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Polyamide 6/wollastonite composites: strength properties and their dependence on humidity and temperature

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The use of wollastonite as a reinforcement for polyamide 6 (PA 6) composites was evaluated using various mechanical test methods. The results suggest that wollastonite acts as a reinforcement for PA 6 at concentrations in the range 25 to 40 wt%, because it increases strength, stiffness and impact strength. Increases of 20 to 200% in these properties were obtained for these wollastonite concentrations. This reinforcing effect was observed when the composite was not exposed to any humidity or temperature treatment; such treatments were found to cause a deterioration in interfacial adhesion as concluded from scanning electron microscopy observations. In conclusion it seems that the present surface treatment system of the wollastonite may be improved and so better the long-term properties of PA 6/wollastonite composites in severe conditions. The short-term tests, however, show that the wollastonite reinforces PA 6, i.e. increases the strength, stiffness and impact strength when it is not exposed to any humidity or temperature treatments.

1. Introduction

Recently, the reinforcing and filling of plastics has gained much attention due to the increasing interest in engineering plastics [1]. In the case of thermosets there is a distinct difference between reinforcing and filling, while it is more difficult to make such a clear distinction where thermoplastics are concerned. On the other hand, it ought to be noted that compounding, for thermoplastics, is a cost-increasing step in production, whereas for thermosets it does not usually affect production costs markedly. By using these additives it is possible to tailor the properties of the compounds to different end-use requirements by simultaneously affecting the mechanical, thermal and electrical properties [1]. It is therefore difficult to distinguish between filling and reinforcing. Consequently, it is more correct to talk about compounding and, if needed and possible, specify the type of effect the additive has.

For thermoplastics a great variety of materials have been tried. Probably most powders which can be subdivided have been tested. These additives can be classified in many ways, e.g. organic/inorganic, synthetic/natural, according to size and shape, etc. At present glass fibre, in different forms, mica and talc are probably those which are most frequently used in thermoplastics. In addition, certain groups of additives such as carbon, aramid and synthetic ceramic fibres are of great technical importance, although they are used in smaller quantities [2, 3].

The compounding of thermoplastics has encountered many problems, many of which are not easily solved. Therefore efforts in the production of thermoplastic-based composites have largely been restricted to the development of individual compounds for certain applications, i.e. development work has concentrated on solving problems related to the additives [4]. In the next section we will briefly review some of the central problems and their solutions with reference to the additives.

2. Properties of relevance for composites

The size and shape distributions have to be mastered in such a way that it is possible to obtain an optimal combination of properties [5]. In the case of fibrous additives it ought to be possible to control the length and thickness distributions to achieve a sufficient aspect ratio. When several different additives are used, suitable size distributions are dictated by the optimal or highest packing density desired in the final composite. Natural materials usually require grinding and fractionation possibly followed by a recombination of relevant fractions to obtain the desired result. In the case of wollastonite the acicular shape is critically dependent on the grinding process.

One of the central problems with thermoplastics is how to obtain adhesion between the additive and the matrix [6]. The problem is more pronounced with thermoplastics than with thermosets because the long molecular chains of thermoplastics are usually less reactive and thus less disposed to adhere to the additive

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surface. Furthermore, certain additives are inclined to react with the surrounding atmosphere, e.g. moisture, which is still supported by the large effective specific surface. In this respect certain processes such as reaction injection moulding (RIM) offer advantages.

To obtain sufficient interfacial adhesion, adhesion promoters or coupling agents have been developed. They are usually bifunctional molecules able to react with the additive as well as with the matrix [7]. Common promoters are silanes and titanates, but new and more effective promoters are being developed. The purpose of the promoters is to link together the two phases by primary chemical bonds, in order to increase the composite's resistance to severe conditions, e.g. the combination of humidity, water and heat.

The quantities of adhesion promoters needed are usually quite small; they are proportional to the specific surface of the additive, and mono-molecular layers are usually sufficient. This, however, causes problems in surface treatment of the additive, i.e. to obtain an even and complete coverage. Usually this is not difficult when surface treatment and adsorption are effected from a solution, but in the case of dry powders the result is often unsatisfactory.

The properties of thermoplastic composites may thus be tailored to match the requirements only if it is possible to control the function of the additives [8]. Consequently, the properties of the additives should not be allowed to change during the processing steps. One of the most critical factors is the reduction in length due to breaking of fibres in the mixing step. Glass fibres with a length of 200 to 600 μm, for example, are easily shortened in the extruder to sizes which are no longer able to reinforce the material. Finally, the fibre orientation strongly affects the composite properties. It is therefore important to bear in mind that most forming and mixing processes affect the orientation, and the composite may obtain an isotropic properties which may alter throughout a finished composite part.

3. Test materials

This study is concerned with the influence of wollastonite on the properties of polyamide 6. The wollastonite used as an additive is natural calcium silicate, which is not very common and which can be ground to needle-shaped particles. The wollastonite used in this investigation was obtained from Oy Partek AB, Lappeenranta limestone mining facility in Finland. The chemical and physical properties are shown in Table I.

It is worth noting the length (~ 10 to 20 μm) and the thickness (~ 1 μm) giving the particle an aspect ratio of about 10 to 20, which is small compared with commercial short glass fibres, whose ratios usually are in the range 30 to 100. The present wollastonite sample was subjected to a grinding process which yields particles with a high aspect ratio. Before being mixed with the polyamide, the particles were surface-treated with a suitable silane adhesion promoter, which was mechanically mixed with the wollastonite. The distribution of silane on the surface of the particles was not studied since no suitable method was available.

TABLE I Chemical composition and physical characteristics of wollastonite

Chemical composition (wt %)		
SiO_2	51.80	
CaO	44.50	
MgO	0.80	
Al_2O_3	0.60	
Fe_2O_3	0.20	
Na_2O	0.10	
K_2O	0.10	
TiO_2	0.05	
MnO	0.01	
P	0.01	
S	0.01	
F	0.01	
Loss on ignition	1.70	
Physical properties		
Shape		Acicular
Aspect ratio, *L/D*		15:1
Minus 10 μm (1250 mesh) (%)		98
Surface area (BET) ($m^2 g^{-1}$)		2.1
Specific gravity		2.9
Bulk density ($kg l^{-1}$)		0.4
Brightness (MgO = 100%) (%)		90
Hardness (Mohs scale)		4.5
pH on 10% slurry		10–11
Oil absorption (ASTM1483) (%)		55
Melting point (° C)		1395–1410
Coefficient of thermal expansion (° C^{-1})		7.5×10^{-6}

The matrix material was a commercial grade polyamide (BASF, Ultramid 35), which was only dried normally to drive off adsorbed moisture before mixing and injection moulding.

3.1. Mixing and preparation of test specimens

The polyamide/wollastonite mixtures were prepared using two laboratory twin-screw extruders, Leistritz, and Werner and Pfleiderer. The mixing was done in the laboratories of the two companies using the mixing parameters suggested by the respective company according to their previous experience. The parameters were assumed not to damage the matrix materials structurally. These mixtures were designated L1, L2, W1 and W2.

For the test specimens an Arburg 305-210-700 injection moulding machine was used. The mould was prepared at the Tampere University of Technology, and the dimensions of the specimens are shown in Table II. The small size of the specimens was chosen to obtain more specimens from less test material. The specimen for the tensile test is not standard, while the specimen for impact tests (also used for the flexural strength tests) follows DIN standards. Previous work has shown that the results using the present specimen for tensile strength measurements do not significantly differ from those results obtained by using specimens of standardized dimensions [9].

3.2. Materials testing and the results

The properties of the mixtures were recorded only by static measurements of tensile, impact and flexural strength. Table II shows the dimensions of test specimens, standards used and detailed test conditions. Dynamic tests were not included at this stage because

TABLE II Testing methods, specimen dimensions and arrangements

Test	Standard	Specimen	Test arrangements
Impact strength	DIN 53453	Dimensions 50 mm × 6 mm × 4 mm Notch: width 0.8 ± 0.1 mm depth 1.3 ± 0.2 mm length 6 mm	Charpy impact strength test
Tensile strength	–	Dimensions 60 mm × 20 mm × 5 mm Deformation length 15 mm Width of deformation length 10 mm	Tensile strain rate 5 mm min^{-1}
Flexural strength	DIN 53452 (kleinstab)	Dimensions 4 mm × 6 mm × 50 mm	Bending strain rate 5 mm min^{-1} Support distance 40 mm
Flexural modulus	Flexural strength test according to ASTM D 790 ISO standard		

if the static strength properties are not sufficient, then the dynamic strength properties cannot possibly suffice.

TABLE III The combined humidity and temperature pre-treatment conditions used

	Temperature (°C)	Relative humidity (%)	Time (h)
A	70	*	24
B	20	100	48
C	20	100	240
D	20	†	240
E	100	100	24
F	100	†	24

*Not measured. †Submerged in distilled water.

Owing to the fact that PA 6 is known to be a material which absorbs considerable amounts of water and is even very sensitive to humidity, absorbing moisture directly from the air, the mixtures were subjected to various humidity treatments before being tested. In addition, the humidity treatments were combined with heat treatments. The purpose of these tests was to study their influence on interfacial adhesion between the additive and matrix.

The combined humidity/heat treatments are explained in Table III and the results from the mechanical tests are shown in Table IV. The results obtained are also presented graphically in Fig. 1.

In addition to the mechanical tests, including the various treatments, the fracture surfaces were investigated by SEM. Additive loadings were determined by burning off the organic material, using randomly chosen specimens.

TABLE IV Strength properties of the polyamide 6/wollastonite composites

Material	Wollastonite content (wt %)	Pre-treatment	Tensile test		Bending test: *E*-modulus (GPa)	Impact test (10^3 J m^{-2})
			Tensile strength (MPa)	Elongation to fracture (%)		
L1	24.1	A	85.1 ± 1.4	17.1 ± 3.3	3.4 ± 0.1	9.8 ± 2.5
	.	B	78.8 ± 0.5	17.4 ± 1.1	2.6 ± 0.1	16.5 ± 1.6
	.	C	–	–	–	–
	.	D	59.8 ± 0.5	18.3 ± 1.7	1.1 ± 0.05	23.8 ± 2.0
	.	E	–	–	–	–
	25.0	F	37.1 ± 0.3	101 ± 11	0.6 ± 0.06	36.1 ± 6.6
L2	28.1	A	89.0 ± 0.5	15.4 ± 2.3	3.8 ± 0.2	10.8 ± 1.0
	.	B	82.5 ± 1.1	15.2 ± 2.6	3.1 ± 0.1	17.6 ± 3.0
	.	C	66.1 ± 0.8	17.0 ± 1.5	1.4 ± 0.1	16.7 ± 1.1
	.	D	63.6 ± 0.4	15.6 ± 0.5	1.3 ± 0.03	21.9 ± 1.3
	.	E	40.0 ± 1.0	49 ± 4	0.8 ± 0.02	17.3 ± 4.0
	29.9	F	39.4 ± 0.7	65 ± 6	0.8 ± 0.02	29.8 ± 2.1
W1	31.0	A	94.4 ± 0.5	14.4 ± 2.0	4.3 ± 0.2	12.1 ± 1.6
	.	B	88.2 ± 0.5	17.7 ± 1.4	2.8 ± 0.3	16.9 ± 2.4
	.	C	69.5 ± 0.8	16.4 ± 1.5	1.6 ± 0.06	13.4 ± 2.9
	.	D	66.0 ± 0.6	15.6 ± 0.9	1.3 ± 0.01	23.6 ± 2.6
	.	E	43.0 ± 0.5	46 ± 2.8	0.9 ± 0.04	15.8 ± 1.2
	31.8	F	40.5 ± 0.3	52 ± 3.5	0.8 ± 0.05	18.8 ± 0.5
W2	39.2	A	104.7 ± 0.3	11.7 ± 1.1	5.6 ± 0.07	12.5 ± 2.2
	.	B	97.1 ± 0.3	12.1 ± 1.0	3.1 ± 0.08	16.1 ± 0.9
	.	C	78.4 ± 0.8	11.8 ± 0.8	2.1 ± 0.09	17.9 ± 0.0
	.	D	74.7 ± 0.7	11.2 ± 0.7	1.9 ± 0.05	23.5 ± 2.0
	.	E	47.5 ± 1.2	26.1 ± 4.5	1.1 ± 0.2	12.5 ± 0.7
	40.6	F	47.5 ± 0.6	23.2 ± 4.1	1.1 ± 0.7	17.7 ± 0.5
PA6	–	A	77.8 ± 7.8	350 ± 90	2.0	8.5 ± 2.5
		B	78.1 ± 2.3	400 ± 10	1.2	17.1 ± 1.4
		C				
		D	78.7 ± 4.4	500 ± 70	0.35	48 ± 0.8
		E				
		F	52.1 ± 3.4	430 ± 80	0.27	38 ± 0.3

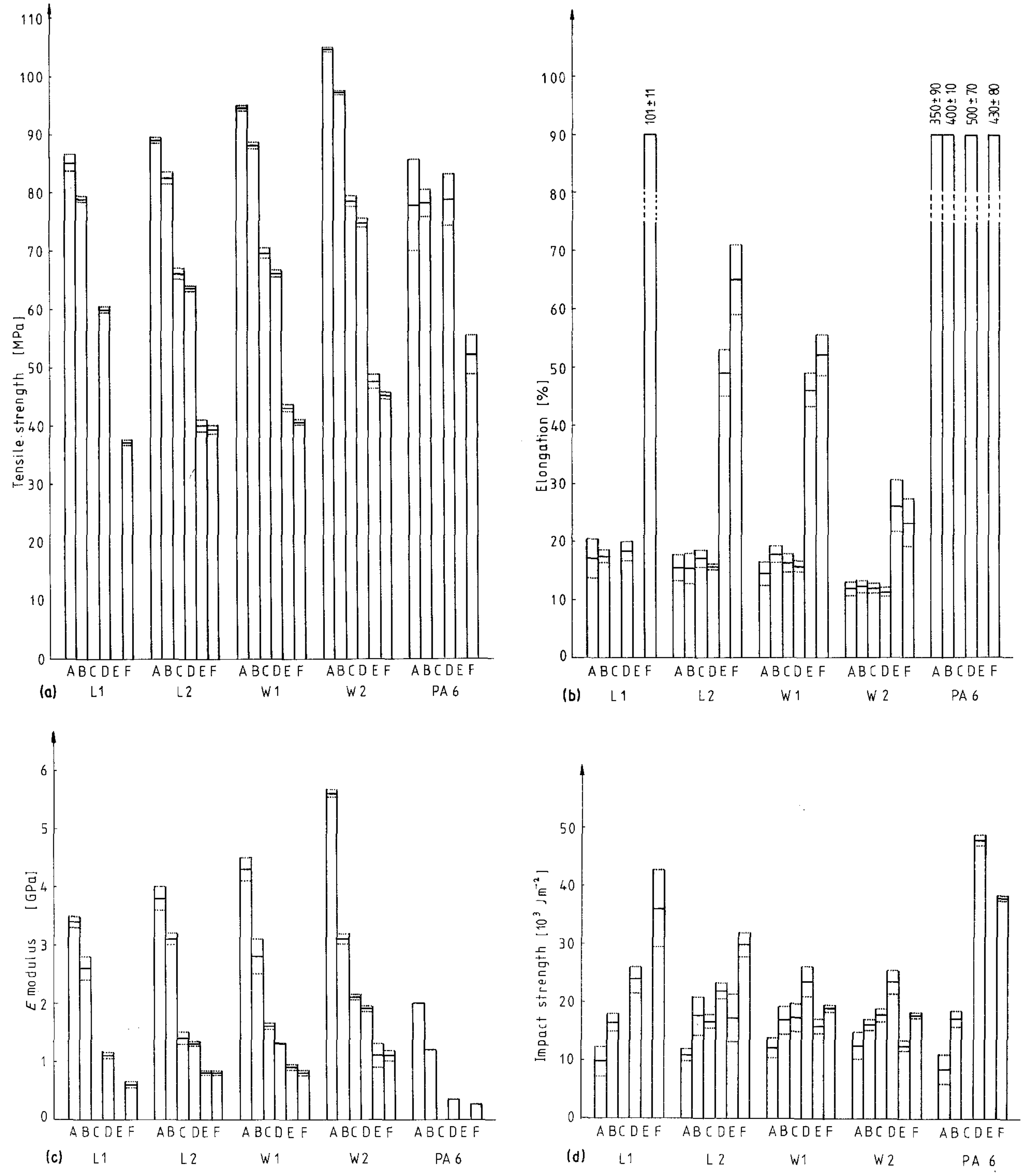

Figure 1 Mechanical strength values and their scattering of four different (L1, L2, W1 and W2) polyamide 6/wollastonite composites and unfilled polyamide 6 (PA 6) after different temperature and humidity treatments (A, . . . , F, see Table II). The numerical strength values are shown in Table III. (a) Tensile strength, (b) elongation to fracture, (c) E modulus (bending), (d) impact strength.

4. Results and discussion

4.1. Materials testing

The effect of wollastonite addition compared with pure polyamide will first be examined. The modulus increases to the double with wollastonite loadings up to 30 wt %, i.e. the stiffness of the composite increases and consequently the usefulness for constructive purposes is greatly improved. An improvement in tensile strength of about 10 to 15% can also be observed. Simultaneously, the elongation at fracture decreases to about 1/20 of that of the pure matrix material.

With this type of additive it is common for the impact strength to decrease and the material to become more brittle. In the present case, wollastonite, there was a slight *increase* in impact strength. The scattering in the data was small in all measurements, suggesting that the results are sufficiently reliable.

Increasing the additive concentrations from 30 to 40 wt % clearly improves all the strength properties. Impact strength, especially, increases markedly while elongation fracture in the tensile tests decreases by half.

These results suggest that, in the case of untreated material (humidity and heat treatment), wollastonite reinforces the polyamide by simultaneously increasing the strength, stiffness and impact strength of the

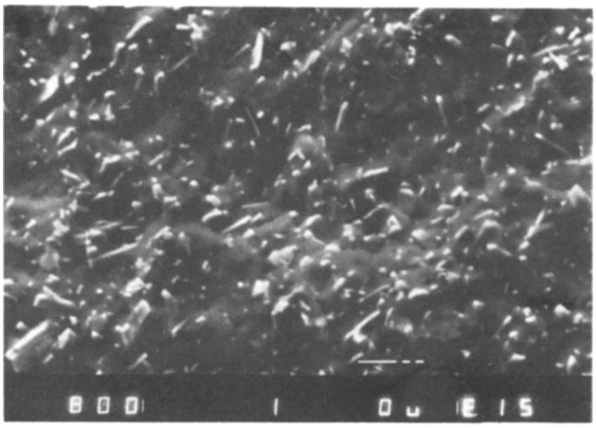

Figure 2 SEM picture of a typical polyamide 6/wollastonite fracture surface, where the wollastonite is evenly distributed in the matrix (material W1, treatment A, impact test). Long scale bar = 10 μm.

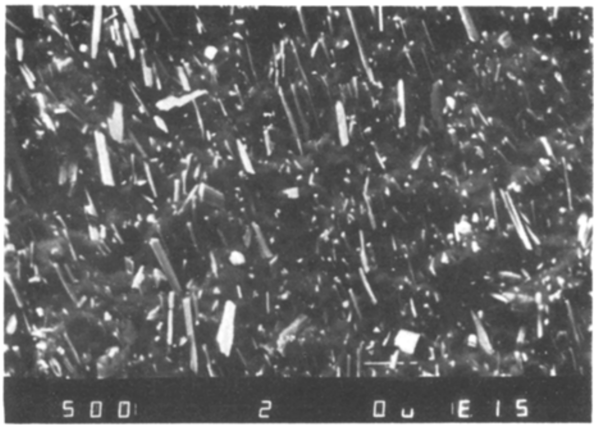

Figure 3 SEM picture of specimen from impact test (material L2, treatment F) where typical orientation of the wollastonite particles can be seen (due to injection moulding). Long scale bar = 10 μm.

material. The increase is in all cases 40 to 200% at wollastonite concentrations of 40 wt %.

For discussion of the influence of the combined humidity/heat treatments on the composite, we will first examine the behaviour of the pure polyamide. As can be seen in Figs 1a to d, there is a significant decrease in strength properties. All the treatments reduce the stiffness and increase the impact strength, while the tensile strength is only significantly affected after the boiling treatment. These results are in accordance with relevant data on polyamide 6 found elsewhere [10].

For the composites there is a clear deterioration in the strength properties, stiffness and tensile strength, starting even at the milder treatments.

In the case of impact strength for the composites, it can be seen that the increase in ductility is smaller than for the pure material. Thus it may be concluded that all the properties of the composites are improved compared with the pure polyamide, with the exception of tensile strength. Consequently, it is very difficult to draw any conclusions concerning the nature of interfacial adhesion.

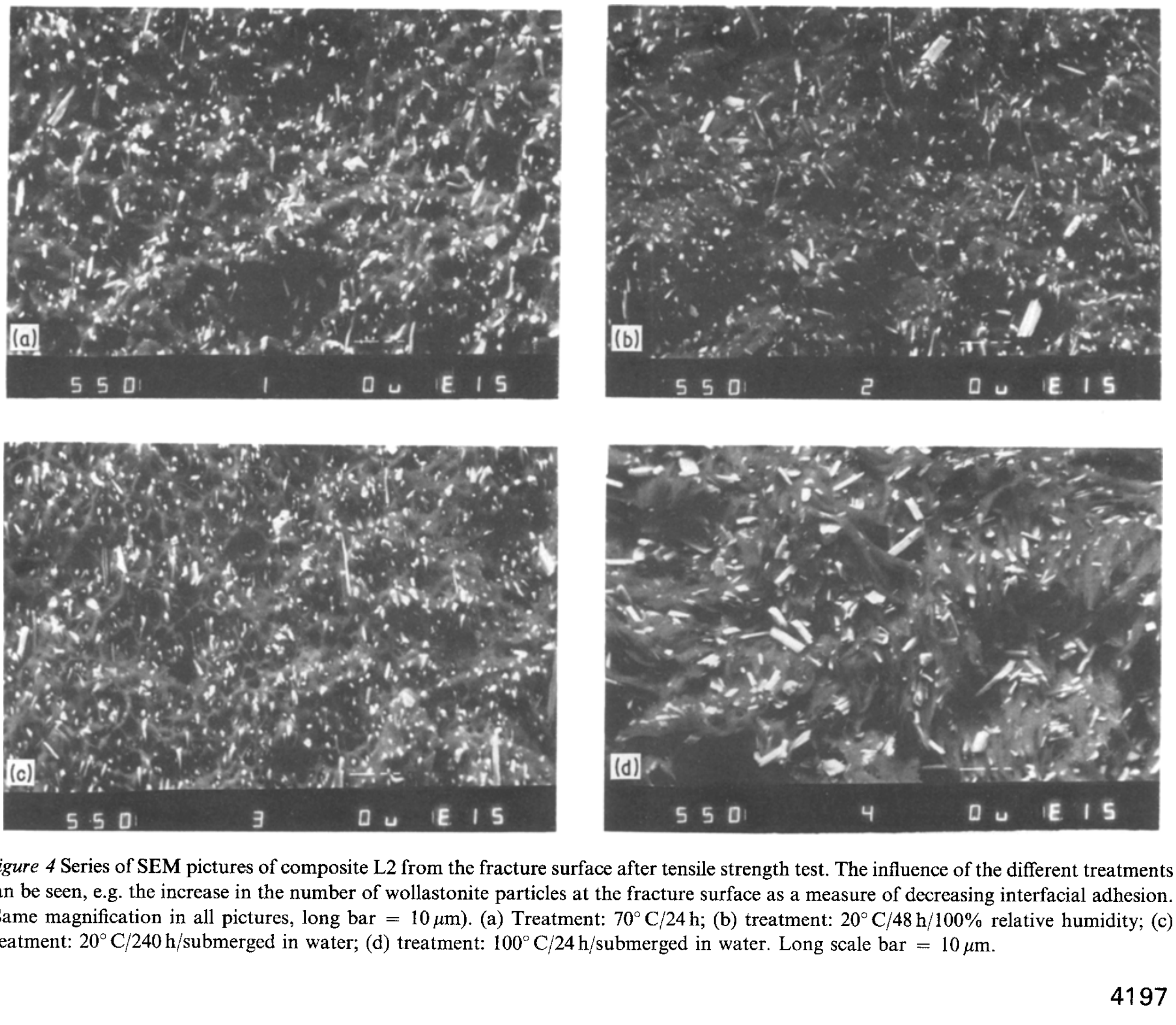

Figure 4 Series of SEM pictures of composite L2 from the fracture surface after tensile strength test. The influence of the different treatments can be seen, e.g. the increase in the number of wollastonite particles at the fracture surface as a measure of decreasing interfacial adhesion. (Same magnification in all pictures, long bar = 10 μm). (a) Treatment: 70° C/24 h; (b) treatment: 20° C/48 h/100% relative humidity; (c) treatment: 20° C/240 h/submerged in water; (d) treatment: 100° C/24 h/submerged in water. Long scale bar = 10 μm.

4.2. The microstructure of the fracture surfaces

This examination was made with an ISI 40-SEM scanning electron microscope which was specially equipped for the study of non-conducting materials (plastics and ceramics), having several different recording facilities, e.g. photographs and video. The main purpose of the SEM examination was to establish the distribution of additives and study the additive/matrix interface.

The wollastonite was found to be well dispersed and distributed througout the matrix (Fig. 2), reflected by the very homogeneous structure of the fracture. In a few cases only, was there a slight orientation of the wollastonite particles. The orientation can probably be attributed to the injection-moulding process used for preparation of the specimens. Such an orientation is shown in Fig. 3. Also the variation in the contents of wollastonite, as determined by burning, was very small, typically less than ± 1 wt %, which in practice lies within the range of accuracy of the method.

The adhesion between the additive and matrix is clearly reflected in the nature of the fracture. It is obvious that a fracture in the composite with the untreated additive results in a fracture surface which reveals considerably more wollastonite particles than when surface-treated wollastonite is used. This is clearly shown in Fig. 4. Obviously it may be concluded that the combined humidity/heat treatment adversely affects the composite by decreasing the adhesion between the additive and matrix.

The present results would thus indicate that a strong enough (primary) bond in the structure wollastonite and polyamide 6 interface has not been obtained. Probably the interfacial bond consists of secondary bonds to a large extent, e.g. physical adsorption of the adhesion promoter.

There are several possible reasons for the weak interfacial adhesion, many of which can be affected by further optimization of the surface treatment and the choice of adhesion promoter [11]. It is unlikely that the heat treatment, both during processing and the treatment of the finished specimen, affects the adhesion promoter physically or chemically adsorbed at the interface. The influence of water may also be fatal, if the hydrolysis reaction of the promoter and surface is displaced. Finally, it is possible that unsuccessful surface treatment leaves the additive partially uncovered and thus hydrophilic, which does not favour adhesion; it is rather to be expected that water molecules due to capillary forces might penetrate the interface and thus destroy additive/matrix adhesion.

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