JOURNAL OF MATERIALS SCIENCE 26 (1991) 4878–4882

Peculiarities of mechanical response of heavily filled polypropylene composites

Part I *Elastic modulus*

J. JANCAR*, J. KUCERA
Chemopetrol, Research Institute of Macromolecular Chemistry, Tkalcovska 2, 65649 Brno, Czechoslovakia
P. VESELY
State Textile Research Institute, 66471 Veverska Bityska, Czechoslovakia

A concentration dependence of a dynamic storage E'_c modulus was investigated for polypropylene filled with microfibrous magnesium hydroxide, $Mg(OH)_2$. The non-monotonous shape of E against filler volume fraction dependence was explained as a consequence of the filler agglomeration.

A simple stochastical model for the dependence of an agglomerate size on the filler volume fraction was developed. A qualitative agreement was obtained between experimental data and proposed theory. A critical filler volume fraction, when an "infinite" agglomerate origins, was determined from the model as well as from percolation conception to be around $v_f^{crit} = 0.2$.

Notation

r_f	average fibre aspect ratio at given v_f
v_f	fibre volume fraction
$v_{f,1}$	volume fraction of nonagglomerated fibres
S_1	relative area occupied by nonagglomerated fibres on the composite perpendicular cross section
$i = 2, 3 \ldots n$	number of fibres in the i-fibre agglomerate
$v_{f,i}$	fibre volume fraction in the agglomerate (considered constant and equal to v_f^{max}/q)
q	parameter of agglomeration
S_i	relative area occupied by i-particle agglomerate
r_i	aspect ratio of i-particle agglomerate
v_f^{max}	fibre maximum volume fraction (hexagonal space packing $v_f^{max} = 0.907$)

1. Introduction

Further extension of application of particulate filled polypropylene requires reduced flammability. Commonly used halogen flame retardants are toxic and corrosive when burned or processed [1]. $Mg(OH)_2$ is a new noble flame retardant and smoke suppressant filler for polyolefins, as the decomposition temperature is about 340 °C. A quantitative understanding of structure-property relationships, capable of the rationalizing the material design, is an important goal of both basic and applied research [2–5]. This is even more emphasized when the high filler loading has to be incorporated (25–60 vol %).

In our previous paper [6], the importance of filler agglomeration was described as well as changes of the matrix morphology when PP is filled with high loading of $Mg(OH)_2$. As particles in the agglomerate are bonded by physical bonds and the agglomerates possess viscoelastic behaviour similar to that for real chemical network [7], term physical network (PN) was used. It was also shown that PP immobilized on the filler surface can create a continuous phase and bonds particles in PN.

The objective of this paper is to develop a simple theoretical model for origin of PN and to analyse isothermal concentration dependences of E'_c modulus for PP filled with $Mg(OH)_2$ microfibres.

2. Experimental procedure

Commercial polypropylene Mosten 58.412 (Chemopetrol, Czechoslovakia), melt index (210 °C, 21.6 N) 4g/10 min was used as a matrix. Microfibrous magnesium hydroxide KISUMA 7B (Kyowa, Japan) was used as a filler (Table I). $Mg(OH)_2$ was surface treated with about 2 wt % of stearic acid by the producer. The components were mixed in the PLE 651 Brabender Plasticorder (chamber W50H, charge 50 cm^3) at 200 °C, 50 r.p.m., 10 min. Out of the compounded materials, plaques 1 mm thick were compression moulded at 210 °C. The specimens cut out of the plaques were annealed for 1.5 h at 114 °C and then slowly

*On leave at The University of Connecticut, Institute of Materials Science, U-136, 97 North Eagleville Road, Storrs, CT 06268, USA.

TABLE I Characteristics of the fillers

Chemical nature	Grade	Specific surface area ($m^2 g^{-1}$)	Density ($g cm^{-3}$)	Young modulus[a] E (GPa)	Shear modulus[a] G (GPa)	Average aspect ratio
CaCO	Durcal 2	3.3	2.71	72	28	irregular approximately spherical/p 1
Mg(OH)	Kisuma 5B	7	2.36	64	25	hexagonal lamellae/p 5
	Reachim	6.8	2.36	64	25	hexagonal lamellae/p 5
	Kisuma 7B	37	2.36	64	25	needles/p 25

[a] The values E and G moduli of Mg(OH) were estimated considering the relation between elastic moduli and hardness of materials.

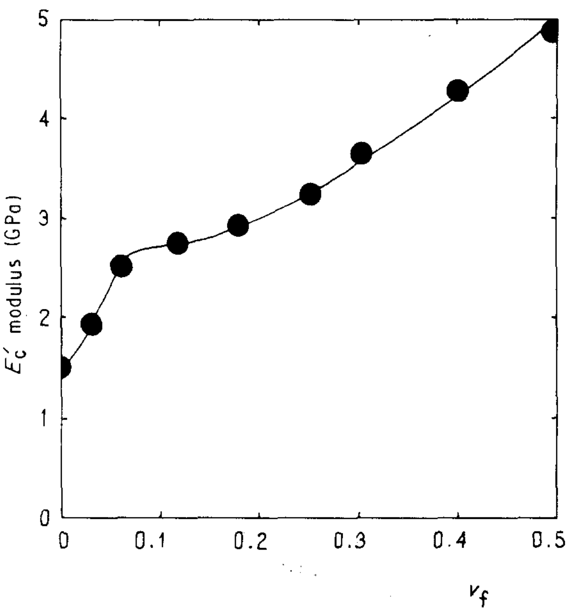


Figure 1 The composition dependence of the dynamic E'_c modulus for the PP/$Mg(OH)_2$ needle composite obtained from experiment (random fibre orientation).

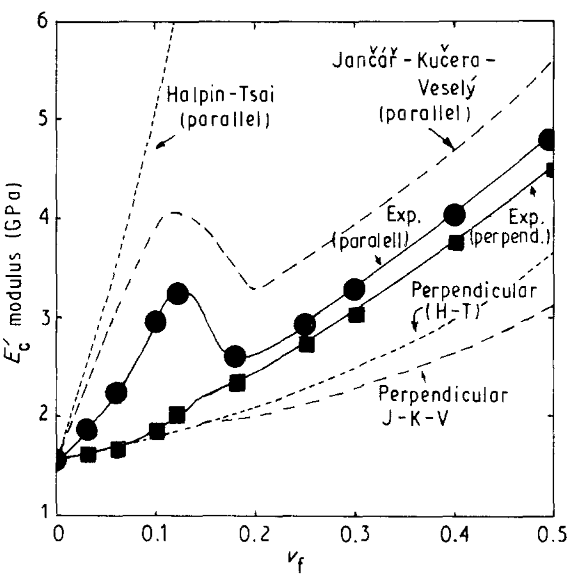


Figure 2 The composition dependence of the Young E'_c modulus for the PP/$Mg(OH)_2$ needle composite with unidirectionally aligned needles. (●) parallelly measured E^L_c modulus, (■) perpendicularly measured E^T_c modulus, (-------) theoretical curve calculated from the Haplin-Tsai equation (Equations 9–11), (– – – –) theoretical curve calculated from here proposed model.

cooled down at a rate of about $5\,°C\,min^{-1}$. Composites with aligned needles were obtained via a simple technique. Strings out of compounded materials were extruded through the nozzle of M200 Plastograph (nozzle dia. 2 mm). Then, strings were aligned parallelly in the mould and compression moulded at the same conditions as described above. The dog-bone specimens were cut out parallel and perpendicularly to the string-in-mould formal direction. Small shear rate during the string extrusion and consequent recrystallization in the course of compression moulding and annealing did not cause the matrix orientation. Moduli measurements were carried out on the Dynamic Mechanical Thermal Analyzer (PL DMTA, PL Thermal Sciences, UK) at the exciting frequency 1 Hz (23 °C).

3. Theory, results and discussion

3.1. The agglomerate (bundle) origin

For unidirectionally aligned fibrous composite, fibres are represented by circles of radius, R, on the material perpendicular cross section (Fig. 3a). The area fraction occupied by circles, S_f, is equal to v_f. Let us assume that on the fibre surface there is a uniform layer of immobilized matrix. This interlayer "effective" thickness is ΔR. To describe the space packing, we have considered the cross section divided in hexagons (Fig. 3b). For a given v_f, the probability p that a circle will be located in a hexagon is given by:

$$p = \frac{v_f}{v_f^{max}} \tag{1}$$

The maximum filler volume fraction is equal to 0.907 for hexagonal parallel space packing considered [10]. When the distance between two neighbouring circles is equal to twice the interlayer thickness, i.e. $2\Delta R$, new hexagons are drawn around circles with the side $(R + \Delta R)$ long. The area occupied by these two hexagons represent the area of two-particle agglomerate (Fig. 4a). Physically, the bond between two particles is created via interpenetration of particle interlayers of molecules immobilized on the fibre surface. The interpenetration probably occurs in the melt and during the solidification, when the molecular mobility in the interlayer is not so significantly reduced.

The concentration of agglomerates on the cross section is:

$$v_{f,A} = \frac{Q_{A,2}\, v_f^{max}}{q} \tag{2}$$

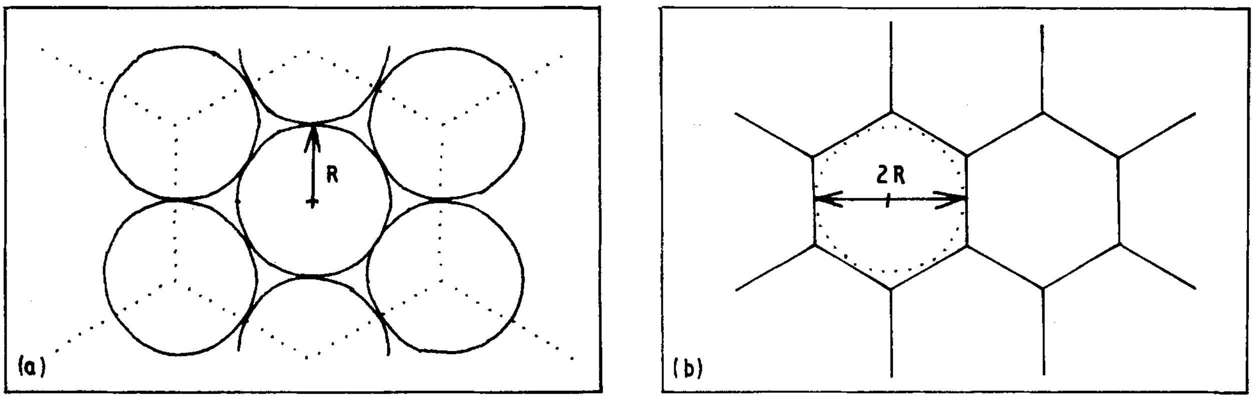


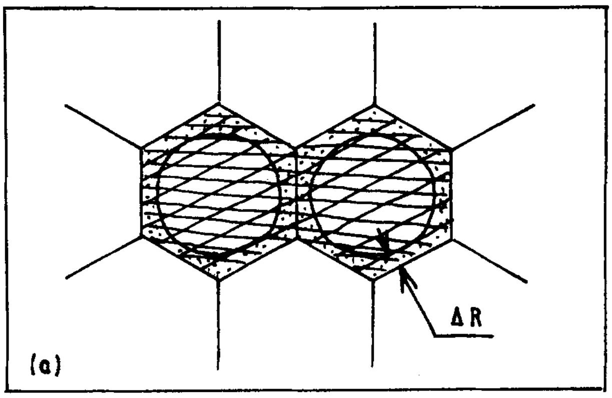
Figure 3 (a) The hexagonal parallel space packing of fibres on the perpendicular cross section at $v_f^{max} = \pi\sqrt{(3/6)} = 0.906$. (b) A network of identical hexagons fully dividing the cross section area.

In Equation 2, $Q_{A,2}$ is the area fraction occupied by all agglomerates and q determines the effect of interlayer thickness:

$$q = (1 + B)^2 \tag{3}$$

where

$$B = \frac{\Delta R}{R} \tag{4}$$



The concentration of non-agglomerated particles is:

$$v_{f,1} = \frac{v_f - v_{f,A}}{1 - Q_{A,2}} \tag{5}$$

Each agglomerate is characterized by its elastic modulus E_A and its aspect ratio r_A. We suppose, that agglomerates behave as new reinforcing elements possessing different physical and geometrical characteristics in comparison to $Mg(OH)_2$ single fibres.

3.2. Elastic response of the composite with agglomerated microfibrous reinforcement

Two basic assumptions were considered. Firstly, the reduction of the fibre aspect ratio with increasing filler volume fraction was accounted. This reduction was partly due to the mechanical destruction of fibres in the course of compounding and partly due to the agglomeration. Effect of the mechanical destruction

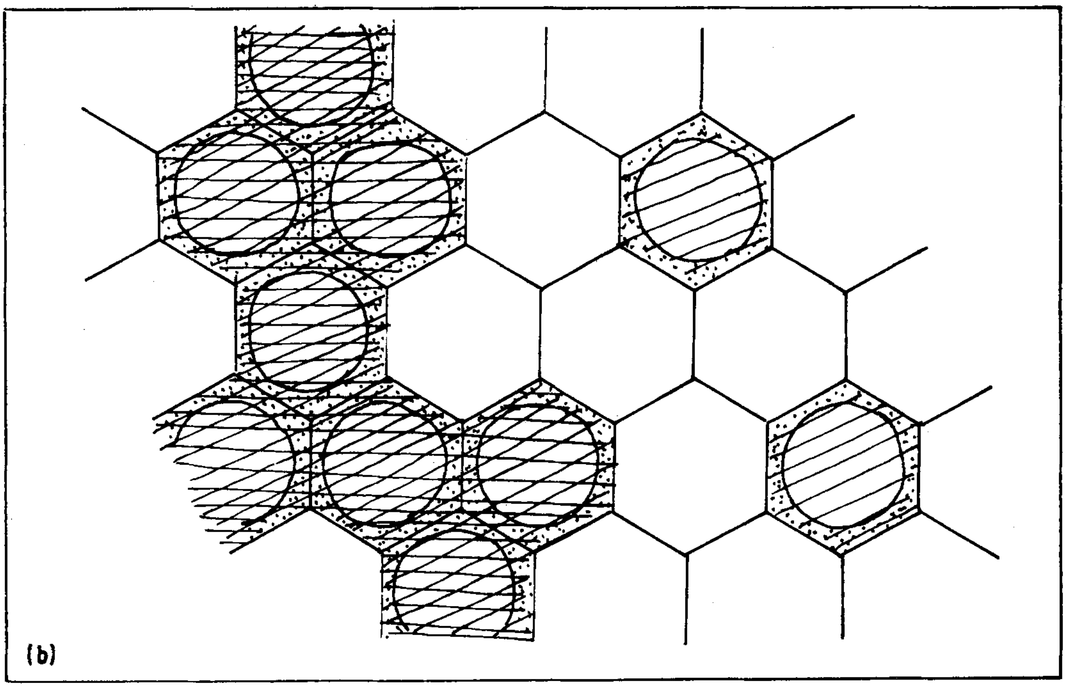


Figure 4 (a) 2-particle agglomerate origin on the composite cross section as represented by the hexagonal network considering the presence of physical "bonding" agent—the immobilized interlayer. ▨ filler, ░ interlayer, ▤ originated agglomerate. (b) n-particle agglomerate origin on the composite cross section. ▤ originated agglomerate.

was determined experimentally earlier [8, 9]. An additional "apparent" reduction due to the agglomeration can be calculated using results of the previous paragraph:

$$r_f = v_f^{-1}(S_1 v_{f,1} r_{exp} + \Sigma(S_i v_{f,i} r_i)) \quad (6)$$

Secondly, a reduction of the effective elastic modulus of the bundle of fibres, in comparison to the single fibre, was accounted. The single $Mg(OH)_2$ fibre has elastic modulus determined by its chemical nature and crystallographic structure (64 GPa). In the case of agglomerate containing both high modulus fibres and low modulus matrix, the effective elastic modulus of such a complex "reinforcing element" has to be necessarily lower than that for a single fibre. The nature of the proposed model has led us to assume a constant value of the elastic modulus of an agglomerate independently on the number of agglomerated fibres. The value of 7 GPa was obtained by the simple extrapolation of the experimental composite E_c modulus for the low filler volume fraction to $v_f^{max} = 0.907$. As we characterized polydisperse filler by average parameters, we have made the same averaging procedure for the effective filler modulus as for the aspect ratio in previous paragraph:

$$E_f^{eff} = v_f^{-1}(S_1 v_{f,1} E_f + E_{A,2}(v_f^{max} q^{-1})\Sigma S_i) \quad (7)$$

To find the concentration dependence of the elastic modulus of composite with unidirectionally aligned microfibrous rigid filler and to account the effect of agglomeration, we have substituted the geometrical constants A and B in the Halpin-Tsai Equation 10* by constants A^{eff} and B^{eff} calculated using values of r_f and E_f^{eff} (Equations 6 and 7). The expressions for the constants are as follows:

$$A^{eff} = 2r_f \quad \text{for parallel } E \text{ modulus}$$

$$A^{eff} = \tfrac{1}{2} \quad \text{for perpendicular } E \text{ modulus} \quad (8)$$

$$B^{eff} = (E_f^{eff}/E_m - 1)/(E_f^{eff}/E_m + A^{eff}) \quad (9)$$

Then, the modified Halpin-Tsai equation can be expressed in the form:

$$E_c/E_m = (1 + A^{eff} B^{eff} v_f)/(1 - B^{eff} v_f) \quad (11)$$

Using Equation 11, a qualitative agreement was obtained between experimental data and calculated values of E_c modulus over the entire concentration region investigated (Fig. 2).

3.3. Critical filler volume fraction

An attempt was made to evaluate the critical fibre volume fraction v_f^{crit} when the "infinite" agglomerate of fibres occurs first. The estimation of v_f^{crit} was made from both our model and percolation theory. Critical filler volume fraction can be considered as a percolation threshold, as the mechanical response change the character steeply. Consistently with the proposed model, we have used the "site percolation model". In this model, two sites are bonded when elipsoids, representing the filler particles, with the centres in the neighbouring sites and with a given aspect ratio, overlap. At the same time, a vector character of percolation had to be accounted and unidirectional alignment of fibres was considered.

Balberg [11, 12] has suggested that the critical volume fraction of fibres of length L and diameter $2R$ at the percolation threshold can be expressed as

$$v_f^{crit} = 2.65(L/R)^{-1} \quad (12)$$

Considering the average aspect ratio (L/R) equal to 12, as it was determined experimentally, we have obtained from Equation 12 the critical fibre volume fraction equal to 0.22. The v_f^{crit} was then estimated from concentration dependences of r_f and E_f^{eff} as the position of the turning point (Fig. 5). The critical fibre volume fraction determined by this way was within the interval from 0.17 to 0.20. In spite of very rough assumptions for the proposed model, values determined from percolation theory and from our model are in an agreement.

4. Conclusions

The effect of fibre agglomeration on the dynamic mechanical modulus of PP filler with microfibrous $Mg(OH)_2$ was investigated. A simple statistical model

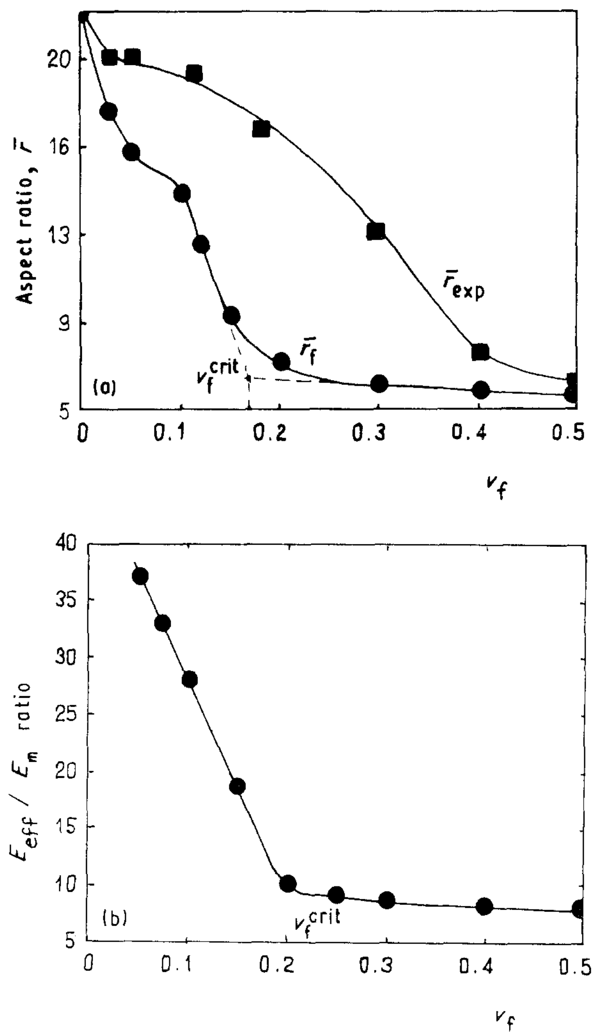


Figure 5 (a) The concentration dependence of the Mg(OH) needle average aspect ratio $\bar{r}$ calculated taking into account both experimentally determined $\bar{r}$ reduction and that calculated from Equation 6. (b) The concentration dependence of the average "effective" filler modulus E_{eff} from Equation 7.

*Unmodified equation not given in text.

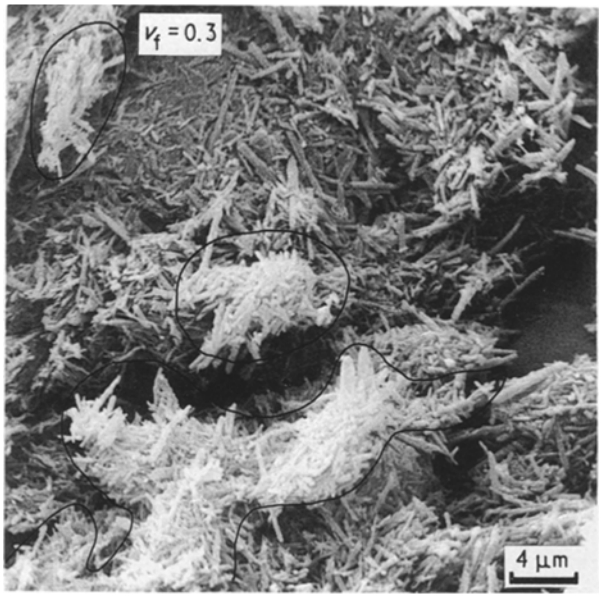


Figure 6 SEM micrograph of the extracted bundles of $Mg(OH)_2$ needles (hot decaline 130 °C, 2 h).

was proposed to describe the concentration dependence of the origin of *n*-particle agglomerates. The layer of immobilized PP on the fibre surface was considered as a "bonding agent" for these agglomerates. It is believed that the bond is due to origin of sufficient number of entanglements between interpenetrated interlayers of neighbouring particles. The interlayers interpenetrated either in the melt in the course of compounding or compression moulding, when the mobility of molecules in the interlayer is not significantly reduced.

The Halpin-Tsai equation was modified to find the description of the concentration dependence of the dynamic E'_c modulus accounting agglomeration of unidirectionally aligned fibres. Qualitative agreement was obtained between theory and experimental data assuming that agglomerates act as new reinforcing elements with elastic modulus and aspect ratio different in comparison to single $Mg(OH)_2$ fibres.

The steep change of the character of concentration dependence of E'_c modulus of the composites investigated led us to the suggestion about percolation threshold appearance. The site percolation model was considered as a proper theoretical model for the description of the effect of agglomeration on the mechanical response of the system. The critical fibre volume fraction when "infinite" agglomerate occurs first was determined from both the percolation theory and from our simple model. For the composite studied, both theories provided critical fibre volume fraction around 0.2.

Acknowledgement
The authors wish to thank Professor Eugene Guyon (ESPCII Paris, France) for providing them with a basic source of knowledge about percolation theory.

References

1. P. N. HORNSBY and C. L. WATSON, *Plast. Rubb. Proc. Appl.* **6** (1986) 169.
2. J. HUGO, J. KUCERA and F. RYBNIKAR, in MPC Symposium on Mechanics of Polymer Composites, edited by R. A. Bares (Prague, 1986).
3. E. GUYON, in The Physics of Random Matter, Les Houches, Session XLVI (North Holland, 1987).
4. Y. KANTOR and I. WEBMAN, *Phys. Rev. Lett.* **52** (1984) 1891.
5. J. VAREILLE, E. GUYON and S. ROUX, *Revue Phys. Appl.* **22** (1987) 1361.
6. J. JANCAR, J. KUCERA and P. VESELY, *J. Mater. Sci. Lett.* **7** (1988) 1377.
7. P. VESELY, in Proceedings of the 4th European Symposium on Thermal Analysis and Calorimetry, E-6 (Jena, Germany, 1987).
8. J. JANCAR, *J. Mater. Sci.* **24** (1989) 3947.
9. *Idem., ibid.* **24** (1989) 4268.
10. L. E. NIELSEN, "Mechanical Properties of Polymers and Composites", Vol. 2 (Dekker, New York, 1974).
11. I. BALBERG, N. BINENBAUM and N. WAGNER, *Phys. Rev. Lett.* **52** (1984) 17.
12. I. BALBERG, C. H. ANDERSON and N. WAGNER, *ibid.* **B-30** (1984) 3939.

Received 26 February 1990
and accepted 31 January 1991