Figure 4*. Here again the effect of different crystallinities is clear. For films obtained in different solvents, a transition starts below −20°C and the storage modulus gradually decreases. Near 30°C, the modulus decreases more drastically and finally reaches a plateau. The magnitude of this plateau depends on the solvent used in the film preparation. The plateau is higher in samples with a higher degree of crystallinity (samples obtained in butanol). Crystallites usually act as physical crosslinks and increase the modulus, inhibiting the polymer flow. Only near 200°C do the films start to flow as a consequence of melting. As a first approximation, the storage modulus above $T_g$ is related to the degree of crystallinity ($w_c$) according to equation (3):

$$\log G = 6.763 + 4.66 w_c \tag{3}$$

where $G$ is the shear modulus[37], analogous to the storage modulus $E'$, but obtained in torsion experiments.

*Figure 5* shows the dynamic-mechanical behaviour as a function of the incorporation of the inorganic

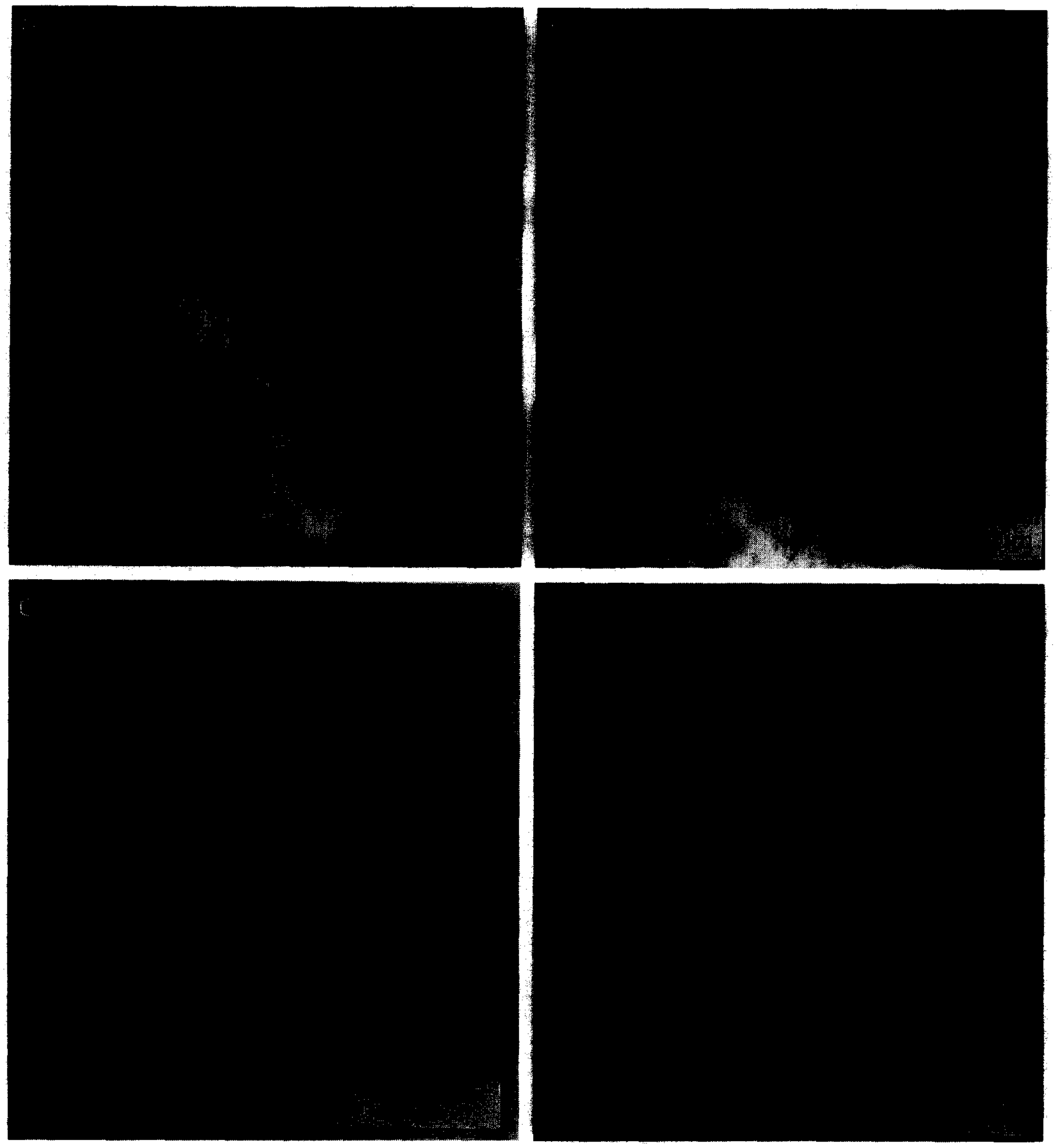


**Figure 7** Transmission electron microscopy of (a, c) pure Pebax and (b, d) 60 : 40 Pebax/TEOS hybrids prepared in (a, b) 1 : 1 HCOOH : THF or (c, d) *n*-butanol

component. Curves for films obtained in different solvents followed the same pattern and only the results for HCOOH : THF are shown here. Curves of log $E'$ as a function of temperature have the same tendency, except that the plateau $T_g$ and melting is higher for higher inorganic content. This is usually observed also in polymer samples with fillers[37].

Curves of log $E''$ as a function of temperature did not change much with the silica content, at least as far as $T_g$ is concerned. For films obtained in butanol, the curves are even more coincident, also with regard to $T_g$. Since there is no shift in $T_g$, the inorganic phase is probably acting as an inert filler without preferential interaction with the polymer.

With regard to curves of log tan$\delta$ as a function of temperature, the incorporation of silica caused an enlargement of the $T_g$ peak. Besides this peak enlargement, independently of the solvent, the curves for hybrids in the region of the transitions are above the curve for pure Pebax. On the other hand, for temperatures above the transition region (higher than 50°C), the tan $\delta$ curve for pure Pebax is above those for hybrids. This complex behaviour can be associated with the different damping mechanisms which may occur in 'filled' polymers. The enlargement of $T_g$ peaks may indicate some phase segregation, although no domain could be observed by electron microscopy at the same composition.

In a further comparison of hybrids with particulate-filled polymers, the most pronounced effect of fillers is the broadening of the transition region at high filler concentrations. Fillers often decrease the damping as expressed by $E''/E'$[37]. The damping of rigid fillers is very low compared to that of the polymer. However, there are numerous cases where fillers increase the damping, probably by the introduction of new damping mechanisms which are not present in the pure polymer. These new damping mechanisms include: (a) particle–particle friction with particles touching one another as in weak agglomerates; (b) particle–polymer friction without any adhesion at the interface; and (c) excess damping of polymer near the interface because of induced thermal stresses or changes in polymer conformation or morphology[37]. The increased damping in hybrids here is more probably the result of particle–polymer friction.

### *Morphological characterization*

*Figure 6* shows scanning electron micrographs of Pebax/TEOS hybrids, prepared using 1 : 1 HCOOH : THF or *n*-butanol. When 1 : 1 HCOOH : THF was used, a phase separation was observed at higher silica contents (as shown in *Figure 6b* for 22 : 78 Pebax/TEOS). When *n*-butanol was used, even for 22 : 78 Pebax/TEOS, domains were not detected. Morphologies similar to that in *Figure 6c* were observed independently of Pebax/TEOS composition.

Ultrathin films (70 nm thick) were cut and observed in a transmission electron microscope with a spectrometer which uses inelastic electrons to form element-specific images. When the electron beam passes through the sample, interaction with electrons of different elements results in characteristic energy losses. A prism–mirror system deflects electrons with different energies to different angles so that only electrons with a well defined energy can be selected. If only elastic electrons are chosen ($\Delta E = 0$) a bright field image with reduced chromatic

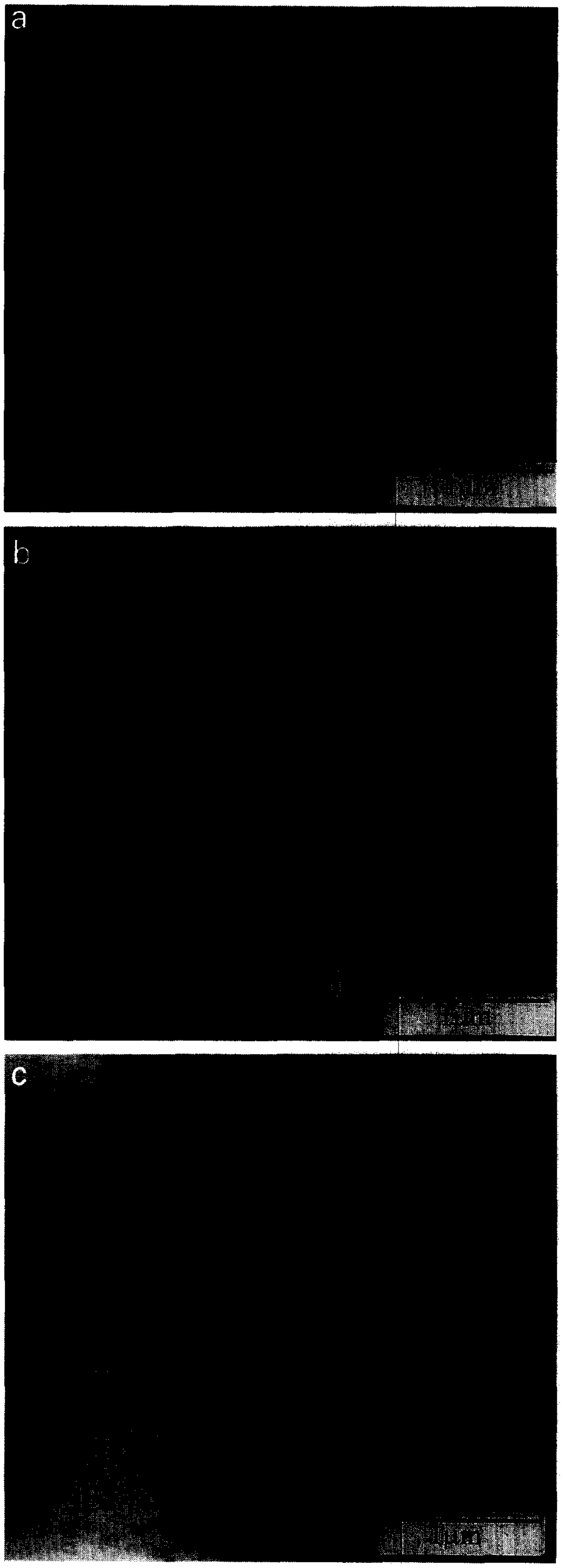


**Figure 8** Transmission electron microscopy of 75/25 Pebax/TEOS hybrids prepared in *n*-butanol. Images obtained with (a) elastic electrons, $\Delta E = 0\,\mathrm{eV}$, and electron spectroscopic images selective for (b) nitrogen, $\Delta E = 401\,\mathrm{eV}$ and (c) carbon, $\Delta E = 285\,\mathrm{eV}$

aberration is obtained. When monochromatic inelastic electrons are selected, electron spectroscopic images are formed showing the local concentration of a particular element (bright regions).

*Figure 7* shows the elastic image of a pure Pebax film and 60/40 Pebax/TEOS, prepared from solutions in 1/1 HCOOH : THF or *n*-butanol. Similar morphologies were observed for all other hybrids with TEOS contents up to 40 wt%. The presence of silica (up to 40%) seems not to change the morphology. For samples obtained from solutions in HCOOH : THF, a morphology typical of crystalline polymers with dendritic/fibrillar structures was observed. For samples obtained from solutions in *n*-butanol, dispersed globular structures could be seen. The composition of these globular structures was evaluated, obtaining images with inelastic electrons with an energy loss $\Delta E = 420\,\mathrm{eV}$, above the ionization edge of nitrogen (401 eV), and $\Delta E = 380\,\mathrm{eV}$, below it. The subtraction is shown in *Figure 8*. A local concentration of nitrogen was detected. The difference in morphology observed by electron microscopy concerns the supermolecular structure and does not reflect a change in the degree of crystallinity.

X-ray analysis showed that Pebax hybrids prepared in *n*-butanol have higher degrees of crystallinity than those prepared in HCOOH : THF, as shown in *Figure 2*. Different kinds of structure (globular and fibrillar/dendritic) were also reported for polyamides in different solvents[40]. For instance, a polyamide film obtained by casting a glycerin/polymer solution showed globular structures, while polyamide films obtained from a formic acid/polymer solution showed fibrillar or dendritic structures[40]. Pebax solutions in butanol, although less concentrated (3 wt%), are much more viscous and are usually gels at room temperature. The high viscosity does not favour the formation of the ordered supermolecular structures observed in samples obtained from solutions in HCOOH : THF.

No silica domains were observed by transmission electron microscopy in samples with TEOS content up to 40 wt%. Either the silica is well distributed in the matrix or the silica domains are smaller than the detection limit.

## CONCLUSIONS

Organic–inorganic hybrids of Pebax and silica were prepared by hydrolysis-condensation of tetraethoxysilane by acid catalysis. Using different solvents for the polymer, the degree of crystallinity and morphology were dramatically changed. As a result, some changes in the stress–strain and dynamic-mechanical behaviour were observed. Independently of the synthesis conditions, the incorporation of silica in Pebax promotes a hardening effect, which was confirmed by the increase in the Young's modulus as a function of silica content. Under specific conditions, hybrids with much better mechanical properties than the pure polymer (higher yield strength, elastic modulus and toughness) were obtained. This was the case with 75/25 Pebax/TEOS prepared in HCOOH : THF. On the other hand, no morphology change was detected with the incorporation of silica in Pebax, at least for TEOS contents up to 40 wt%. But for samples with 78 wt%, TEOS showed phase separation when observed by scanning electron microscopy.

The sol–gel process is an alternative procedure to generate silica in the form of small and well dispersed particles. Practically no agglomeration, a usual problem in filled elastomers, occurs. These characteristics are very desirable for polymer reinforcement.

## ACKNOWLEDGMENTS

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