

Low-Filled Toughened Composites of Poly(hexano-6-lactam)-*block*-polybutadiene-*block*-poly(hexano-6-lactam)/Wollastonite by Polymerization Casting

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ABSTRACT: Composites consisting of 10–15 wt % wollastonite as an acicular filler and poly(hexano-6-lactam)-*block*-polybutadiene-*block*-poly(hexano-6-lactam) matrix (5–15 wt % polybutadiene blocks) were prepared by anionic polymerization of hexano-6-lactam. Hydroxyterminated polybutadiene *in situ* functionalized with toluene-2,4-diyl diisocyanate (TDI) was used as an initiator and sodium salt of hexano-6-lactam as a catalyst. To achieve a good dispersion and high adhesion to the matrix, the filler was modified with (3-aminopropyl)triethoxysilane and then functionalized either separately with *N,N'*-benzene-1,3-dicarbonylbis(hexano-6-lactam) or *N*-benzoyl-hexano-6-lactam or *in situ* functionalized with TDI. The increase in Young's modulus and decrease in elongation were achieved along with a moderate decrease in impact resistance.
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Key words: block copolymer; nylon 6; polybutadiene; wollastonite filler

INTRODUCTION

Practical experience reveals that the filling of the polymer matrix with short fibers below a certain limit of volume fraction does not improve the mechanical strength of the composite, instead often deteriorating it. Commercially available filled polyamide plastics contain 30 vol % or more of fibrous fillers.^{1,2} However, a low filling has been used for articles from toughened plastics,³ especially those produced by reactive processing such as reaction injection molding (RRIM)^{4,5} and polymerization casting. This serves for fine tuning of mechanical properties in the enhancement of

Young's modulus, which always decreases by incorporation of a toughening rubber phase with a low glass transition temperature (T_g).

Adhesion between the filler and matrix is of the utmost importance for composite properties. High adhesion can be best secured by binding the filler surface with polymer matrix using surface modification of the filler.^{3–5} Covalent bonds are preferred, but ionic bonds, H bonds, and other interactions may play an important role. This can be critical in the systems where the toughened polymer matrix is based on block copolymers prepared by polymerization carried out on reactive end groups of an elastomeric prepolymer. Interactions between blocks of the copolymer may have different characters and may change during polymerization. Possible solutions for such a complex system consisting of wollastonite, low-molecular weight hydroxyterminated polybutadiene, and hexano-6-lactam (HL) are presented in this

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study. An analogous system without filler, suitable for nylon RIM and polymerization casting by anionic polymerization of HL, was recently studied.⁶

EXPERIMENTAL

Materials

Wollastonite [TREMIN™ (AST 939-300)] had needle particles of 20–100 μm length and 1.5–4 μm diameter. It was surface modified by slow stirring of its 20% (w/v) dispersion in the mixture (3-aminopropyl)triethoxysilane (APTES, Merck, pract.)-acetic acid-water 10 : (1–2) : 100 (v/v/v, pH 4) at room temperature for 60 min, washing with water, and drying (in air and then at 60°C/130 Pa); or 30 min refluxing of the 20% dispersion in APTES-toluene-acetic acid 1 : 10 : 1 while slowly distilling off the released ethanol, washing with toluene, drying, dispersing in distilled water, washing, and drying.

α,ω -Dihydroxypolybutadiene (PBD), produced by (Kaučuk Co., Kralupy) living anionic polymerization and endcapping with oxirane, had the following characteristics: number-average molecular weight (\bar{M}_n) 4910; weight-average molecular weight (\bar{M}_w) 5840; $c_{\text{OH}} = 0.378 \text{ mmol g}^{-1}$; average functionality 1.87; butadiene structure units: 1,4-*cis* 14.3, 1,4-*trans* 26.7, and 1,2- 59%; volatiles 0.4%. PBD was dried and kept over activated 4-Å molecular sieves under an argon atmosphere at 0°C.

HL (DSM, The Netherlands) was distilled in a vacuum and kept under dry Ar. *N,N'*-Benzene-1,3-dicarbonylbis(hexano-6-lactam), *N,N'*-isophthaloyl-bis-6-hexanelactam (IPBL), and *N*-benzoyl-hexano-6-lactam (BL) were prepared as described earlier.⁷

Tolulene-2,4-diyl diisocyanate (TDI, Fluka, $\geq 98\%$ 2,4-isomer) was used without distillation and kept under an inert atmosphere.

Sodium salt of HL (NaL) was prepared from HL in excess and the solution of sodium *tert*-butoxide in THF.⁸

Separate Functionalization of Wollastonite

Dry wollastonite after modification with APTES (50 g) was dispersed in 100 mL dry toluene, 3 g IPBL, or 1.8 g BL and 1 mL triethylamine was added. Then the mixture was heated to 50°C for

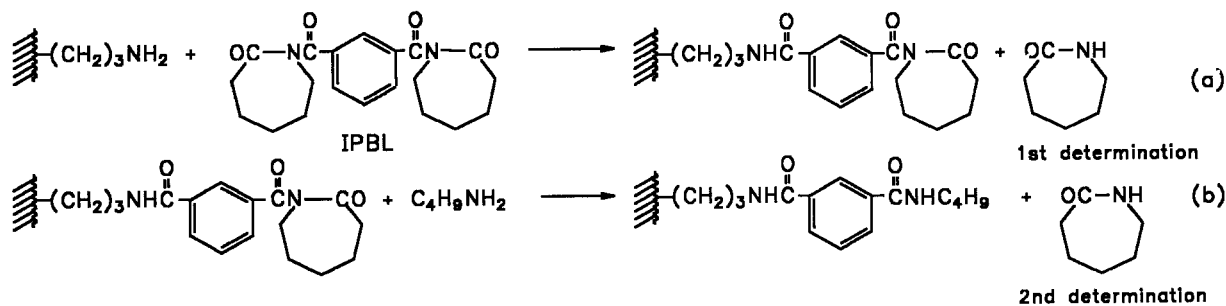
100 h. The filler was filtered off, washed 5 times with hot toluene, and dried at 60°C/130 Pa.

Monitoring of Modification with APTES

A sample of the washed and dried modified filler (1 g) was placed in an ampoule; 1.5 mL dry toluene, 60 mg IPBL, and 14 μL triethylamine were added. The ampoule was sealed and heated to 80°C for 100 h. The cleaved HL was determined in the reaction mixture by the HPLC method⁹ using 12-dodecanolactam as an internal standard (first determination, Scheme 1). The filler was then extracted with toluene and dried. Approximately 200 mg was placed in an ampoule and 0.250 mL dry toluene and 15 μL butylamine were added. The ampoule was sealed and heated to 80°C for 100 h. The cleaved HL (second determination, Scheme 1) was determined in the same way.

Polymerization

The polymerizations were performed at 160°C for 30 min either in glass ampoules (ID 11 mm, length ~ 130 mm) under an Ar atmosphere or in a two-part aluminum mold with a $4 \times 140 \times 155$ mm cavity and an upper opening for casting, which was rinsed before casting with an Ar stream. The polymerization mixture was prepared in a two-necked 250-mL flat-bottomed glass vessel with an inlet and outlet of inert gas through a T valve and a magnetic stirrer. The APTES modified and either nonfunctionalized or subsequently functionalized wollastonite was dispersed in about 85% HL under an Ar atmosphere at 100°C by moderate stirring. In the case of *in situ* functionalized filler, TDI was added with a syringe in the amount corresponding to the OH groups of the PBD and reacted for 30 min at 100°C. Then PBD was added and the temperature was raised to 115°C for complete dissolution of the PBD in the HL and slowly decreased to 105°C during 30 min. With the separately functionalized wollastonite, PBD and toluene-2,4-diyl diisocyanate (TDI) were added successively and reacted for 30 min at 115–105°C as in the second stage of the previous procedure. A low polymerization shrinkage of the composite and the presence of surface modified inorganic filler bring about problems with demolding of the casting. Nonfilled cured silicon rubber proved to be an efficient separation agent for the aluminum molds used. The inner walls of the mold were separated with a thin



Scheme 1

layer of two-component silicon rubber (Rhodosil RTV141, Rhône-Poulenc) that was cured at 100°C, together with a silicon rubber mold sealing.

Composite Characterization

The matrix was characterized by the residual HL content determined by HPLC in the toluene extracts.⁹ The matrix was always slightly cross-linked and hence incompletely soluble in *m*-cresol.

The filler gradient (wt %/cm) caused by sedimentation was determined from the difference of ash contents in two composite samples from the middle part of the ampoule plug or mold-cast plaque that were vertically distanced from each other by 10 cm (Fig. 1). Combustion was carried out in porcelain crucibles in a muffle furnace at

temperatures increasing to 600°C within ~ 30 min and at 600°C for 3 h.

Scanning electron micrographs of fracture surfaces prepared at liquid nitrogen temperature were taken by a Jeol JSM 35 microscope after sputter coating with gold in a Balzers apparatus. Samples were fractured in three-point bending; the razor-blade notch was cut in the center of the tensile side of the sample.

Mechanical Properties

Tensile tests were carried out with beam-shaped dry specimens (2 × 4 mm cross-section dimensions, cut from the middle part of a plaque) on an Instron instrument with a clamp distance of 100 mm, a displacement rate of 1 mm min⁻¹, and at 23°C. Notched impact resistance (a_k) was measured with a Charpy pendulum on 50 × 2 × 4 mm specimens at an average notch depth of 1 mm and at 23°C. The distance of the supports was 40 mm, and the pendulum velocity at impact was 2.9 m s⁻¹.

RESULTS AND DISCUSSION

Wollastonite Filler

Wollastonite has often been used as a natural acicular filler for polyamides.^{1,2,10} Its advantages are that it is a relatively small health hazard in comparison with other fibrous inorganics (such as asbestos and fibrous talc¹), and, for the anionic polymerization of HL, it has a low water adsorption (up to 0.5%) and alkaline reaction of this type of calcium metasilicate (pH of water dispersion,² ~ 9.9). The aspect ratio (length to diameter of needlelike particles), which is decisive for the reinforcing effect of the commercial wollastonite used, was ~ 23 in the starting material and was

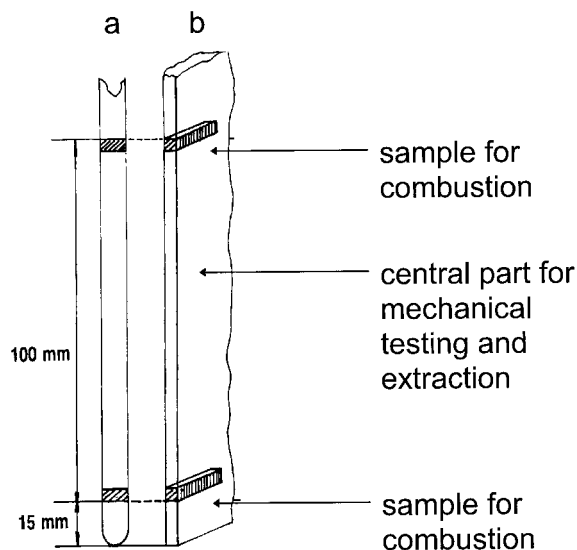


Figure 1 Location of the samples used for the characterization of composites in a plug from the (a) ampoule and (b) mold-cast plaque.

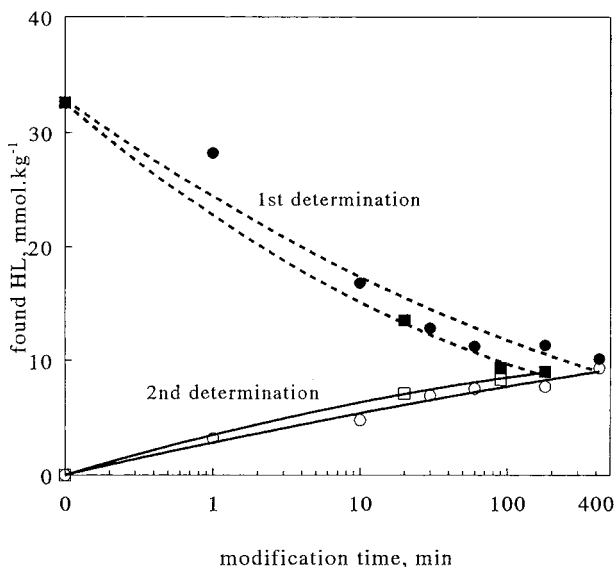


Figure 2 Monitoring of the modification of wollastonite with (3-aminopropyl) triethoxysilane in (●, ○) aqueous acetic acid at room temperature or (■, □) toluene at 100°C: (●, ■) hexano-6-lactam (HL) cleaved from *N,N'*-benzene-1,3-dicarbonybis(6-hexanelactam) (first determination) and (○, □) HL cleaved in the subsequent aminolysis with butylamine (second determination).

somewhat reduced during surface modification and functionalization. However, the critical aspect ratio of 10 : 1 calculated¹⁰ for the wollastonite surface modified with APTES and polyamide 6 (PA6) matrix was always exceeded.

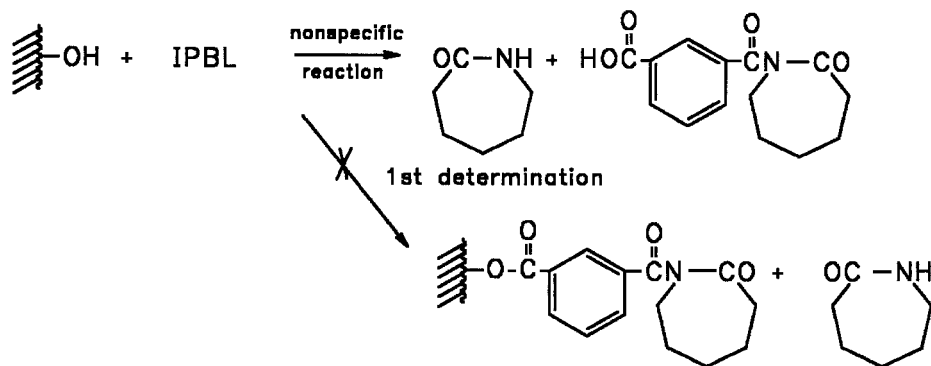
The upper limit of filling is given by the dispersibility of wollastonite in molten HL. The free flowing dispersion suitable for mold casting is obtained up to the weight ratio of wollastonite/HL of (15–20) : (85–80) [i.e., 6–9 vol % of the filler (wollastonite density⁸ = 2.9)]. At a higher con-

tent of the filler, a thick to pasty system is obtained.

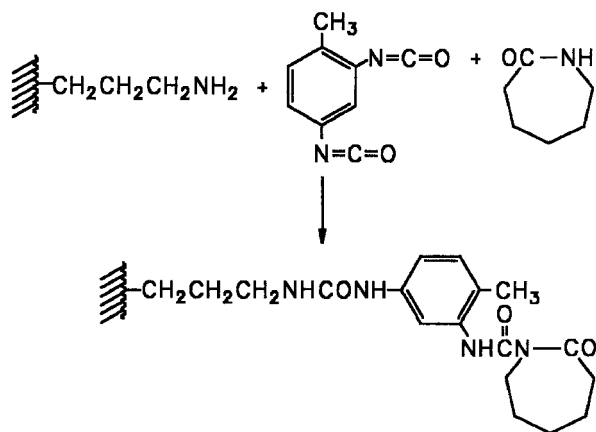
Surface Treatment of Wollastonite

Two methods of surface modification with APTES were used (see the Experimental section), both giving similar results. The reaction in aqueous acetic acid, which is recommended by APTES producers for glass fibers, should be preferred because the modification in boiling toluene resulted in aggregation of particles and hence required final dispersion in water. The modification of the glass-fiber surface is usually performed in the aqueous dispersion for only for 1 min at room temperature. Because we intended to introduce growth centers for the anionic polymerization of HL by reacting the NH_2 groups on the filler surface with an excess of IPBL, we used this functionalization reaction to monitor the surface modification. The analysis was based on two determinations of HL cleaved off from IPBL in the functionalization step [Scheme 1(a)] and, subsequently, by aminolysis of the functionalized filler with butylamine [Scheme 1(b)].

As follows from Figure 2, the highest amount of HL split off in the first step was found with wollastonite before its modification with APTES. This was obviously caused by a nonspecific reaction of IPBL with reactive surface groups (e.g., by alkaline hydrolysis; Scheme 2). This reaction proceeds by cleavage of an HL molecule without binding the rest of the IPBL molecule to the filler, because the subsequent aminolysis did not yield any HL. The amount of HL released in functionalization slowly decreases with the extended time of modification, whereas the HL formed in aminolysis attains the limit value of ~ 10 mmol



Scheme 2



Scheme 3

kg^{-1} after only about a 60-min reaction with APTES. Similar time plots were obtained for the reaction carried out in water and toluene.

Functionalization of the filler surface (i.e., incorporation of acyl lactam groups or growth centers) was carried out as a separate step in the toluene dispersion [Scheme 1(a)] or *in situ* by the reaction with TDI in the dispersion in molten HL then used directly for polymerization (Scheme 3).

An alternative to the functionalization was the reaction with BL (Scheme 4). In this case the filler can be bound to the polyamide part of the matrix by the amide exchange reaction. The advantage of *in situ* functionalization is, besides its simplicity, in avoiding the particle aggregation.

Considering the upper limit of filling of ~ 20 wt %, the functionalization cannot provide more than 0.03 mol % initiator (acyl lactam groups) for the homopolymerization of HL. This is, however, an insufficient amount for initiating the anionic polymerization of HL with only the functionalized filler.

Block Copolymerization

The procedure for the preparation of triblock copolymers PA6-*block*-PBD-*block*-PA6 by anionic polymerization of HL was studied in detail.⁶ The same method was used for the preparation of com-

posites consisting of the PA6-*block*-PBD-*block*-PA6 matrix and the wollastonite filler, including the PBD prepolymer with OH end groups, *in situ* functionalization of PBD with diisocyanate (in our case TDI), and sodium salt of HL (NaL) as a catalyst.

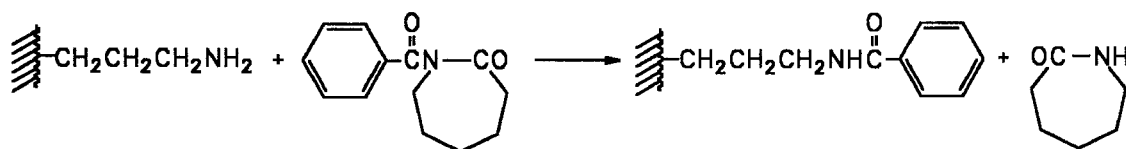
The presence of wollastonite brings about the following phenomena that can be influenced by modifying the copolymerization procedure.

Interaction of Filler with Added PBD

Dispersibility of wollastonite in molten HL is little affected by its surface modification; only fluidity of the dispersion is better with the APTES modified filler. On the other hand, the behavior of PBD in the filler-HL dispersion strongly depends on the surface treatment of wollastonite. PBD coagulates on the surface of the APTES modified filler giving the system dispersion of nonmodified wollastonite in an HL-PBD solution. A proper APTES modification and functionalization of the surface that blocks free polar and amine groups is a prerequisite for the preparation of a stable system for polymerization casting. This means that *in situ* functionalization of wollastonite and PBD also has to be performed in two steps: first the functionalization of the filler with an excess of TDI (of the amount corresponding to the OH groups in PBD, only a small part is consumed) and then the reaction of PBD with the remaining TDI.

Retarded Anionic Polymerization

In the presence of APTES modified wollastonite, the anionic polymerization of HL is slowed down, probably due to the acetic acid that remains adsorbed on the filler surface in a higher amount than corresponds to amine acetate groups, even after washing and drying in a vacuum. Another reason may be the cation exchange between the Ca cations on the filler surface and NaL leading to the Ca salt of HL that is less active. The molar ratio OH end groups/TDI/NaL 1 : 1 : 1 used in the preparation of PA6-*block*-PBD-*block*-PA6 co-



Scheme 4

Table I Composites Consisting of Wollastonite Filler and PA6-*block*-PBD-*block*-PA6 Matrix

Wollastonite		PBD ^b (wt %)	Dispersion in HL	OH/TDI/NaL (mol %) ^c	Residual HL ^d	<i>G</i> (wt %/cm)
Pretreatment ^a	Content (wt %)					
—	10	0	Fine	—/0.5/0.5	1.0	— ^e
—	10	15	Coagulation	0.7/0.7/0.7	1.3	— ^f
M	10	0	Fine	—/0.5/0.5	40	—
F1	10	15	Coagulation	0.7/0.7/0.7	17	— ^f
F2	10	15	Fine	0.7/0.7/0.7	4	<0.01
F2	10	15	Fine	0.7/0.7/1.4	0.7	0.02
F2	15	10	Fine	0.5/0.5/1.0	0.6	0.06
F2	15	15	Fine	0.7/0.7/1.4	0.8	0.02
F2	15	15	Fine	0.7/0.7/1.2	1.1	<0.01
F2	10	10	Fine	0.5/0.5/1.0	0.8	0.05
FIP	10	10	Rough fraction	0.5/0.5/1.0	2.0	0.37
FIP	15	15	Rough fraction	0.7/0.7/1.4	1.2	0.35
FB	10	10	Rough fraction	0.5/0.5/1.0	1.7	0.15
FB	15	15	Rough fraction	0.7/0.7/1.4	1.1	0.11
FB	13	10	Fine	0.5/0.5/1.0	1.4	0.17

G, sedimentation gradient of the filler.

^a Wollastonite modified with (3-aminopropyl)triethoxysilane (M) *in situ* functionalized with TDI together with PBD in one step (F1) or before addition of PBD (F2) separately functionalized with *N,N'*-benzene-1,3-dicarbonylbis(hexano-6-lactam) (FIP) with *N*-benzoyl-hexano-6-lactam (FB).

^b In matrix.

^c Concentration of OH end groups of PBD, TDI, and NaL relative to HL.

^d Residual HL in the matrix.

^e Brittle composite.

^f Filler and rubber sedimented.

Table II Mechanical Properties of Polymerization Cast Composites PA6-*block*-PBD-*block*-PA6/Wollastonite^a

Wollastonite		PBD (wt %) ^c	<i>G</i> (wt %/cm)	<i>a_k</i> (kJ cm ⁻²)	<i>E_t</i> (GPa)	σ_z (MPa)	ϵ_r (%)
Pretreatment ^b	wt %						
—	0	0	—	4	2.7	—	—
—	0	5	—	7	2.3	70	13
—	0	10	—	nb	1.3	48	52
—	0	15	—	15	1.4	28	27
F2	10	5	0.34	5	2.5	—	—
F2	10	10	0.14	9	2.3	60	5
F2	10	15	0.01	7	2.1	44	5
F2	15	10	0.03	8	2.5	62	5
F2	15	15	0.12	7	2.1	44	5
FIP	10	10	0.37	4	2.2	49	3
FIP	15	15	0.35	—	1.2	22	2
FB	10	10	0.15	4	2.2	53	4
FB	15	15	0.11	—	1.2	22	2
FB	13	10	0.17	5	2.1	47	4

G, sedimentation gradient of the filler; *a_k*, notched impact resistance (Charpy pendulum; nb, does not break; *E_t*, tensile modulus; σ_z , tensile strength; ϵ_r , elongation at break).

^a Dry specimens, 23°C, residual hexano-6-lactam < 2 wt %.

^b See Table I.

^c In the matrix.

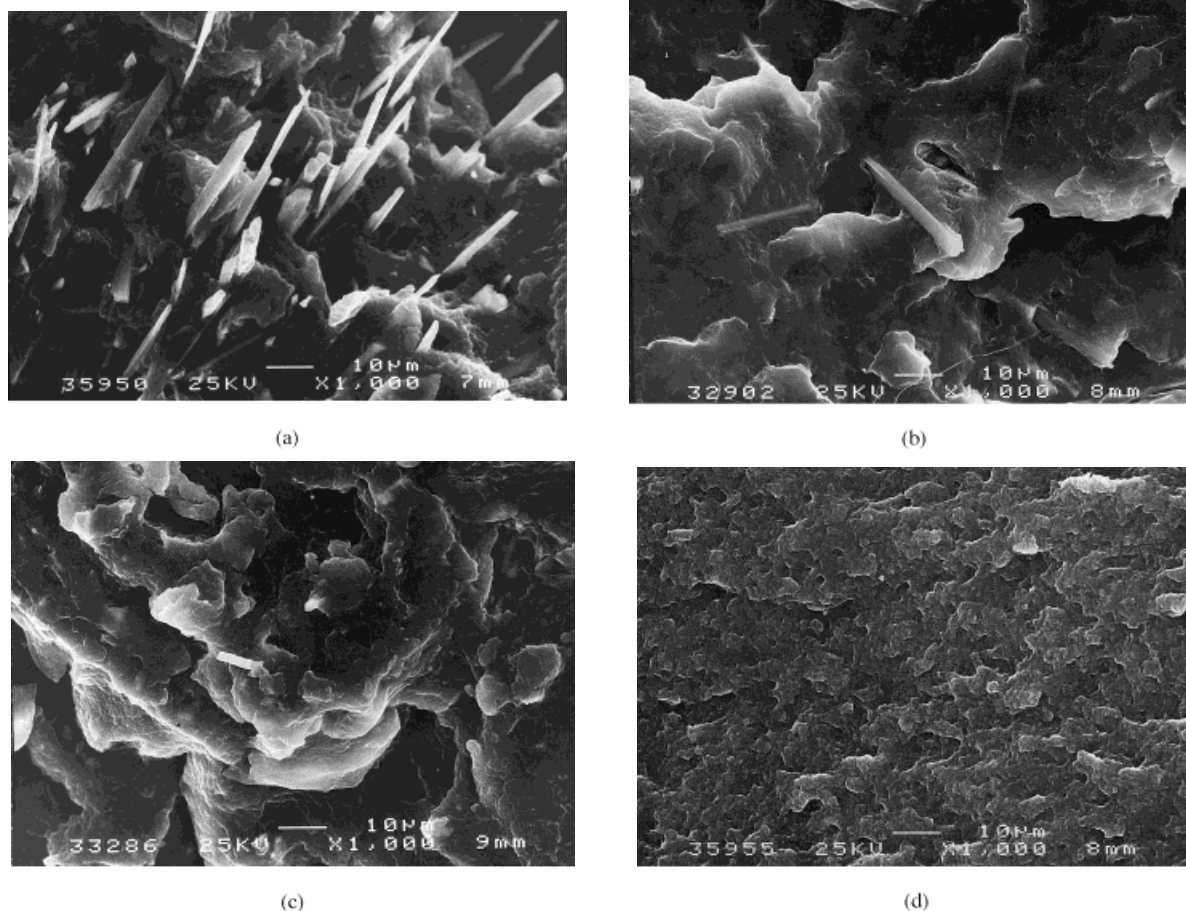


Figure 3 Scanning electron micrographs of the fracture surface of (a) polyamide 6-untreated wollastonite composite, (b) polyamide 6-(3-amino-propyl)triethoxysilane (APTES) modified wollastonite, (c) composite consisting of APTES modified and *in situ* functionalized wollastonite and matrix of PA6-*block*-polybutadiene-*block*-PA6, and (d) PA6-*block*-polybutadiene-*block*-PA6 without filler.

polymers⁷ has to be changed to 1 : 1 : 2 in order to complete the polymerization with a higher content of the filler (Table I).

Sedimentation of Filler

The different densities of molten HL and wollastonite leads to sedimentation that is retarded by viscosity of the dispersion medium. The effect was characterized as the filler gradient determined from the incombustible matter of the composite samples taken at 10-cm distances in the vertical direction of the casting (Fig. 1). The results in Tables I and II show that a lower gradient was found with a higher concentration of PBD, nonaggregated filler particles from *in situ* functionalization, and faster polymerizations.

Adhesion Filler–Matrix

The effect of the treatment of wollastonite on the adhesion between the filler and matrix is clearly seen on scanning electron micrographs of fracture surfaces of the composites [Fig. 3(a–d)]. Figure 3(a) shows the composite, prepared by anionic homopolymerization of HL, containing dispersed untreated wollastonite as an example of poor adhesion in which filler particles were drawn off the matrix during break and protrude from the surface without traces of adhering matrix on their surface. Better adhesion was attained in the HL homopolymerization in the presence of wollastonite treated with APTES; needles of the filler protruding from the fracture surface in Figure 3(b) are coated with the matrix material. In composites of properly modified and functionalized wol-

lastonite and PA6-*block*-PBD-*block*-PA6 matrix, the filler particles are hidden beneath the fracture surface [Fig. 3(c)], which is coarser than that of the matrix material without filler [Fig. 3(d)].

Mechanical Properties

Table II surveys the results of the mechanical testing of the composites prepared with properly surface treated wollastonite and the block copolymer matrix. In all cases the content of residual HL was less than 2% in relation to the initial HL concentration. The Young's modulus increased with filling as expected (i.e., 2 or 3 times) in comparison to the unfilled matrix material, while ultimate tensile strength was moderately increased by fine filling. Elongation at break dramatically decreased. Notched impact resistance of the matrix material decreased on filling with the finely dispersed *in situ* functionalized filler as well, but it remained twice as high in comparison to the unfilled and nonmodified PA6. The reason why the filling effect on tensile strength is not as pronounced as expected may be defects caused by imperfect degassing of the dispersion before casting. Degassing, which is almost impossible in gravitation casting due to heavy foaming in a vacuum, could be solved in the RRIM technique.

CONCLUSIONS

To increase adhesion between wollastonite and PA6-*block*-PBD-*block*-PA6 copolymer matrix, the filler has to be properly silanized with (3-aminopropyl)triethoxysilane. The subsequent functionalization introducing *N*-acyllactam or secondary amide groups can be performed *in situ* or separately but always before the PBD prepolymer is added. The *in situ* functionalization with diisocyanate is preferred because it prevents aggregation of filler particles. The concentration of the basic

catalyst should be increased to complete the polymerization rapidly and to a high conversion. Because specific interactions of the filler surface with all components of the polymerization system are important for the preparation and resulting properties of the composite, the conditions of filler modification and polymerization have to always be found for every system leading to a filled and toughened polyamide composite (e.g., for filled copolymers with soft blocks of polyethers or rubbers other than PBD).

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