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Reinforcement of biodegradable poly(ester-urethane) with fillers

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Two novel poly(ester-urethanes) (PEUs: PEUa and PEUb) were reinforced by blending in a batch mixer with organic and inorganic fillers of different particle sizes and shapes. In most experiments the filler contents were 0, 5, 15, 30, and 50 wt.%. In general, both the particulate and fibre-like fillers increased the stiffness almost linearly with increasing filler content, but the tensile and impact strengths and strain at break showed a downward trend. Exceptionally, improvements in tensile strength were achieved with glass fibre, as expected, and, surprisingly, also with some blend compositions containing silicate-type fillers. In addition, slightly improved impact strength was achieved with a small amount of fine talc. Dynamic-mechanical thermal analysis confirmed the reinforcing effects and showed some slight changes in the glass transition temperature of the PEU. Scanning electron microscopy studies on the morphology revealed relatively good mixing and contact between all the fillers and PEU. © 1997 Elsevier Science Ltd.

(Keywords: poly(ester-urethane); fillers; reinforcement)

INTRODUCTION

The general classification of filler particles is normally based on two primary properties, particle size and surface area, both of which are directly measurable and serve as a basis for systematising the functions of the filler. Fillers are characterised by the particle size distribution, the shape of the particles and, as a consequence, by the manner in which the particles pack together. Most fillers are ground rock or ores, processed to obtain the material in particulate form. As such, they do not fracture uniformly and the particles tend to be of irregular size and shape. The particles of certain fabricated fillers, such as silicates and calcium carbonates, are more uniform. In addition to size and shape, the chemical composition of the filler is essential in deciding upon its use. The chemical nature determines the degree of reactivity with the matrix material, which is important for good adhesion between the different phases. When the use of a filler is first considered, it is often with a view to reduce the cost of the product. Although cost considerations are certainly important, fillers often in addition impart property improvements to plastics: properties such as mechanical reinforcement and greater thermal resistance. The natural filler materials, like wood, cotton and cellulose, are generally much less expensive than the polymers with which they are compounded, and they are also degradable, which recommends their use in blends of biodegradable polymers. Both natural and synthetic organic fillers also offer important functional effects, including, frequently, improvements in processability and desirable modification of properties of the final compound. The most prominent physical effect of fillers is the increase in stiffness, which depends on the packing characteristics, size, shape, and interfacial bonding. The most commonly used fillers are rigid, with virtually no elongation to fracture, and their composites are, therefore, stiff but brittle[1].

The proportions of the basic polymer and filler in the blend can vary over a wide range. The optimum composition of the blend will depend to a significant extent on the choice of filler, the intended end-use, the characteristics or properties desired in the product, e.g. mechanical properties, and the rate and degree of biodegradability. Blends of biodegradable and non-biodegradable polymers have also been studied to increase the often very low heat distortion temperature of biodegradable polymers[2–5].

Biodegradation rates have been reported for blends consisting of two or more biodegradable polyesters exhibiting different degrees of biodegradability[6]. The degradation rates of the blends were found to differ from those of the component polymers. It would be expected that a component made from a blend of two or more polymers subject to biodegradation would eventually consist only of the slower degrading polymer, the quicker degrading polymer simply disappearing over time. In fact, a single characteristic value has been observed, and the component members of the blend persist over time. This has been particularly surprising because biodegradation is believed to depend on the chemical structure, which would not be affected by polymer blending.

The compositions of biodegradable polyesters with preferably 20 to 50 wt.% of organic degradable filler have been reported in a recent patent application[7]. The cellulose-based fillers that were mentioned included starch, functionalised starch, cellulose, functionalised cellulose, wood flour, flour of nut shells, cotton and linen fibre and flour or a mixture thereof. The fillers may be acting as nucleating agents to increase the rate and/or degree of crystal formation in the compositions. Conventional additives, such as heat- and light-stabilisers and antioxidants, processing aids, such as mould release aids and lubricating agents,

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and other well-known additives have been added in amounts up to about 15 wt.%, though more usually from 0.1 to 10 wt.%.

Lactic-acid-based polyesters are especially well-known biodegradable polymers, which have seen increasing use not only in biomedical applications but also in packaging and consumer goods. However, large-scale lactide production continues to be relatively complicated and expensive, so that alternative polymerization routes for lactic acid are of interest. In previous papers, we have described the synthesis of lactic-acid-based thermoplastic poly(ester-urethane) (PEU) by a two-step process and the basic characteristics of this new polymer[8,9]. In our present study, two novel PEUs (PEUa and PEUb), a linear and a branched one, were reinforced through blending with several organic and inorganic fillers of different particle sizes and shapes. The aim of the work was to study the feasibility of filling these polymers, in particular to reinforce them, and to understand the relationships between the morphology and properties of the composites.

EXPERIMENTAL

Materials

Two lactic-acid-based PEUs (PEUa and PEUb), a linear and a branched one, were used as the polymer matrix. The polymers were synthesised in a two-step process in a bench-scale reactor (volume 6.2 l). First the lactic acid was condensation polymerised to obtain a low molecular weight prepolymer and then the molecular weight was raised to an appropriate level by adding diisocyanate as chain extender. The hydroxyl-terminated prepolymer was made through condensation polymerisation of L-lactic acid and 2 mol% of 1,4-butanediol. The synthesis and characterisation of the PEU have been described in detail elsewhere[9,10].

Several inorganic or organic fillers of different particle sizes and shapes were added to modify the properties of the biodegradable PEU. The inorganic particulate fillers were two grades of talc ($Mg_3SiO_{10}(OH)_2$) of different particle size (Finntalc M05SL and M20SL; Finnminerals), ultrafine kaolin, sometimes called china clay (SPS Powder; ECC International), two silicate fillers (Aktisil VM 56, produced by modifying the surface with vinyltriethoxy silane, and Sillikolloid P 87, a natural combination of corpuscular quartz and lamellar kaolinite; Hoffmann Mineral), calcium carbonate or whiting ($CaCO_3$, Winnofil S; Zeneca) and two differently coated, ultrafine titanium dioxide (TiO_2) pigments: UV-TITAN P160, acicular crystals, and P580, oval crystals (Kemira Pigments). Generally, P160 imparts high transparency and UV-protection and P580 excellent exterior durability and UV-protection. Wood dust was studied as an example of an organic filler (two grades with sifted particle sizes < 0.5 mm and < 1.0 mm). The fibre-like materials investigated were wood fibre (length up to 18 mm; Deutsche Fibrit) and glass fibre (XG 2089, average diameter 17 μm, sizing for PP; PPG). The glass fibres were cut to a length of about 10 mm. It should be noted that the wood-based materials exhibited relatively wide size distributions and differences in shape. In most of the experiments the filler contents were 0, 5, 15, 30, and 50 wt.%, while with the two TiO_2 grades, a lower content (2 wt.%) was studied as well. It should be noted that, owing to the different densities, the actual volume fraction of the light wood-based fillers ($\rho < 1$ kg m^{-3}) was much higher than that of the inorganic ones ($\rho = 2$–3 kg m^{-3}).

Blending

Different amounts of the fillers were blended with the PEU matrix at 140°C (5 min, 75 rev min^{-1}) in a Haake Rheomix 600 batch mixer equipped with a Haake Rheocord 9000 controlling unit.

Compression moulding

The composites and the unfilled PEUs were compression moulded to the form of plates at 160°C with a Darragon press. The moulding process consisted of three steps: 6 min melting, 4 min compression and 3 min cooling. Test specimens for dynamic-mechanical thermal analysis (DMTA) and impact and tensile testing were sawn from these plates.

Tensile tests

Tensile properties were characterised by using an Instron 8031 tensile testing machine running at a test speed of 5 mm min^{-1}, following the standard ISO 527. Note that the samples sawn from the compression-moulded plates were rectangular in shape and that their dimensions (3 mm × 10 mm × 90 mm) were thus not according to the standard.

Impact strength

The toughness of the materials was characterised by Charpy impact tests of unnotched samples. The tests were carried out with a pendulum-type impact tester (Zwick, pendulum of 0.5 J) at room temperature following the standard ISO 179-1982(E). The samples (4 mm × 6 mm × 50 mm) were sawn from the compression-moulded plates.

DMTA

The dynamic-mechanical properties of the materials were studied with a dynamic-mechanical thermal analyser (RSA from Rheometrics) to evaluate the effects of the fillers on the glass transition temperature and the level of storage modulus. The measurements were made with a dual cantilever procedure on samples (2 mm × 5 mm × 53 mm) sawn from the compression-moulded plates. Temperature was raised by 2°C min^{-1} and a frequency of 6.3 Hz was used.

Morphology

Morphology of the composites was examined by scanning electron microscopy (SEM; Cambridge Instruments, Stereoscan 120) on cross-sections of cryogenically fractured samples. Before SEM analysis the surfaces were coated with a thin layer of gold.

RESULTS AND DISCUSSION

Mechanical properties

Organic and inorganic fillers of different particle sizes and shapes were blended with biodegradable PEUs and the mechanical properties and morphology were studied. The primary aim was to reinforce amorphous linear PEU (referred to as PEUa), which as such is brittle and hard. For comparison, some studies were made with a branched PEU (PEUb). In an earlier study aimed at improving toughness we modified the PEU with biodegradable elastomer-like materials[11].

Mechanical properties of the composites containing different types of filler are presented in *Tables 1–4*. Since the specimens for mechanical testing were cut from plates prepared by compression moulding, the level of mechanical properties reported here should be considered as indicative

Table 1 Mechanical properties of PEUa blended with standard and fine talc, kaolin, Aktisil and Sillikolloid

Sample (wt.%/wt.%)	Modulus (MPa)	Tensile strength (MPa)	Strain at break (%)	Charpy impact strength (kJ m^{-2})
PEUa[a]	1990 ± 210	29 ± 3	3.2 ± 0.2	8.0 ± 0.7
PEUa[b]	1690 ± 280	38 ± 1	4.2 ± 0.3	8.3 ± 0.8
PEUa 95/standard talc 5	1830 ± 80	36 ± 1	4.0 ± 0.2	6.4 ± 1.4
PEUa 85/standard talc 15	2670 ± 70	34 ± 3	3.1 ± 0.6	4.1 ± 0.1
PEUa 70/standard talc 30	3090 ± 230	28 ± 1	2.4 ± 0.1	2.0 ± 0.2
PEUa 50/standard talc 50	3010 ± 80	31 ± 1	2.5 ± 0.1	1.6 ± 0.6
PEUa 95/fine talc 5	1950 ± 70	35 ± 1	3.6 ± 0.4	11.1 ± 1.8
PEUa 85/fine talc 15	2220 ± 260	33 ± 4	3.0 ± 0.5	5.4 ± 1.0
PEUa 70/fine talc 30	2910 ± 240	29 ± 2	2.4 ± 0.1	5.0 ± 0.4
PEUa 50/fine talc 50	3390 ± 250	27 ± 2	2.0 ± 0.3	1.5 ± 0.3
PEUa 95/kaolin 5	1950 ± 250	30 ± 1	3.2 ± 0.3	7.4 ± 0.7
PEUa 85/kaolin 15	2070 ± 50	31 ± 3	3.1 ± 0.3	7.0 ± 1.4
PEUa 70/kaolin 30	2870 ± 180	31 ± 4	2.4 ± 0.4	4.7 ± 0.5
PEUa 50/kaolin 50	3230 ± 150	32 ± 4	2.2 ± 0.4	2.8 ± 0.3
PEUa 95/Aktisil 5	2130 ± 100	37 ± 4	3.2 ± 0.2	7.2 ± 1.7
PEUa 85/Aktisil 15	2410 ± 60	42 ± 2	3.0 ± 0.2	9.0 ± 1.6
PEUa 70/Aktisil 30	3010 ± 130	41 ± 1	2.4 ± 0.2	6.6 ± 0.3
PEUa 50/Aktisil 50	2390 ± 40	27 ± 3	2.0 ± 0.3	4.8 ± 0.9
PEUa 95/Sillikolloid 5	2020 ± 60	40 ± 5	3.4 ± 0.4	7.2 ± 0.5
PEUa 85/Sillikolloid 15	2620 ± 170	38 ± 2	2.8 ± 0.1	8.3 ± 1.2
PEUa 70/Sillikolloid 30	3040 ± 190	30 ± 5	2.1 ± 0.3	6.3 ± 1.0
PEUa 50/Sillikolloid 50	2810 ± 340	28 ± 2	1.9 ± 0.2	3.9 ± 0.6

[a] Initial
[b] Processed in batch mixer for comparison

Table 2 Mechanical properties of PEUa blended with $CaCO_3$ and two TiO_2 grades

Sample (wt.%/wt.%)	Modulus (MPa)	Tensile strength (MPa)	Strain at break (%)	Charpy impact strength (kJ m^{-2})
PEUa[a]	1990 ± 210	29 ± 3	3.2 ± 0.2	8.0 ± 0.7
PEUa[b]	1690 ± 280	38 ± 1	4.2 ± 0.3	8.3 ± 0.8
PEUa 95/$CaCO_3$ 5	1900 ± 120	33 ± 2	3.2 ± 0.4	5.4 ± 1.5
PEUa 85/$CaCO_3$ 15	2080 ± 50	28 ± 4	2.8 ± 0.5	5.2 ± 0.6
PEUa 70/$CaCO_3$ 30	2610 ± 210	26 ± 2	2.1 ± 0.6	2.8 ± 0.3
PEUa 50/$CaCO_3$ 50	2450 ± 270	18 ± 2	1.3 ± 0.2	1.8 ± 0.2
PEUa 98/TiO_2[c] 2	1780 ± 150	38 ± 1	4.3 ± 0.3	8.4 ± 0.8
PEUa 95/TiO_2[c] 5	1570 ± 100	34 ± 2	4.0 ± 0.3	8.4 ± 0.7
PEUa 85/TiO_2[c] 15	1880 ± 70	31 ± 3	3.3 ± 0.2	2.5 ± 0.2
PEUa 70/TiO_2[c] 30	—	—	—	1.6 ± 0.3
PEUa 98/TiO_2[d] 2	1920 ± 140	33 ± 3	3.7 ± 0.2	6.4 ± 0.6
PEUa 95/TiO_2[d] 5	1890 ± 80	33 ± 1	3.7 ± 0.2	4.4 ± 0.7
PEUa 85/TiO_2[d] 15	1860 ± 100	23 ± 1	2.2 ± 0.3	4.9 ± 0.8
PEUa 70/TiO_2[d] 30	2180 ± 70	15 ± 2	1.4 ± 0.3	1.4 ± 0.9

Blends with 50 wt.% of TiO_2 were not made
[a] Initial
[b] Processed in batch mixer for comparison
[c] Acicular crystal
[d] Oval crystal

and not necessarily the best possible. Blending of the materials in a twin-screw extruder and processing by injection moulding could be expected to result in better properties due to the more intensive mixing and the achievement of a favourable flow-induced morphology.

As a general pattern, addition of filler increased the stiffness almost linearly with increasing filler content, in particular at lower filler loadings. Some compositions exhibited poorer mechanical properties at higher filler concentrations, but this was at least partly due to the blending and processing methods. Nevertheless, it should be noted that, even at highest loading, the filler mixed surprisingly well with the PEU matrix. In general, tensile and impact strengths and strain at break showed, in turn, a downward trend as a function of filler concentration. Such behaviour is typical for filled thermoplastics[1].

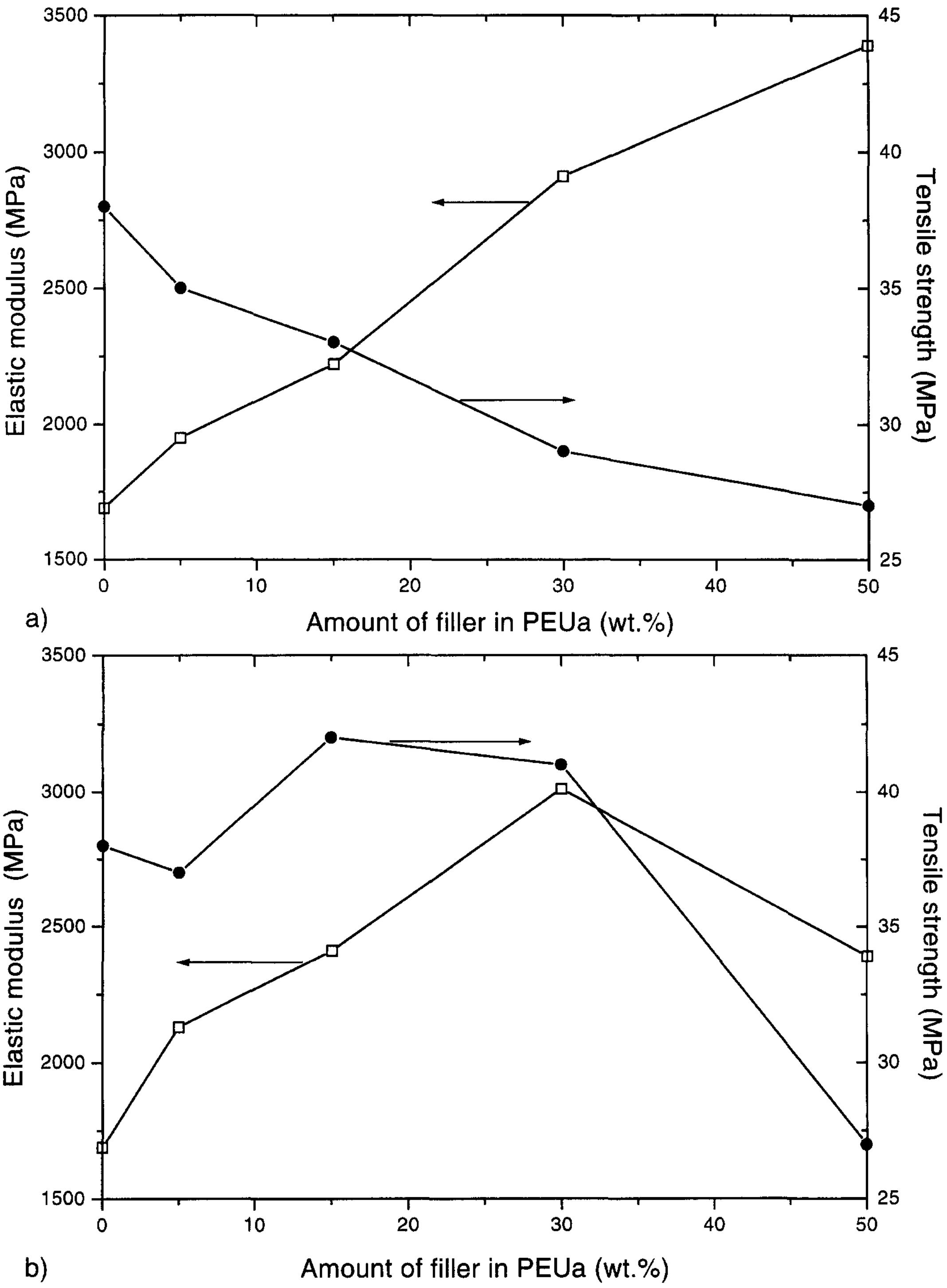


Figure 1 Modulus and tensile strength of (a) PEUa/standard talc and (b) PEUa/Aktisil as a function of filler content

Exceptionally, improvements in tensile strength were achieved with glass fibre and, surprisingly, with some blend compositions containing silicate-type fillers (Aktisil, Sillikolloid). The improvements achieved with the silicate fillers are probably explained by interactions (hydrogen bonding) between the silicate and the hydroxyl end groups of PEU.

Table 1 gathers together the results for blends containing talc, kaolin, and the two silicates. Basically, the effects of these fillers followed the general trends described above. Interestingly, however, improved impact strength was achieved with a small amount (5 wt.%) of the fine talc grade. This is in agreement with our earlier results on PE/PA6 blends modified with small amounts of fine talc[12]. In addition, a significant improvement in stiffness was achieved with the highest amount (50 wt.%) of this talc grade (*Figure 1a*). Use of kaolin as a filler increased the elastic modulus of PEUa with increasing filler content, but the level of tensile strength remained unimproved at all filler loadings. The two silicate fillers (Aktisil and Sillikolloid) improved the mechanical properties of PEUa, especially at additions of 5 and 15 wt.% (Sillikolloid) and 15 and 30 wt.% (Aktisil). As noted above, the silicates were exceptional in producing high values of tensile strength (*Figure 1b*).

Mechanical properties of PEUa modified with $CaCO_3$ and

Table 3 Mechanical properties of PEUa blended with two wood dusts, wood fibre and glass fibre

Sample (wt.%/wt.%)	Modulus (MPa)	Tensile strength (MPa)	Strain at break (%)	Charpy impact strength (kJ m^{-2})
PEUa[a]	1990 ± 210	29 ± 3	3.2 ± 0.2	8.0 ± 0.7
PEUa[b]	1690 ± 280	38 ± 1	4.2 ± 0.3	8.3 ± 0.8
PEUa 95/finer wood dust 5	1790 ± 200	32 ± 3	3.6 ± 0.9	2.5 ± 0.6
PEUa 85/finer wood dust 15	1790 ± 250	38 ± 3	3.9 ± 0.7	2.3 ± 0.4
PEUa 70/finer wood dust 30	2170 ± 230	32 ± 2	2.6 ± 0.4	2.5 ± 0.3
PEUa 50/finer wood dust 50	2270 ± 60	32 ± 1	2.4 ± 0.2	2.6 ± 0.2
PEUa 95/coarse wood dust 5	1880 ± 160	31 ± 3	3.3 ± 0.5	2.9 ± 0.8
PEUa 85/coarse wood dust 15	2160 ± 130	33 ± 1	3.2 ± 0.1	2.3 ± 0.8
PEUa 70/coarse wood dust 30	2210 ± 190	33 ± 2	2.7 ± 0.2	2.3 ± 0.5
PEUa 50/coarse wood dust 50	2260 ± 120	31 ± 2	2.3 ± 0.1	1.5 ± 0.1
PEUa 95/wood fibre 5	1900 ± 50	28 ± 4	2.8 ± 0.4	2.9 ± 0.8
PEUa 85/wood fibre 15	2350 ± 140	34 ± 1	3.0 ± 0.2	2.5 ± 0.1
PEUa 70/wood fibre 30	2800 ± 250	35 ± 5	2.7 ± 0.4	3.4 ± 0.4
PEUa 95/glass fibre 5	2080 ± 130	37 ± 1	4.0 ± 0.2	4.9 ± 1.1
PEUa 85/glass fibre 15	2110 ± 110	41 ± 1	4.1 ± 0.2	5.4 ± 0.7
PEUa 70/glass fibre 30	3660 ± 10	52 ± 4	2.9 ± 0.4	6.9 ± 1.4

Blends with 50 wt.% of wood and glass fibres were not made

[a] Initial

[b] Processed in batch mixer for comparison

Table 4 Mechanical properties of PEUb blended with fine talc, Aktisil, Sillikolloid, wood fibre and glass fibre

Sample (wt.%/wt.%)	Modulus (MPa)	Tensile strength (MPa)	Strain at break (%)	Charpy impact strength (kJ m^{-2})
PEUb[a]	2220 ± 80	39 ± 1	2.4 ± 0.3	6.3 ± 0.2
PEUb[b]	2200 ± 100	39 ± 1	2.5 ± 0.2	7.3 ± 1.1
PEUb 70/fine talc 30	3850 ± 260	38 ± 3	2.0 ± 0.5	2.8 ± 0.5
PEUb 70/Aktisil 30	3440 ± 150	39 ± 3	1.6 ± 0.3	7.4 ± 1.3
PEUb 70/Sillikolloid 30	3400 ± 160	37 ± 1	1.5 ± 0.2	7.2 ± 0.3
PEUb 70/wood fibre 30	2880 ± 60	31 ± 3	1.4 ± 0.2	4.1 ± 0.7
PEUb 70/glass fibre 30	3850 ± 210	48 ± 4	2.2 ± 0.5	8.7 ± 0.7

[a] Initial

[b] Processed in batch mixer for comparison

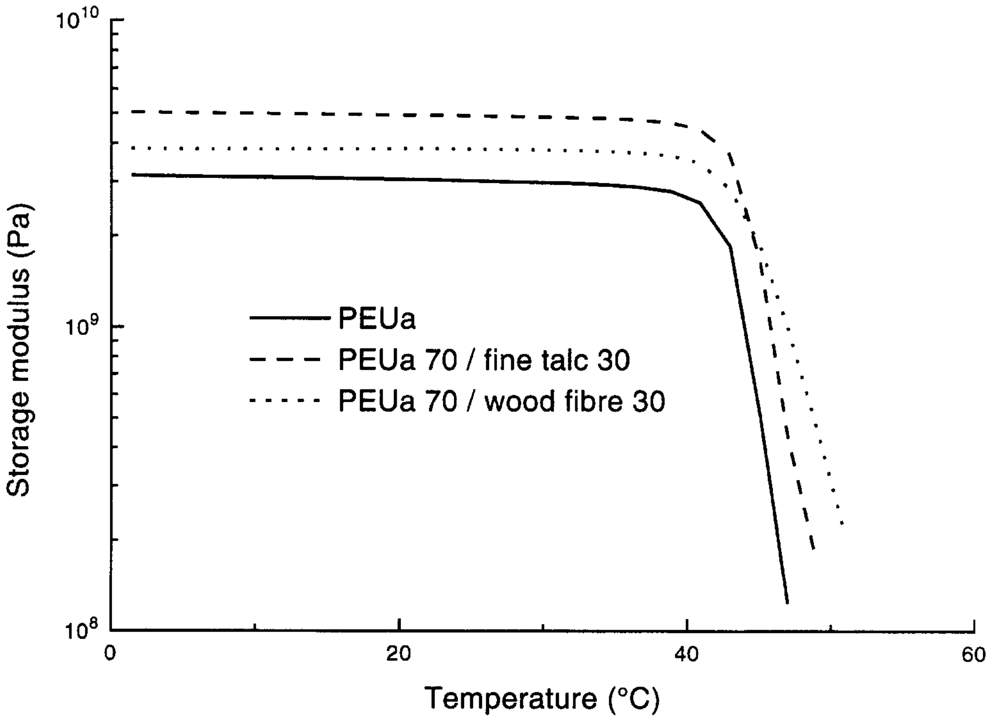
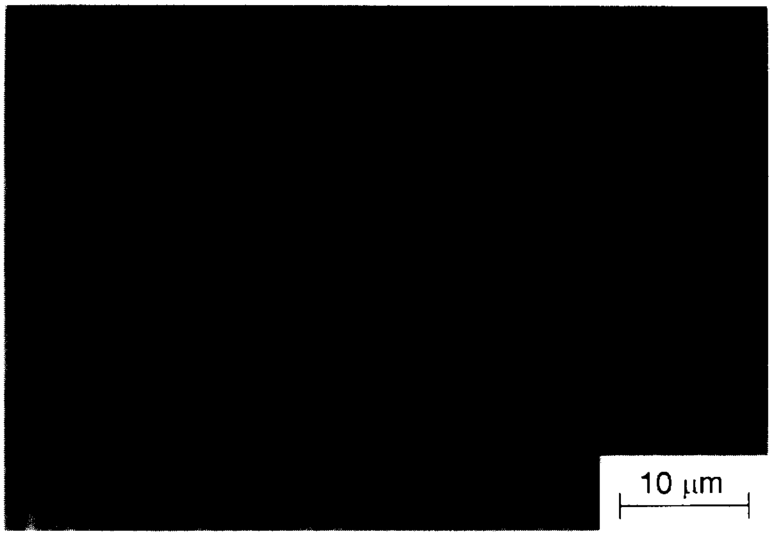
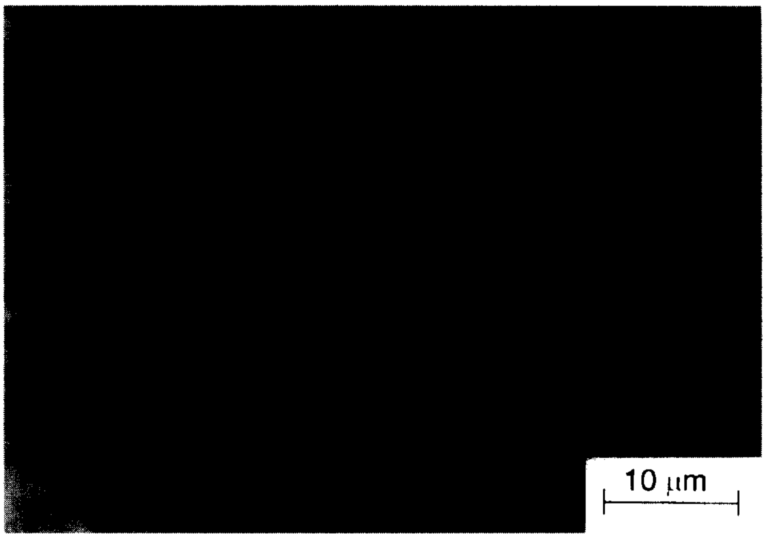


Figure 2 Storage modulus E' in DMTA of neat PEUa and PEUa blended with fine talc and wood fibre



a)



b)

the two TiO_2 grades are set out in *Table 2*. $CaCO_3$ increased the elastic modulus of PEUa, but all other mechanical properties showed poorer values. The TiO_2 grade with acicular crystals did not reduce the toughness of the material at small contents (2 and 5 wt.%), whereas the one with oval crystals served better as a reinforcement. The TiO_2 grades did not really reinforce the PEUa polymer, however, not even at higher loadings. In fact, 30 wt.% of TiO_2 in PEUa made the composite extremely brittle. The difference in crystal shape did not affect the properties strongly owing to the extremely small particle size. Our initial idea was not to use the expensive TiO_2 grades simply for reinforcing. As it turned out, even in a small amount, they lightened the characteristic brown colour of the material, which might be an advantage for some applications. Similar, though less pronounced, colour effects were achieved with other blends, in particular those filled with $CaCO_3$ and the fine talc.

Table 3 shows the effects of wood dust (two grades) and wood and glass fibres on the properties of PEUa. The wood dust is a waste material obtained when sawing wood. The dust was sieved through two different sieves to obtain different particle sizes. Owing to the sawing the particles were of irregular size and shape; some of them were even fibre-like, which could have had some effect on the results. The tensile strength of the composites continued fairly high. Wood fibre seemed to provide slightly better reinforcement than the two wood dusts, evidently due to the more regular shape. As expected, the highest levels of elastic modulus and tensile strength were achieved with the composites containing glass fibres. It should be noted that, since the specimens were made by compression moulding, the fibres did not have any particular orientation in the sample. Injection moulding of the composites containing glass or wood fibres would lead to orientation of the fibres in the flow direction and presumably to significant improvements in properties, especially in elastic modulus. If the results are compared with those obtained with the inorganic fillers, it should be kept in mind that the actual volume fraction of the wood-based fillers in the blends was much higher due to their lower density.

To investigate the effects of the matrix polymer on the mechanical properties of PEU-based composites, a branched PEU grade (referred to as PEUb) was tested as well. Composites consisting of 70 wt.% of PEUb and

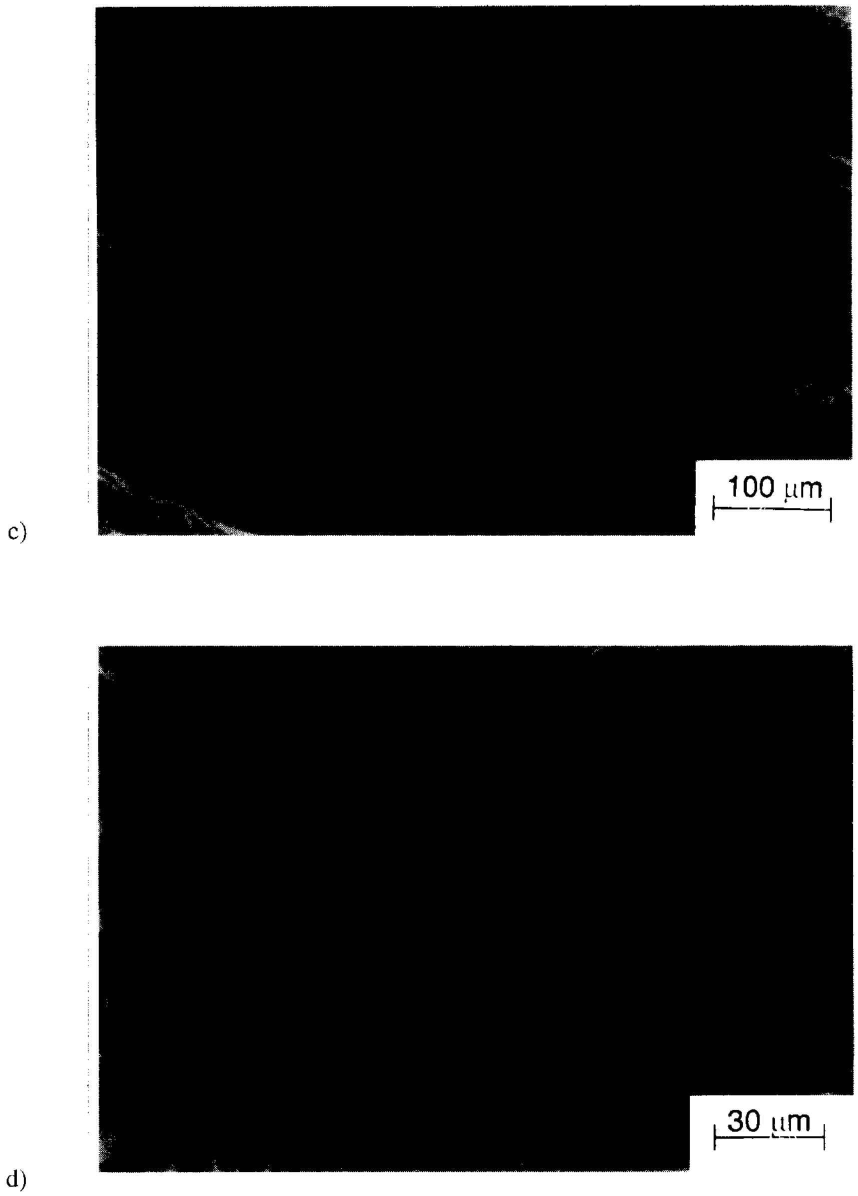


Figure 3 SEM micrographs of (a) PEUa 70/standard talc 30, (b) PEUa 70/Aktisil 30, (c) PEUa 70/finer wood dust 30, and (d) PEUa 70/glass fibre 30 blends

30 wt.% of fine talc, Aktisil, Sillikolloid, wood or glass fibres were prepared and studied according to the same procedures as discussed above. All the materials mixed well with the PEUb and the mechanical properties of the composites (see *Table 4*) showed trends comparable with those based on the linear PEU grade (PEUa).

Dynamic-mechanical thermal properties

Dynamic-mechanical thermal properties of the PEUs and the composites containing 30 wt.% of filler were studied to evaluate the effects of the fillers on the glass transition temperature T_g and the level of storage modulus E'. The DMTA measurements were done as flexural tests made with the dual cantilever procedure. Shifts in glass transition temperatures often serve as an indication of interactions between the blended materials[13]. The glass transition temperature of PEUa was 43°C or 51°C, depending on whether this was determined from the maximum of loss modulus E'' or tan δ respectively. Values only 1–2°C higher were measured for the composites, which means that the fillers did not significantly change the T_g of PEUa. These small changes were not related to interactions, but to the stiffening effect induced by the fillers. This effect can be seen in *Figure 2* as higher values of storage modulus E' for the composites than for the neat PEUa, especially at temperatures close to the T_g of the matrix polymer. DMTA thus provides further evidence of significant reinforcing, achieved in particular with the fibre-like fillers (wood and glass fibres) and talc.

Morphology

As mentioned above, the fillers used in this study were of different particle sizes and shapes. It is well known that these basic characteristics, together with the filler content, influence strongly the properties of the composites. In addition, the interfacial adhesion between the filler and the matrix polymer is critically important for the properties. To discover how well the fillers were mixed with the matrix, the morphologies of composites containing 30 wt.% filler were studied by SEM.

Figure 3a–d shows the SEM micrographs of PEUa blended with standard talc, Aktisil, fine wood dust, and glass fibres respectively. In general, all the fillers mixed surprisingly well with the PEU matrix, even at high concentration. Talc particles were flakes (*Figure 3a*), standard talc exhibiting particle sizes below 10 μm (85%) and fine talc below 5 μm (80%). Kaolin was in the form of both flakes and spherical particles, whereas Aktisil was in the form of spherical or slightly irregular agglomerated particles (*Figure 3b*) with average sizes ranging from 1 to 7 μm, and Sillikolloid existed as small spheres or flakes of the order of 1–6 μm. $CaCO_3$ exhibited a small average particle size of 60–90 μm, and the two TiO_2 grades having acicular and oval crystals formed particles of ca. 17 μm and 30–35 μm respectively. As mentioned above, the wood dusts consisted of relatively large particles of irregular shape (like rough compressed flakes). These slightly fibrillar particles appeared to be bunched together, which might be responsible for the poor contact with the matrix, as seen in *Figure 3c*. The different mixing may be at least partly explained by the different densities of the fillers. While the actual volume content of the high-density inorganic fillers was much less than their weight fraction, that of the wood-based materials was even somewhat higher. The wood fibres were flat, whereas the glass fibres exhibited a round cross-section with a diameter of about 17 μm. *Figure 3d* suggests that the glass fibres were well embedded in the PEU matrix. Overall, the SEM micrographs showed there to be relatively good mixing and contact between all the fillers and PEU.

CONCLUSIONS

Two novel biodegradable PEU polymers were modified by blending with several fillers of different particle sizes and shapes with the purpose of studying the effects of the fillers on mechanical properties and morphology. In general, addition of particulate or fibrous filler increased the stiffness almost linearly with filler content, particularly at lower filler loadings. The most significant reinforcement was achieved with glass fibres, even though processing of the samples by compression moulding did not contribute to orientation. In addition, some blend compositions containing particulate silicate-type fillers showed improvement in tensile strength. This finding is probably explained by interactions like hydrogen bonding between the silicates and the hydroxyl end groups of PEU. DMTA did not show any significant changes in the glass transition temperature of the PEU, but further evidence of stiffening was obtained. In general, all fillers exhibited surprisingly good mixing and contact with the PEU matrix, even at relatively high concentrations.

Despite the reinforcing effect of the fillers, the composites were still brittle, and further toughening or compatibilisation is required. Recently, we successfully toughened the PEU matrix with some elastomeric biodegradable polymers[11]. In future work, we aim to combine the toughening and reinforcing effects, and study the effects of the fillers on biodegradability. To further improve the properties of the composites, more intensive mixing and injection moulding will be applied.

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REFERENCES

1. Katz, H. S. and Milewski, J. V., *Handbook of Fillers and Reinforcements for Plastics*, van Nostrand Reinhold Company, London 1978, p. 652.
2. Clendinning, R. A., Potts, J. E. and Niegisch, W. D., US Patent No. 3932319, 1976.
3. Nemphos, S. P. and Kharas, G. B., European Patent Application, 0540182A3, 1993.
4. Sinclair, R. G. and Preston, J. R., PCT, WO 92/04413, 1992.
5. Kharas, G. B. and Nemphos, S. P., European Patent Application 0515203A3, 1992.
6. Pitt, C. G., European Patent Application 0281482A1, 1988.
7. Kwok, J., Lunt, J., Makuc, J. M. and Castriotta, M., European Patent Application 0533314A3, 1993.
8. Härkönen, M., Hiltunen, K., Malin, M. and Seppälä, J. V., *J. Macromol. Sci. Pure Appl. Chem.*, 1995, **A32**(4), 857.
9. Hiltunen, K., Seppälä, J. V. and Härkönen, M., *J. Appl. Polym. Sci.*, in press.
10. Hiltunen, K., Härkönen, M., Seppälä, J. V. and Väänänen, T., *Macromolecules*, in press.
11. Hiljanen-Vainio, M., Kylmä, J., Hiltunen, K. and Seppälä, J. V., *J. Appl. Polym. Sci.*, in press.
12. Heino, M., Holsti-Miettinen, R., Kirjava, J., Hietaoja, P. and Lankinen, E., Research Report 16.08.1995, Helsinki University of Technology, Finland.
13. Holsti-Miettinen, R., Heino, M. and Seppälä, J. V., *J. Appl. Polym. Sci.*, 1995, **57**, 573.