

Micellar reinforcement of polystyrene with grafted rigid-chain polyesters

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Abstract

Two decades ago, the concept of molecular reinforcement of thermoplastics was advanced: it was predicted that thermoplastics of regular flexible-coil polymers are strongly reinforced by rigid-rod polymer chains that are molecularly dispersed in the thermoplastic matrix, acting as “molecular fibres”. However, it proved difficult to test this concept because rigid-rod and flexible-coil polymers are usually demixed. Rigid-rod chains do not dissolve in normal thermoplastic matrices but form a separate phase. A related concept bearing more promise, i.e. the “micellar reinforcement”, is introduced in this paper: rigid chains that are provided with flexible grafts can form reinforcing cylindrical micelles in thermoplastic matrices. The micelles of such rod-coil graft copolymers have a thickness on the submicroscopic scale, not far above the molecular scale. This concept was explored in a polyester–polystyrene system based on rigid-chain polyesters (PES) containing double-bond units. Graft copolymers PSgPES were prepared by a mechanism of “grafting-through” which amounts to a random copolymerisation of styrene and the double bonds in the PES chains. Synthetic problems were (i) achieving high molecular weights, in particular of the PS chains, and (ii) avoiding crosslinking which occurs easily via multigrafting. After attempts with initiators in the bulk and in solution, thermal polymerisation without an initiator yielded long-chained PSgPES graft copolymer products with only moderate shares of ungrafted PS and PES byproducts. These graft products formed cylindrical micelles of PES in a PS matrix which doubled the modulus of PS. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymers are inherently softer and weaker than steel. They are competitive only when reinforced with high-modulus fibres. Conventional fibre–polymer composite materials contain fibres, some micrometers thick and millimeters long, dispersed and oriented in the polymer matrix (Fig. 1(a)). The market is dominated by glass fibres but organic fibres of rigid-chain liquid crystalline (LC) polyaramides are meanwhile used as well [1,2]. In the search for novel principles of reinforcing thermoplastics, the concept of *molecular reinforcement* of thermoplastics has been advanced two decades ago [3–7], of which the extreme case is indicated in Fig. 1(b): rigid chains, molecularly dispersed in the flexible-chain matrix of thermoplastics, can act as reinforcing fibres on the single-chain (“molecular”) level. Rigid-chain polymers might be composed of rigid-rod [8] or hairy-rod chains [9,10] that exhibit liquid crystalline (LC) order. That this concept works, in principle, has recently been demonstrated theoretically [11].

However, the situation in Fig. 1(b) is unrealistic. Rigid-rod and flexible-coil chains are usually incompatible [12–

16] which keeps the rigid chains from dissolving in the matrix (only special systems with polyionic chains, prepared in solution, appear to permit a true single-chain dispersion of rigid chains [17]). Therefore, instead of single-chain composites, only “nanocomposites” have so far been developed in which rigid-rod polymers form tiny submicroscopic fibres that consist of many (definitely more than one) chains [18–20]. These composites are analogues to nanocomposites with submicroscopic inorganic fillers, in particular nanowhiskers [21] and exfoliated silicate layers [22,23].

The topic of this paper is a novel concept of reinforcing thermoplastics which is related to molecular reinforcement, i.e. *micellar reinforcement*. This concept is based on the thermodynamic stability of the nanophases of block and graft copolymers [24–27]: rod-coil block [28–30] or graft copolymers consisting of rigid and flexible blocks should be able to form, in the flexible-chain matrix of thermoplastics, anisotropic micellar structures with a hard rigid-rod core and a soft flexible-coil shell. This paper deals with rod-coil graft copolymers. As shown in Fig. 1(c), these copolymers should form oriented cylindrical micelles of rigid-rod chains that are tied to the matrix by a fur of flexible-coil grafts. These micelles are high-modulus fibres on an almost

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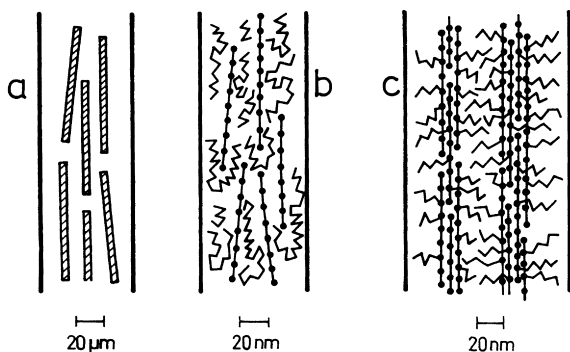


Fig. 1. Oriented thermoplastics, reinforced with: (a) macroscopic fibres or (b),(c) rodlike polymer chains in (b) molecular or (c) micellar dispersion.

molecular level. Compatibility of the rigid and coiled chains is not required.

The viability of this concept will be demonstrated. Graft copolymers of rodlike aromatic LC copolyesters and flexible polystyrene will be discussed, first the strategy and the synthesis, then the morphologies and the mechanics.

2. Strategy

Most graft copolymers are prepared via the mechanisms of *grafting-from* or *grafting-onto*. Grafts (gPB) get laterally attached to a backbone chain (gPA) so a T-shaped copolymer PAgPB results. In this study, however, the less common

mechanism of *grafting-through* was employed, the principle of which is indicated in Fig. 2(a). A vinyl monomer B is copolymerized with double bonds in a polymer PA, which leads to a X-shaped copolymer since the gPB chain runs through the gPA chain. Reasonably, the longer chain, gPA or gPB, should be viewed as the backbone and the other one as the graft so the resulting copolymers are either of type PAgPB or type PBgPA.

Chain structures based on such X-shaped graft points are shown in Fig. 2(b) and (c) where either a gPA chain connects several gPB chains (Fig. 2(b)) or a gPB chain connects several gPA chains (Fig. 2(c)). These multigraft copolymers must be carefully designed. Combinations of the chain architectures in Fig. 2(b) and (c) lead easily to a chain network where gPB chains run through several gPA chains and vice versa. Unsaturated polyester resins are commercial systems of this network type [31]. Evidently, crosslinking must be avoided when graft copolymers are aimed at.

The polyester–polystyrene system in Fig. 3 was introduced in Ref. [32] and is discussed in this paper:

- *Copolyester (Fig. 3(a))*: A rigid-chain copolyester of terephthalic and 2,5-dihexoxyterephthalic acid as well as phenylhydroquinone was chosen. This copolyester is a thermotropic main chain LC polymer with a relatively low clearing point ($T_{lc-i} = 270^{\circ}\text{C}$), due to the hexoxy and phenyl substituents [9]. The polymer can be dissolved at moderate concentrations in several solvents.

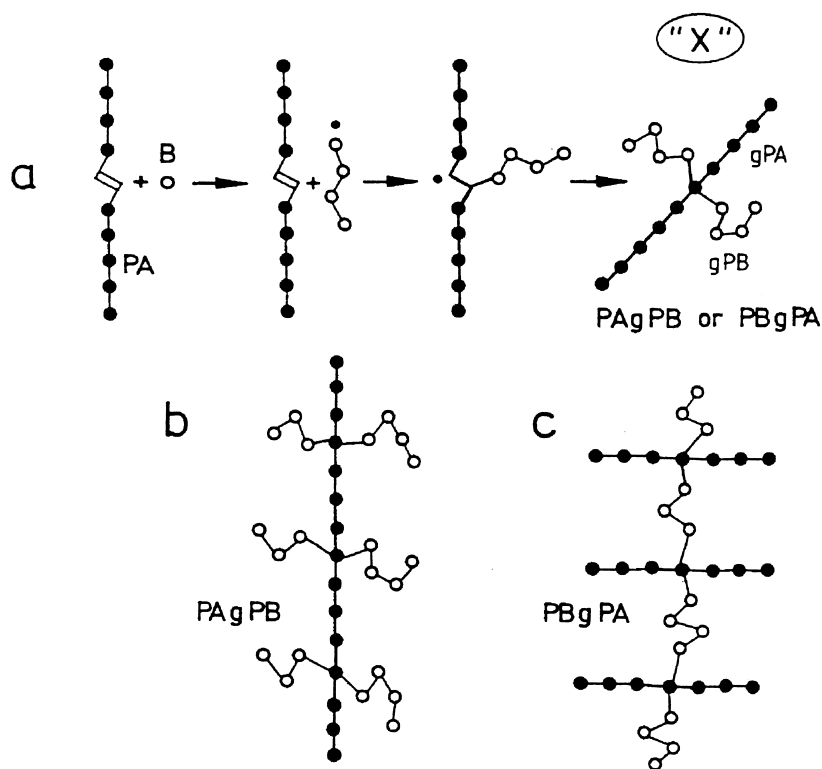


Fig. 2. Grafting-through: (a) "X" shaped graft copolymers (PAgPB or PBgPA), prepared by random copolymerisation of a monomer B and double bonds in a polymer PA; (b),(c) multigraft architectures with a back bone (b) gPA or (c) gPB.

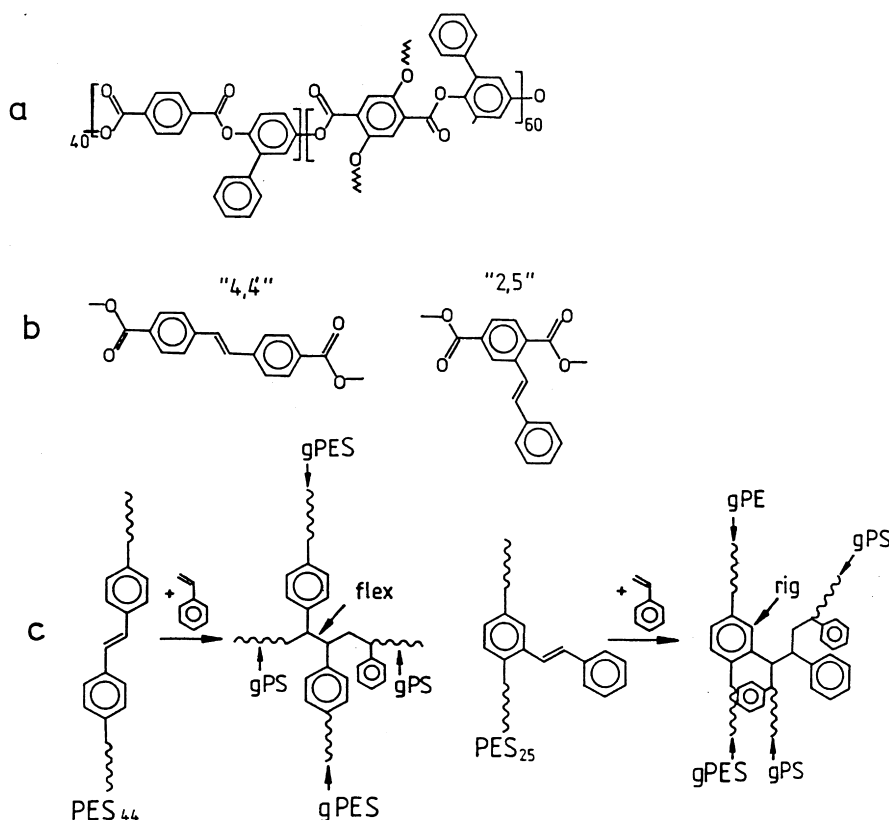


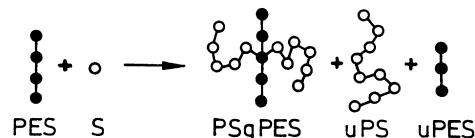
Fig. 3. Polyester–polystyrene system: (a) basic polyester; (b) double bond containing stilbene co-units for the modified polyesters PES₄₄ and PES₂₅: 4,4'-dicarboxystilbene ("4,4'") and 2,5-dicarboxystilbene ("2,5'"); (c) grafting of styrene chains through the double bonds, producing a flexible (flex) link in PES₄₄ but leaving PES₂₅ rigid (rig).

- *Copolyesters PES* (Fig. 3(b)): The chains of this copolyester were provided with 4,4'- or 2,5-dicarboxystilbene units which contain double bonds that cannot homopolymerize but can copolymerize with styrene (as to the abbreviations: the modified copolyesters will be referred to by "PES" and sometimes by "PES₄₄" and "PES₂₅", to specify the double bond unit).
- *Graft copolymers PSgPES* (Fig. 3(c)): The modified copolyesters PES₄₄ and PES₂₅ were grafted with styrene. For the performance of the resulting rod-coil graft copolymers PSgPES, it is mandatory that the grafted gPES chains be as rigid as the original PES chains. This was definitely the case with PES₂₅ but not entirely with PES₄₄. Since the double bonds of the 2,5 units are laterally attached, grafting leaves the PES₂₅ chains rigid. But the double bonds of the 4,4' units are incorporated in the PES₄₄ chains so grafting (whereby double are turned into single bonds) introduces flexible chain links.
- *Architecture of PSgPES*: For competitive products PSgPES, two conditions had to be satisfied, i.e. (i) long PS chains and (ii) sufficient grafting without crosslinking. The statistics of grafting-through predict that condition (ii) means that the PSgPES chains must predominantly be built as in Fig. 2(a), like an X, with one gPS backbone and one gPES graft.

3. Theory of grafting-through

Analyzing graft copolymerisations is always difficult. It is usually impossible to arrive at an exact and comprehensive picture of the complex products on the basis of experiments alone. But predictions derived from theory can help. Since the theory of grafting-through processes is basically that of random copolymerisation, predictions are easier than for other grafting mechanisms. The following statistics are especially adapted to the polyester–polystyrene system in Fig. 3.

Grafting-through starts from a solution {S/PES} of PES in styrene (S) in which styrene is copolymerized with the double bonds of PES. The product consists of three components, the graft copolymer (PSgPES), the homopolymer of styrene (uPS) and ungrafted polyester (uPES):



Statistically, the product has four constituents, i.e. the subchains gPS and gPES of the copolymer PSgPES and the byproducts uPS and uPES.

3.1. Polyester PES

The polyesters PES (PES₄₄ and PES₂₅) are random copolycondensates ES_{1-x}D_x of the regular units ES of the original polyester (Fig. 3(a)) and the double-bond units D (Fig. 3(b)), the composition being given by the mole fraction of D units

$$x = \frac{m_D/M_D}{m_{ES}/M_{ES} + m_D/M_D} \quad (1)$$

m_i : mass, M_i : molecular weight.

Characteristic parameters for the polyester chains are the averages of the degree of polymerisation n_{PES} and the number d_{PES} of D units per chain (all statistical averages in this section are number averages):

$$n_{PES} = \sum_n np_n = \frac{1}{1 - \pi}, \quad (2)$$

$$d_{PES} = \sum_n \sum_d dp_{nd} = \frac{x}{1 - \pi} = xn_{PES}. \quad (3)$$

The distribution function p_{nd}

$$p_{nd} = p_n(n, d)x^d(1 - x)^{n-d} \quad p_n = \pi^{n-1}(1 - \pi). \quad (4)$$

of the number n of monomers and the number d of D units per chain is controlled by the composition x of PES (Eq. (1)) and the connectivity parameter π (where $(1 - \pi)$ is the share of chain ends) which is calculated from the experimentally determined molecular weight M_{PES} (i.e. from n_{PES} , Eq. (2)).

3.2. Random copolymerisation

In a solution {S/PES} with the PES weight fraction

$$W = \frac{m_{PES}}{m_{PES} + m_S}, \quad (5)$$

the styrene and the D units of PES are copolymerized to a conversion

$$c = 1 - \frac{(m_S + m_D)(t)}{(m_S + m_D)(t=0)} \cong c_S = 1 - \frac{m_S(t)}{m_S(t=0)}. \quad (6)$$

The solution {S/PES} is, in fact, a comonomer mixture {S/D} with the mole fraction of D units

$$Y = \frac{m_D/M_D}{m_S/M_S + m_D/M_D} \cong xW \frac{M_S}{xM_D + (1 - x)M_{ES}}. \quad (7)$$

The copolymerisation is not azeotropic. Values of the copolymerisation reactivity ratios of stilbene (for the double bond units D) and styrene in the literature are [33]

$$r_D \cong 0 \quad r_S \cong 4 \quad (8)$$

so S is favoured over D, in the copolymer S_{1-y}D_y. The composition of S_{1-y}D_y is given by

$$y = \frac{r_D Y^2 + Y(1 - Y)}{r_D Y^2 + 2Y(1 - Y) + r_S(1 - Y)^2} \cong \frac{Y}{r_S}, \quad (9)$$

where the second relation holds for $Y \ll 1$. The copolymer contains less D units than the feed ($y < Y$, Eq. (8)) and the conversion of D units is smaller than that of styrene:

$$c_D \cong \frac{c_S}{r_S}. \quad (10)$$

Although the copolymerisation is not azeotropic (Eq. (8)), the comonomer sequence order in the chains of the copolymer S_{1-y}D_y is, at low conversion c , approximately random.

3.3. Grafting-through product {PSgPES/uPS/uPES}

The random copolymer S_{1-y}D_y is the grafting-through product. More precisely, this product is a blend {PSgPES/uPS/uPES} of grafted and ungrafted chains with the weight fraction of PES (gPES + uPES)

$$w = \frac{m_{PES}}{m} = \frac{W}{W + c(1 - W)}. \quad (11)$$

The statistics of the PS (gPS + uPS) and the PES (gPES + uPES) part of this blend are calculated separately. Characteristic parameters of the products are: (i) the averages of the degree of polymerisation n_i and the number of graft points per chain g_i of all components i ; and (ii) the weight fractions w_i (as to the indices: an index g describes grafted and an index u ungrafted chains while no index describes all chains).

3.3.1. PS = gPS + uPS

The distribution function q_{ng} for the number of monomers (n) and the number of graft points (g) per chain (where g is equal to the number of double bond units D in the PS chains) is given by Eq. (4) with exchanged parameters, i.e. with the composition y of S_{1-y}D_y and the connectivity parameter ψ :

$$q_{ng}(\psi, y) = p_{nd}(\pi, x). \quad (12)$$

The degrees of polymerisation are

$$n_{PS} = \sum_n nq_n = \frac{1}{1 - \psi},$$

$$n_{gPS} = \frac{\sum_n \sum_d nq_{ng \neq 0}}{\sum_n \sum_d q_{ng \neq 0}} = \frac{1 - \psi^2(1 - y)}{(1 - \psi)(1 - \psi(1 - y))}, \quad (13)$$

$$n_{uPS} = \frac{\sum_n nq_{ng=0}}{\sum_n q_{ng=0}} = \frac{1}{1 - \psi(1 - y)}.$$

The connectivity parameter ψ in Eq. (12), which is assumed to be equal for grafted and free chains, is calculated from the experimentally determined molecular weight M_{uPS} (i.e. from n_{uPS} , Eq. (13)).

An important effect in Eq. (13) is that the grafted chains gPS are longer than the average of all PS chains while the

ungrafted chains uPS are shorter:

$$n_{\text{PS}} < n_{\text{gPS}} < 2n_{\text{PS}} \quad 1 < n_{\text{uPS}} < n_{\text{PS}}. \quad (14)$$

The number of graft points per chain is given by

$$g_{\text{PS}} = \sum_n \sum_g g q_{ng} = \frac{y}{1-\psi} = y n_{\text{PS}},$$

$$g_{\text{gPS}} = \frac{\sum_n \sum_g g q_{ng \neq 0}}{\sum_n q_{ng \neq 0}} = \frac{1-\psi(1-y)}{(1-\psi)} = \frac{n_{\text{PS}}}{n_{\text{uPS}}} \cong 1 + g_{\text{PS}}. \quad (15)$$

where g_{PS} is averaged over all PS chains and g_{gPS} only over the grafted gPS chains (note that the limit $y \rightarrow 0$ means $g_{\text{PS}} \rightarrow 0$ but $g_{\text{gPS}} \rightarrow 1$).

The grafting efficiency f_{gPS} leads to the weight fractions w_{uPS} and w_{gPS} :

$$f_{\text{gPS}} = \frac{m_{\text{gPS}}}{m_{\text{PS}}} = \frac{\sum_n \sum_d n q_{ng \neq 0}}{\sum_n n q_n} = \frac{y(1-\psi^2(1-y))}{(1-\psi(1-y))^2}, \quad (16)$$

$$w_{\text{gPS}} = f_{\text{gPS}}(1-w) \quad w_{\text{uPS}} = (1-f_{\text{gPS}})(1-w).$$

3.3.2. PES = gPES + uPES

The PES chains are a bit more complicated than the PS chains in so far as, at a conversion c , only the part c_D (Eq. (10)) of all D units in the PES chains will be grafted. The statistics of the PES chains thus depends on the conversion. The distribution function

$$p_{ndg} = p_{nd}(d, g) c_D^g (1-c_D)^{d-g}, \quad (17)$$

describes the number n of monomers, the number d of

corresponding to q_{ng} (Eq. (12))

$$p_{ng}(\pi, c_D x) = q_{ng}(\psi, y) \quad (18)$$

and all characteristic parameters of the PES chains, i.e.

$$n_{\text{gPES}}, n_{\text{uPES}}, g_{\text{PES}}, g_{\text{gPES}}, f_{\text{gPES}}, w_{\text{gPES}}, w_{\text{uPES}}$$

are given by the respective Eqs. (13)–(16) for the PS chains, after parameter exchanges $\psi \rightarrow \pi$ and $y \rightarrow c_D x$.

3.4. Graft copolymer PSgPES

The overall molecular weight of the graft copolymer PSgPES is approximately given by the molecular weights of the gPS and gPES subchains and the numbers of graft points per subchain

$$M_{\text{PSgPES}} \cong g_{\text{gPES}} M_{\text{gPS}} + g_{\text{gPS}} M_{\text{gPES}} \quad (19)$$

as long as g_{gPS} and g_{gPES} do not approach two where clustering and crosslinking take over. Since M_{gPS} and M_{gPES} are always higher than M_{uPS} and M_{uPES} (Eq. (14)), the molecular weight of PSgPES is always considerably higher than that of the ungrafted byproducts uPS and uPES. The internal composition of the copolymer is

$$i_{\text{PSgPES}} = \frac{m_{\text{gPES}}}{m_{\text{gPS}}} = \frac{f_{\text{gPES}}}{f_{\text{gPS}}} \frac{w}{1-w}. \quad (20)$$

3.5. Parameter evaluation

Those parameters of the product {PSgPES/uPS/uPES} that cannot be determined experimentally must be calculated. The calculations are based (i) on the parameters x , y , w and π , all of which are determined experimentally before a grafting-through run starts, and (ii) on the parameters c and ψ which must be extracted from the product. The calculation proceeds as follows:

$$\begin{array}{l} \underline{y} \xrightarrow{+M_{\text{uPS}} \rightarrow n_{\text{uPS}}} \psi \rightarrow \underline{g_{\text{gPS}}} \\ \rightarrow n_{\text{gPS}} \rightarrow \underline{M_{\text{gPS}}} \\ \rightarrow f_{\text{gPS}} \rightarrow \underline{w_{\text{gPS}}, w_{\text{uPS}}} \\ \\ \underline{M_{\text{PES}}} \rightarrow n_{\text{PES}} \rightarrow \pi \xrightarrow{+c_D x} n_{\text{gPES}} \rightarrow \underline{M_{\text{gPES}}} \xrightarrow{+n_{\text{gPS}} \cdot g_{\text{gPS}}} n_{\text{PSgPES}} \rightarrow \underline{M_{\text{PSgPES}}} \\ \xrightarrow{+c_D x} \underline{g_{\text{gPES}}} \\ \xrightarrow{+c_D x} \underline{f_{\text{gPES}}} \rightarrow \underline{w_{\text{gPES}}, w_{\text{uPES}}} \rightarrow \underline{i_{\text{PSgPES}}} \end{array} \quad (21)$$

D units and the number g of graft points per chain, where p_{nd} is given by Eq. (4). However, only n and g are interesting. Therefore, p_{ndg} can be reduced to a function p_{ng}

The parameters f_{gPS} and f_{gPES} can be measured, via extraction of the byproducts uPS and uPES, so theory and experiment can be compared. As in all graft copolymerisations,

Table 1
Graft products prepared by methods I–III from the polyesters PES₄₄ and PES₂₅; composition variables x , W and Y , conversion c , molecular weights M_h , grafts per chain g_i and grafting efficiencies f_i

PES _D	x (%) exp	M_{PES} (10^{-3}) exp	W (%) exp	Y (%) exp	c (%) exp	M_{uPS} (10^{-3}) exp	M_{gPS} (10^{-3}) exp	M_{uPES} (10^{-3}) exp	M_{gPES} (10^{-3}) exp	g_{gPS}	g_{gPES}	f_{gPS} (%) exp	f_{gPES} (%) exp
I	44	10	5	0.081	41	33	68	8	18	1.10	1.22	18	24
	25	9	5	0.116	42	48	105	7	16	1.22	1.28	33	28
	44	10	25	0.44	46	12	29	8	18	1.23	1.23	34	36
II	25	9	25	0.58	49	11	25	7	15	1.25	1.33	36	30
	44	10	5	0.081	20	96	225	9	19	1.33	1.11	44	79
III	44	19	5	0.116	20	110	260	8	17	1.59	1.14	61	80
	25	10	5	0.116	20	110	260	8	17	1.59	1.14	61	80

very many measured and calculated parameters are involved in Eq. (21). A transparent discussion is difficult. Therefore, the data will later be presented in schematic pictures (see Fig. 5) which are more descriptive than the tables and the text.

4. Synthesis

4.1. Copolyesters PES

Copolyesters PES₄₄ and PES₂₅ (Fig.3b) were prepared with contents of the double-bond units D of $x = 3\%$, $x = 7\%$, $x = 10\%$ and $x = 15\%$. The regular monomers of the polyester (Fig. 3(a)) and the double-bond monomers (Fig. 3(b)), the diacids in the form of their acid chlorides, were copolycondensed as described in Ref. [32]. Grafting test runs with these copolyesters revealed an optimum of x between insufficient grafting and crosslinking. Only the polyesters with the following optimum compositions will be discussed:

$$\text{PE}_{44} : \quad x = 7\% \quad \text{PE}_{25} : \quad x = 10\%.$$

The original polyester is glassy up to $T_g = 60^\circ\text{C}$ and liquid crystalline up to the clearing point $T_{\text{lc-i}} = 270^\circ\text{C}$. Incorporation of the double bond units raises both transitions slightly:

$$60 < T_g < 100^\circ\text{C}, < hsp \text{ sp} = 0.25 > 270 < T_{\text{ni}} < 300^\circ\text{C}.$$

Molecular weights were determined via solution viscometry, using the Mark–Houwink equation in Ref. [32]. All PES had similar molecular weights, $M_\eta \cong 20 \times 10^3$. The number average molecular weights M_n which enter the calculations (Eq. (21)) are listed in Table 1 ($M_n = M_{\text{PES}}$) as obtained from M_η with the approximation

$$M_{\text{PES}} \cong M_\eta/2. \quad (22)$$

Gel permeation chromatography was useless since PS calibration overestimated the molecular weights approximately by a factor of three, due to the rodlike shape of the polyesters PES.

MALDI spectroscopy revealed that the comonomer sequence in the PES chains is not entirely random. At low conversion c , 2,6-hexoxyterephthalic acid units were preferentially built into the oligomers. While this changes the local sequence order, the entire chains can still be treated as random copolymer chains.

4.2. Grafting-through

The grafting-through copolymerisation was carried out in feed solutions {S/PES}, isothermally with nitrogen protection, under three different conditions (Table 3) where BPO is dibenzoylperoxide and AIBN azobisisobutyronitrile.

I, III: Styrene was polymerized in a feed {S/PES} with a PES content of $W = 5\%$. The polymerisation was started

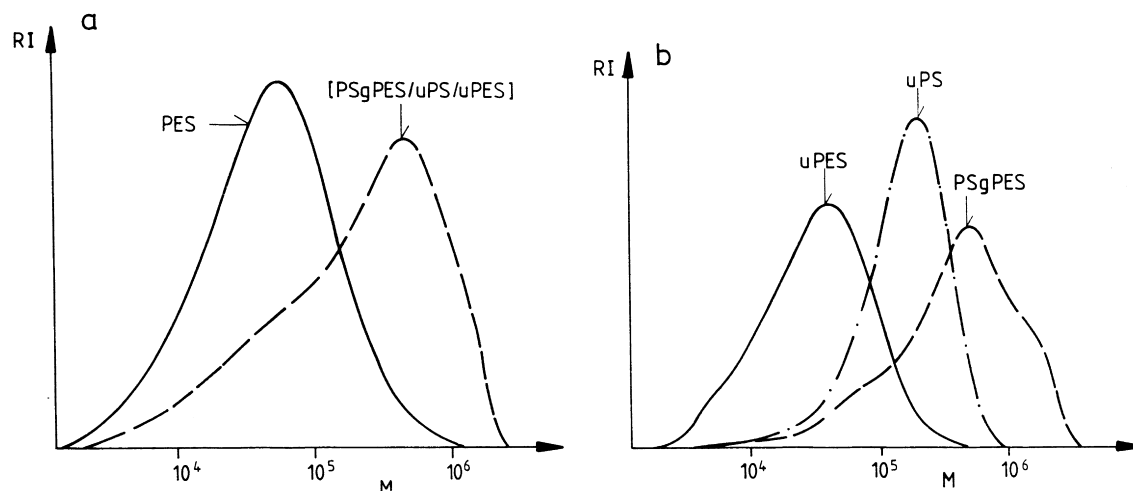


Fig. 4. GPC curves of (a) the original PES₂₅ and the raw graft product {PSgPES/uPS/uPES}, (b) the extracted components uPS, uPES and PSgPES.

Table 2

Graft products prepared by methods I–III from the polyesters PES₄₄ and PES₂₅ with the composition x : weight fractions w_i , total molecular weight M_{PSgPES} and composition i_{PSgPES} of the copolymer

	x (%)	w_{uPS} (%)	w_{gPS} (%)	w_{gPES} (%)	w_{uPES} (%)	M_{PSgPES} (%)	i_{PSgPES} (10^{-3})
I	7	72	16	4	8	100	0.25
	10	60	29	4	7	150	0.14
II	7	40	20	15	17	60	0.75
	10	38	22	17	23	50	0.77
III	7	44	35	4	17	280	0.11
	10	31	48	5	16	320	0.10

Table 3

	Medium	Initiator
I	Bulk	BPO
II	Toluene solution	BPO, AIBN
III	Bulk	No

either (I) by the initiator BPO (0.12 mol%) at 80°C, or (III) thermally, without an initiator at 100°C.

II: A feed {S/PES} with a higher PES content, $W = 25\%$, was diluted with toluene so PES had, in the resulting toluene/styrene solution, again a concentration of 5 wt.%. Styrene was polymerized with BPO or AIBN (0.6 mol%) at 80°C.

All systems turned turbid at fairly low conversion, which indicated phase separation. The polymerisation was stopped when the system got too viscous or started crosslinking. The product was precipitated with methanol; the byproducts uPS and uPES were extracted with cyclohexane and hexafluoroisopropanol. The extracted uPS and uPES fractions contained only the extracted component, according to IR tests, but the purity of the remaining PSgPES fraction could not be confirmed.

GPC curves are shown in Fig. 4. Grafting increases the

molecular weight considerably (Fig. 4(a)). The curves of the extracted product components of I and II runs yielded narrow peak widths indicating good extraction [32].¹ But a broad PSgPES peak in Fig. 4(b) indicates that, unfortunately, the extraction was in the particularly important III runs incomplete. The graft copolymer PSgPES was, after extraction, evidently still mixed with some uPS and uPES.

4.3. Mechanism

To confirm that the reaction mechanism is indeed *grafting-through* (Fig. 2) and not *grafting-from*, the initiator BPO was replaced in some runs by AIBN. Grafting-from polymerisations are readily started only by the aggressive oxy radicals of peroxides but not by the carbon radicals of azo compounds. However, AIBN did as well as BPO, indicating a mechanism of random copolymerisation as postulated for the grafting-through mechanism (Fig. 2(a)).

4.4. Products {PSgPES/uPS/uPES}

Graft copolymerisation runs of type I–III led to products that are characterized in Tables 1 and 2. For the calculations,

¹ Unfortunately, the GPC curves in Fig. 2 of Ref. [32] contain an error: “PS” points to the peak of the graft copolymer and vice versa.

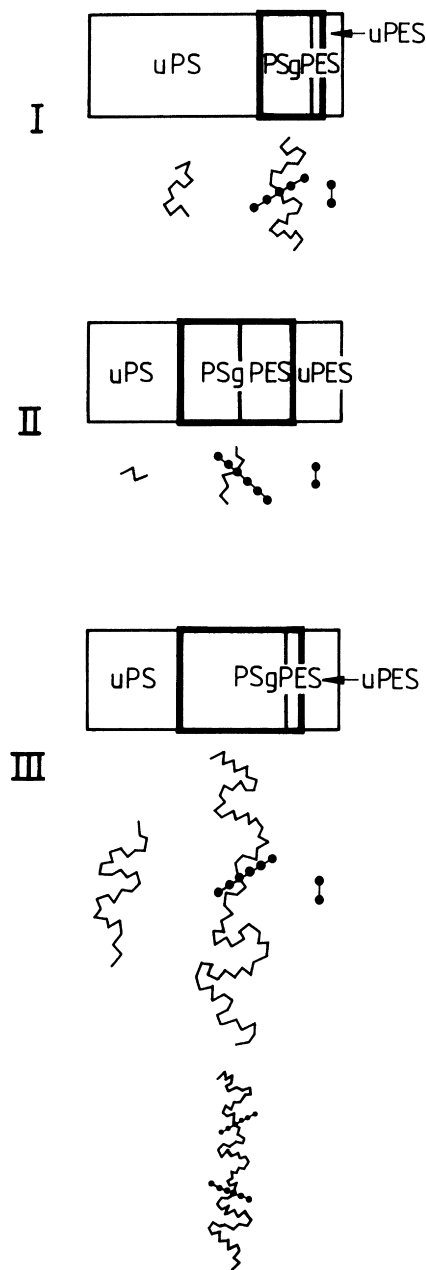


Fig. 5. Composition and architecture of raw products {PSgPES/uPS/uPES} prepared by the methods I–III: weight fractions of all components (uPS, gPS, gPES, uPES) as well as chain lengths of uPS, uPES and PSgPES (kinked: PS, pointed: PES; 1 kink or point corresponds to a molecular weight of 3×10^3).

the experimental parameters quoted in connection with Eq. 21 were used as well as, for the composition y (Eq. (9)) and the conversion c_D (Eq. (10)), the copolymerisation reactivity ratio

$$r_S = 3.$$

This value yielded a fair correspondence with the grafting efficiencies f_i of I and II runs, better than $r_S = 4$ (Eq. (8)). Unfortunately, r_S could not be measured directly. The composition of copolymers of styrene and the stilbene

derivatives (Fig. 3(b)) could not be determined, the two monomers being too similar.

Two effects that are common to all systems are observed in Table 1:

- *Molecular weights M_i* : grafted chains are 2–3 times longer than ungrafted chains.
- *Numbers of grafts g_i* : the majority of copolymer chains PSgPES has the X shaped architecture in Fig. 2(a), with only one chain gPS and gPES each ($1.10 < g_i < 1.59$). The gPS chain is always longer than the gPES chain.

The pictures in Fig. 5 illustrate the composition and architecture of the products {PSgPES/uPS/uPES} better than the Tables. The products from PES₄₄ and PES₂₅ being quite similar, average pictures were designed. The weight fractions of uPS, gPS, gPES, uPES and (emphasized) PSgPES are indicated as well as the molecular weights and the PSgPES architecture. All products consist of a longer-chained copolymer PSgPES and considerably shorter-chained byproducts uPS and uPES.

At the start of this study, copolymerizing {S/PES} feeds in the bulk with an initiator seemed the method of choice [32]. As indicated in Fig. 5(I), the obtained copolymer chains PSgPES are mostly X-shaped ($1.10 < g_i < 1.28$). But unfortunately, the PS chains are not long enough and the grafting efficiency is disappointing. The products are dominated by the homopolymer uPS ($w_{uPS} \cong 65\%$).

This was expected. Like most rigid-chain polymers, the polyesters PES suffer from poor solubility which, in styrene and toluene, is limited to

$$W_{\max} \cong 6\% (25^\circ\text{C}), \cong 11\% (80^\circ\text{C}). \quad (23)$$

The {S/PES} feeds contained $W = 5\%$ PES so the fraction y of D units in the copolymer $S_{1-y}D_y$ and the PES weight fraction w in the products {PSgPES/uPS/uPES} were too small (Eqs. (7) and (10)).

Alternatives to intensify grafting were increasing either (i) the PES content in the feed or (ii) the PS chain length in the product.

In the solution runs II, the PES content W was increased and so were y and w . Indeed, as shown in Fig. 5(II), less homopolymer uPS was obtained ($w_{uPS} \cong 40\%$). The PSgPES chains were symmetric, having gPES and gPS subchains of similar size. Unfortunately, the solution runs suffered from a severe problem: the PS chains got unacceptably short ($M_{uPS} \cong 13 \times 10^3$), due to the dilution effect of the solvent and, perhaps, some chain transfer (similarly short-chained graft copolymers were prepared in Ref. [34] via a macromonomer technique).

The thermally initiated bulk runs III were finally successful, as witnessed by Fig. 5(III). The fraction of the homopolymer uPS was reduced ($w_{uPS} \cong 40\%$) as in the solution runs. But the PS chains grew much longer because the concentration of initiating radicals is very low in thermally initiated PS systems. Molecular weights were obtained in the range of commercial PS ($M_{uPS} \cong 100 \times 10^3$). As a result

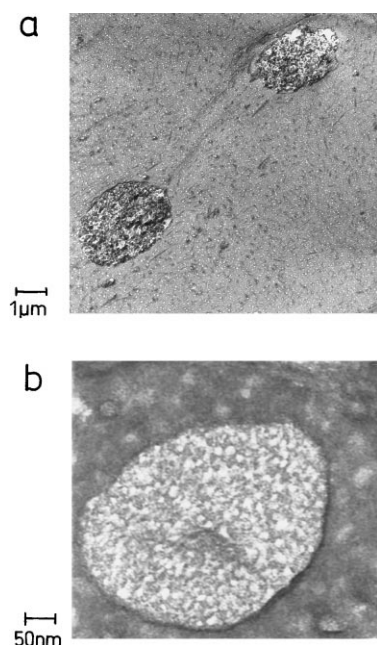


Fig. 6. Morphology of the product {PSgPES/uPS/uPES} from PES₂₅: (a) overview; (b) domain with a co-continuous substructure of PSgPES (gPS dark, gPES white).

of their length, a considerable part of the gPS chains connects two gPES grafts ($1.33 < g_{\text{gPS}} < 1.59$).

The morphology and mechanics of the satisfactory products of the bulk runs III are described in the next section.

The measured and calculated grafting efficiencies f_i agree fairly well, in the I and II runs, but not in the III runs (Table 1). The III runs yielded, experimentally, very high values of f_{gPS} and f_{gPES} . But these values are misleading. It is a general problem of graft copolymer products that seemingly good grafting can simply mean bad extraction of the byproducts. Indeed, the extraction of the long uPS and uPES chains was incomplete. This is reflected in the total molecular weight M_{PSgPES} of the PSgPES chains as reflected by GPC which is much smaller than predicted (Table 2). The GPC curve for PSgPES in Fig. 4(b) proves this point. It has a low-molecular-weight shoulder indicating that the copolymers PSgPES of III runs contain still some uPS and uPES.

5. Morphology and mechanics

The two products {PSgPES/uPS/uPES} of the thermally initiated III runs were studied morphologically and mechanically. Products from PES₄₄ and PES₂₅ behaved similarly. These products are built as follows (Fig. 5,III):

- The graft copolymer PSgPES and the homopolymer uPS are the major, the ungrafted polyester uPES is a minor component.
- The grafted chains gPS and gPES are much longer than the ungrafted chains uPS and uPES.

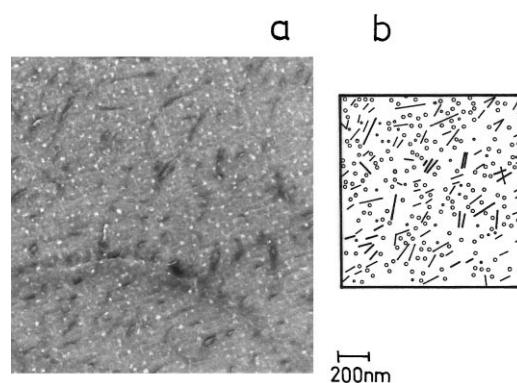


Fig. 7. Cylindric micelles of PSgPES in the gPS matrix (Fig.8a magnified): (a) electron micrograph with points and strands; (b) schematic copy of (a).

- The chains of the PSgPES copolymer are dominated by the long gPS chains.

For graft copolymer systems with this architecture, one would normally predict that the gPS and uPS chains are compatible so PSgPES should form micelles of the type in Fig. 1(c), filled with some uPES, in a matrix of uPS [24–27].

In first tests, films of the products and of the extracted copolymers PSgPES were cast from toluene. Film casting of polymer blends is informative because the solution is very fluid so the polymers can arrange according to their thermodynamic preferences. Unless the solvent is selective, the film morphologies reflect the minimum of the interface tension.

A representative film morphology is shown in Fig. 6(a). Disappointingly, it features large domains of PSgPES. The magnified domain in Fig. 6(b) reveals an extremely fine substructure of nanophases which is caused by intramolecular demixing of gPS and gPES in PSgPES. However, not all PSgPES chains are agglomerated in such domains. The matrix in Fig. 6(a) is filled with many tiny micelles which are magnified in Fig. 7(a). There are white points and black dashes. These are, in fact, the desired cylindric micelles. But Fig. 7 is a bit unsatisfactory, due to a known problem of electron microscopy on rodlike microphases in isotropic disorder: most cylinders are cut perpendicular to their axis and appear as points. Only a few cylinders are cut along their axis and appear as dashes. It is shown later more clearly that the graft copolymer forms really cylindric micelles.

The coexistence of domains and micelles in Fig. 7 suggests that some of the PSgPES chains are compatible with uPS but others, probably those with two gPES grafts on the gPS backbone, are not. This incompatibility is evidence for the pronounced reluctance of rods and coils to mix with each other.

After the tests with cast films, the PSgPES copolymers were characterized in oriented melts. A capillary rheometer and, with more success, a microextruder (DSM Research, 220°C, 120 rpm) were used. An oriented strand of polymer

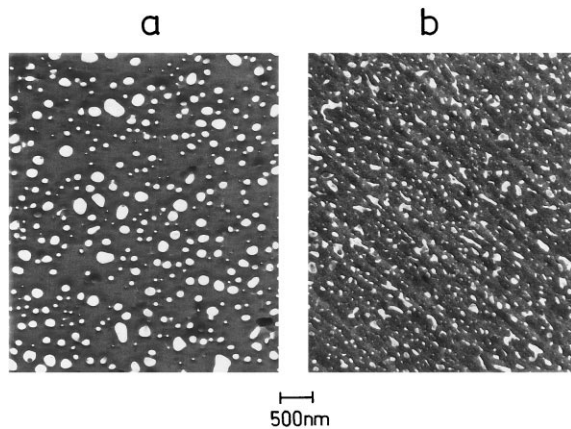


Fig. 8. Oriented melts, cut perpendicular to the extruded strand: circular microdomains in (a) the blend uPS/uPES and (b) the copolymer PSgPES from PES₂₅.

was obtained that was cut, for transmission electron microscopy, in its perpendicular and parallel direction. For comparison, a blend uPS/uPES was investigated as well.

Structures are shown in Figs. 8 and 9. Perpendicular cuts (Fig. 8) display circular microdomains which are larger for the blend and finer for PSgPES. Large domains as in the cast films (Fig. 6) were not found anymore.

The parallel cuts in Fig. 9 demonstrate that the domains in Fig. 8 are indeed oriented cylinders. Even the blend uPS/uPES exhibits in Fig. 9(a) strands of uPES which confirms that rigid-chain polyesters orient easily in flow fields. With related rod-coil blends, however with stiffer chains than PES, the concept of organic nanowhiskers was recently developed [18–20].

The strands of the graft copolymer PSgPES in Fig. 9(b) are much finer than those in Fig. 9(a). These micellar PSgPES strands are exactly what this study was aimed at. They are fibres on an almost molecular level.

As shown schematically in Fig. 10, the rigid gPES chains form, in the core of the cylindric micelles, an ordered LC like structure. A shell of gPS chains on the outside forms the

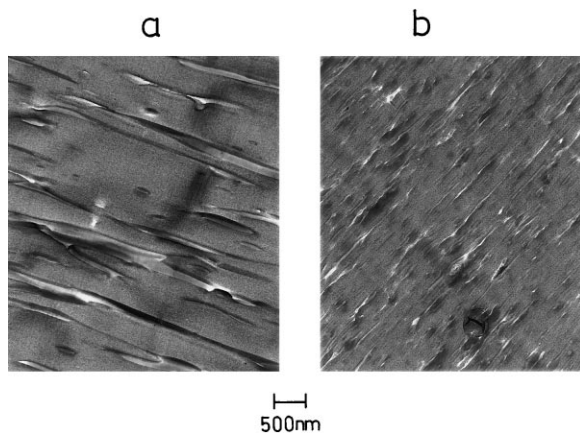


Fig. 9. Melts of Fig. 10, but cut parallel to the extruded strand: cylindric microstrands.

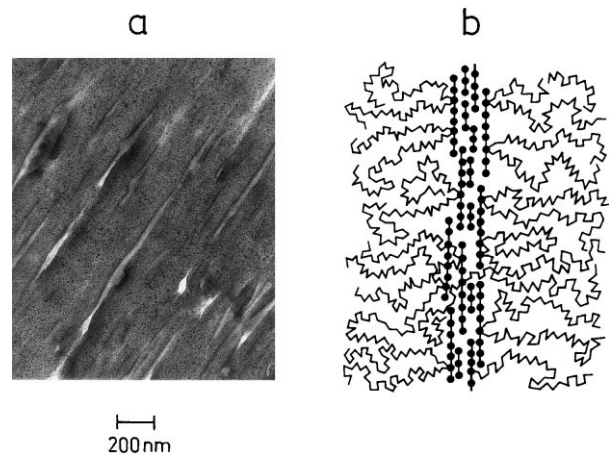


Fig. 10. Cylindric micelles of PSgPES: (a) electron micrograph of Fig. 11(b), magnified; (b) schematic picture.

matrix, together with uPS. At a cross-section diameter of ≈ 40 nm (Fig. 10(a)), the gPES strands are fairly thick. They must be filled with ungrafted uPES. Fig. 10 differs from Fig. 1(c) as far as the rigid chains are in PSgPES quite short and the flexible grafts very long. But the big length difference of gPS and gPES is geometrically not as obvious as one might have suspected because the long gPS chains are coiled while the short gPES chains are straight rods (Fig. 10(b)).

Unfortunately, the length of the cylindric micelles in Fig. 9(b) cannot be determined. The strands are certainly a few micrometers long but probably much longer. Again, this is a problem of electron microscopy: when one long cylinder bends a bit back and forth, leaving and re-entering the ultrathin section, it appears in the picture as a row of many short cylinders. Such rows are observed in Fig. 9(b).

The mechanical behaviour of the graft products {PSgPES/uPS/uPES} and a blend PS/PES of commercial PS and the original PES were examined in tensile tests. The tensile strength was not improved, probably due to a

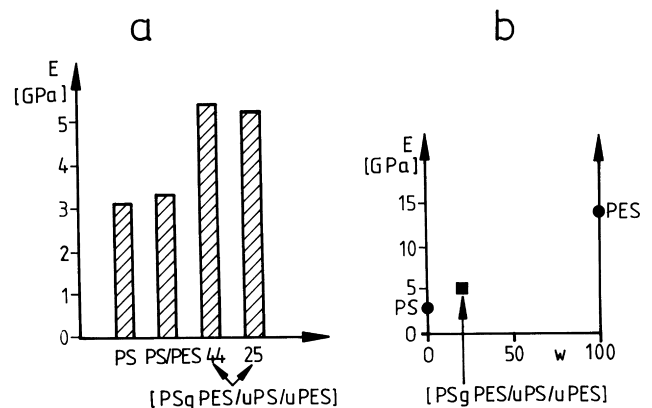


Fig. 11. Youngs modulus E: (a) PS, a blend PS/PES and the graft products {PSgPES/uPS/uPES} from PES₄₄ and PES₂₅; (b) presentation as a function of the PES weight fraction w.

still insufficient molecular weight of the uPS chains. The graft products were as brittle as commercial PS.

However, the stiffness was markedly enhanced (Fig. 11). As shown in Fig. 11(b), uPS has a modulus of $E = 3$ GPa, which is normal for thermoplastics, while the rigid-chain polyesters PES have a much higher modulus of $E = 14$ GPa. The modulus of the graft products is almost twice that of uPS while the blend uPS/uPES has little effect (Fig. 11(a)). This highlights the effect of grafting: to transfer the stiffness of PES to the PS matrix, the PES strands in Fig. 9 must be connected to the matrix, i.e. PS and PES must be coupled in a graft copolymer PSgPES.

The stiffness of the graft product {PSgPES/uPS/uPES} in Fig. 11 is satisfactory: as shown in Fig. 11(b), the modulus of the graft product is just the weighted average of those of PS and PES, meaning that PES transfers its stiffness optimally to the PS matrix as predicted by the Halpin–Tsai equation for fibres of infinite length [35].

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