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Compatibilization of blends of low density polyethylene and poly(vinyl chloride) by segmented EB(SAN-*block*-EB)$_n$ block copolymers

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Hydrogenated segmented poly[butadiene-*block*-((styrene-*co*-acrylonitrile)-*block*-butadiene)$_n$] block copolymers, which were developed by use of the polymeric iniferter technique, were tested for their compatibilizing capacities for (10/90) LDPE/PVC blends. The acrylonitrile content of the SAN blocks of the block copolymers was, as expected, found to be an extremely important factor for their miscibility with the poly(vinyl chloride) phase. When the SAN blocks of the block copolymers have the proper composition, they are excellent agents for the dispersion of the polyethylene phase in the blend into smaller domains. Addition of one percent of block copolymer proved to be sufficient to give a large improvement of the mechanical properties of the blend. These compatibilized blends showed toughnesses comparable to the virgin poly(vinyl chloride). Scanning electron micrographs showed improved adhesion between the dispersed polyethylene phase and the poly(vinyl chloride) matrix. Copyright © 1996 Elsevier Science Ltd.

(Keywords: LDPE/PVC blend; compatibilization; segmented EB(SAN-*block*-EB)$_n$ block copolymer)

INTRODUCTION

Polymer blends can in principle offer a wide variety of mechanical properties, by adjustment of the type and quantity of polymers in the mixture. However, because most polymers are immiscible, the blend components usually phase-separate into distinct, macroscopic domains, and consequently show poor mechanical properties, particularly regarding ductility.

It is well known that block or graft copolymers, containing blocks of the same chemical structure as the hetero phases in an incompatible binary polymer blend, are capable of compatibilizing these polymer mixtures[1–4]. When localized at the interface between the immiscible polymers, the block copolymers lower the interfacial tension, thereby dispersing the polymer blend into small domains due to reduced coalescence of the stabilized particles. Consequently, the blends may show improved ductility, because of enhanced force transfer between the different phases.

Nowadays, polymer blend consumption increases at a rate more than twice that of all plastics. Modification of impact strength, especially at low temperatures, dimensional stability and improvement of processability have been the prime goals of blending. Moreover, the necessity for recycling of plastic waste is a reason for the expanding academic and industrial interest in polymer blending.

In the present study, the compatibilizing effectiveness of newly developed segmented EB (styrene-*co*-acrylonitrile (SAN)-*block*-EB)$_n$ block copolymers [the EB(ethylene-*co*-butylene) blocks being hydrogenated polybutadiene] for low density polyethene (LDPE)/poly(vinyl chloride) (PVC) blends was investigated. Blends of PE and PVC are inherently brittle. During the past decade, there has been a lot of interest in compatibilization of these blends, for use as modified PVC resins, as well as for recycling purposes. Several techniques have been tested to improve the mechanical properties of PE/PVC blends, e.g. co-crosslinking methods[5–7], addition of a rubber or a chlorinated polyethylene as a solid phase dispersant[8], or addition of PE-*g*-PVC or PE-*g*-poly(methyl methacrylate) (PMMA) graft copolymers[9].

SAN copolymers are known to be miscible with a variety of homopolymers, such as PMMA[10–13], poly(carbonate) (PC)[14–15], PVC[16] and poly(ϵ-caprolactone)[17] (within a certain composition range of the SAN copolymer). Therefore, block copolymers of (hydrogenated) polybutadiene (PB) and SAN could have great potential as (multifunctional) compatibilizers for polyolefins with the above mentioned polymers. So far, random copolymer blocks have only been incorporated into a copolymer by grafting them on a polymer chain. These graft copolymers proved to be efficient compatibilizing agents for many different incompatible polymer mixtures[18].

Theoretically, it might be expected that this type of block copolymer, in which one block consists of a random copolymer, is more effective than a simple block

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copolymer. This can be understood by looking at the interactions that exist in a compatibilized blend. First, let us consider the situation of a mixture of homopolymers A and B compatibilized by a block copolymer A-*block*-B. The Flory interaction parameter χ_{AA}, which describes the interactions between the homopolymer A and the A-block of the block copolymer at the interface is obviously zero. Of course, the same applies for the B homopolymer and B-block. A different situation arises taking the same system with a block copolymer consisting of polymer blocks that are chemically different from the homopolymers but are selectively miscible with them. In that case the χ-parameters involved may be negative, reducing the interfacial tension even more, with a corresponding improved compatibilization. Typically, this kind of situation can best be realized by taking blocks consisting of random copolymers[19]. This offers the additional advantage that the interaction between the homopolymer phases and the random copolymer blocks can be tuned by selecting the appropriate copolymer compositions. This observation is the main motivation behind our efforts described here.

As a concrete example we look at a PE/PVC blend, compatibilized by a block copolymer PE-*block*-SAN, where the SAN-block consists of a random copolymer poly(styrene$_y$-*co*-acrylonitrile$_{1-y}$). This system, which is effectively a combination of the common P(A)/P(B)/P(A-*block*-B) case and the most general P(A)/P(B)/P(C-*block*-D) case, will be considered in detail in this paper. The interactions at the interface between the SAN random copolymer block and the PVC can be described[19] by :

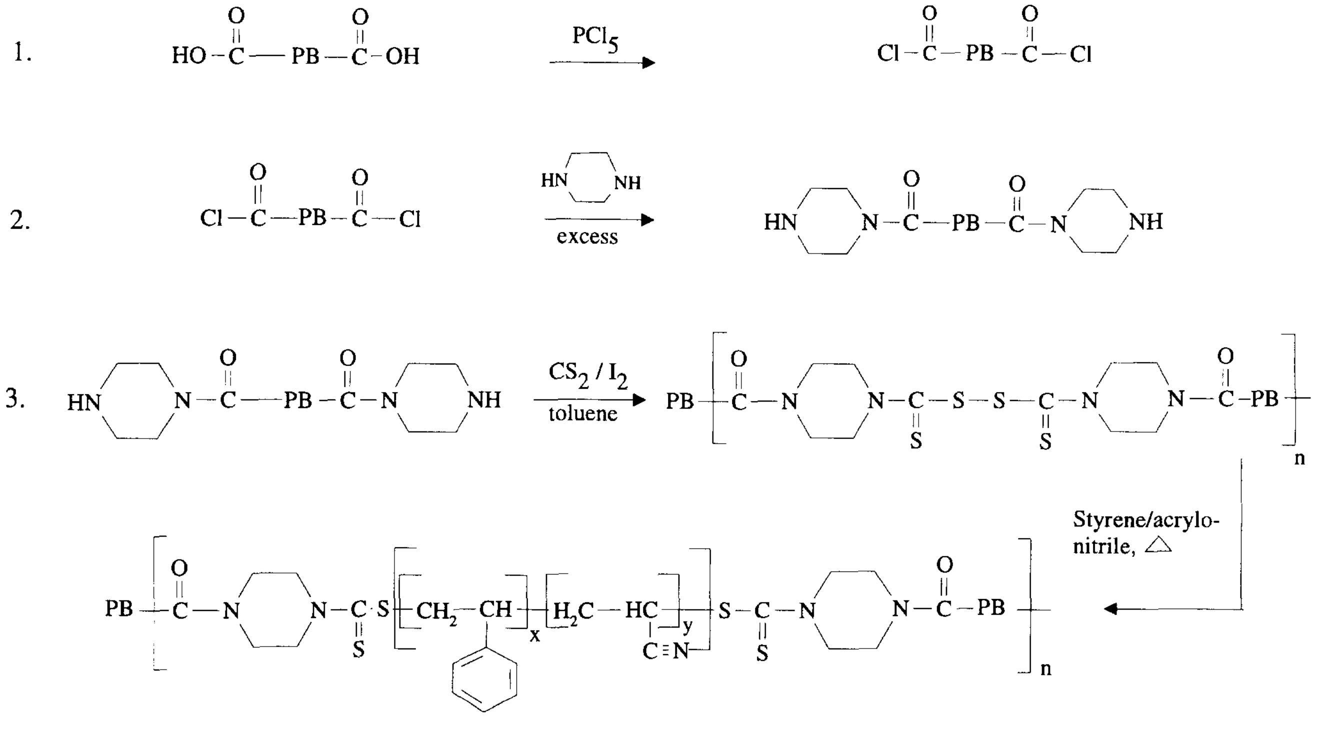
$$\chi_{SAN,PVC} = y\chi_{VC,St} + (1-y)\chi_{VC,AN} - y(1-y)\chi_{St,AN} \quad (1)$$

where χ is the Flory–Huggins interaction parameter and VC, St and AN denote vinyl chloride, styrene and acrylonitrile. Because SAN is a copolymer, in which a large intramolecular repulsion between the styrene and acrylonitrile segments exists ($\chi_{St,AN} \cong 0.8$) due to the large difference in cohesive energy density or solubility parameter values between polystyrene and poly(acrylonitrile), the effective interaction parameter $\chi_{SAN,PVC}$ may even become negative for certain copolymer compositions. In that case the term $y(1-y)\chi_{St,AN}$ outweighs the other terms; the interactions between vinyl chloride and styrene as well as acrylonitrile are more favourable than the intramolecular interactions between styrene and acrylonitrile. This phenomenon is often referred to as the intramolecular repulsion effect[19–21]. However, most of the effect is, as noted by various authors[21–23], merely due to cosolvency.

Since the easiest and most effective way of synthesizing random copolymers is by free radical polymerization, we used an iniferter technique for the preparation of the segmented block copolymers of PB and SAN. The term 'iniferter' is used for free radical initiators with simultaneous chain transfer and terminating properties, providing a pseudo-living polymerization. Segmented block copolymers of PB and SAN were prepared by copolymerization of styrene and acrylonitrile with a synthesized polybutadiene-iniferter. The synthesis of these and related block copolymers, which is presented in *Scheme 1*, was described by us in previous publications[24,25]. Here the thiuram disulfides in the main chain form the iniferter groups, and the copolymerization with this polymeric iniferter can be considered as a polymerization by insertion of styrene and acrylonitrile between the disulfide linkage.

In this study, the synthesized segmented poly[butadiene-((styrene-*co*-acrylonitrile)-*block*-butadiene)$_n$] block copolymers were hydrogenated and tested as a compatibilizer for (10/90) LDPE/PVC blends.

We studied the influence of the addition of various amounts of PB-(SAN-*block*-PB)$_n$ block copolymer on



Scheme 1 Synthesis of segmented PB(SAN-*block*-PB)$_n$ block copolymers via a polymeric iniferter

the mechanical properties and morphology of this blend. Furthermore we looked at the effect of the composition of the SAN blocks of these block copolymers on their compatibilizing capacities. The SAN composition is a key factor in the miscibility behaviour of SAN and PVC, as explained above.

EXPERIMENTAL

*Synthesis of segmented EB(SAN-*block*-EB)$_n$ block copolymers*

The synthesis of the polybutadiene iniferter and corresponding block copolymers was performed as described previously[24].

Hydrogenation reactions of the segmented block copolymers were carried out in a three-necked flask, equipped with a reflux condenser, under nitrogen atmosphere. The segmented PB(SAN-*block*-PB)$_n$ block copolymer was placed in the vessel and dissolved in dry toluene (approximately 1 g per 50 ml toluene). Upon complete dissolution of the polymer, *p*-toluenesulfonyl hydrazide (as the diimide producing species) and tri-*n*-propyl amine (to avoid protonation of the unsaturated polymer and consequent addition of the *p*-toluenesulfinate anion) were added to the solution (both in a molar ratio of 2 per site of unsaturation in the block copolymer). The TSH is only slightly soluble in toluene at room temperature, but dissolves completely upon heating. The system was heated to reflux (110°C) for 2 h. The polymer was isolated by washing the toluene solution twice with 100 ml deionized water, and precipitating the polymer into methanol. The recovered polymer was dried *in vacuo*. Hydrogenation efficiency was checked by ^{1}H nuclear magnetic resonance (n.m.r.) and found to be > 99% in all cases.

Blend preparation by melt mixing

Blends of PVC (PVC-LOX; Wavin KLS Hardenberg, The Netherlands) and LDPE (Stamylan LD 2100 TN00; DSM Geleen, The Netherlands) were prepared by mixing the components for 5 min at a chosen temperature and a rotation speed of 75 rpm in a co-rotating twin-screw micro-extruder. After processing, the blend was immediately cooled into cold water.

Furthermore, for comparison, blending of PVC (Lucovyl RB 8010) with LDPE (StamylanLD 1808 A; DSM Geleen, The Netherlands) was performed in a Brabender Plasticorder at the chosen temperature for 5 min at a rotation speed of 100 rpm. Di-*n*-octyltinbis (isooctylthioglycolaat) (Irgastab Mok 17A; 2.5 wt%) was added to the PVC as a stabilizer.

*Preparation of blends of PB(SAN-*block*-PB)$_n$ block copolymer and PVC by precipitation from tetrahydrofuran solution*

A mixture of a (non hydrogenated) segmented PB(SAN-*block*-PB)$_n$ block copolymer and PVC (Lucovyl RB 8010) was dissolved in tetrahydrofuran (THF, 2.5% solution). The SAN/PVC ratio was kept at 50/50 in all cases. The THF solution was poured into a 10-fold excess of methanol. The material was collected and dried for 3 days in a vacuum oven at 50°C.

Blend characterization

Tensile specimens (ASTM D1708) of the obtained blends were prepared by compression moulding at 180 or 190°C. After a preheating time of 4 min and subsequential thorough degassing of the mixture, the specimens were compression moulded for 3 min and finally quenched into cold water. The tensile properties were measured in an Instron tensile tester at room temperature, using a crosshead speed of 10 mm min^{-1}. The results were averaged from 4 tests per sample.

Differential scanning calorimetry (d.s.c.) was performed on a Perkin Elmer DSC-7 apparatus, using a scanning speed of 10°C min^{-1}.

The morphology of the blends was studied by carrying out scanning electron microscopy (SEM) on cryo-fractured specimens, using a Jeol 6320 F Field Emission SEM.

RESULTS AND DISCUSSION

Block copolymers used in this study

In this work we studied the compatibilizing behaviour of EB(SAN-*block*-EB)$_n$ block copolymers with different compositions and molecular weights. These block copolymers were prepared by synthesizing a polybutadiene-iniferter, followed by thermal copolymerization of the required amounts of styrene and acrylonitrile, using the polymeric iniferter as the initiating species (see *Scheme 1*). The characteristics of the synthesis of this type of block copolymer were described previously[24].

The hydrogenation of the PB blocks was performed by a diimide reduction technique[26–27], using toluene sulfone hydrazide as the diimide generating species. Hydrogenation efficiency was checked by n.m.r. and found to be practically quantitative (≥ 99%). In *Table 1* the characteristics and code names of the segmented block copolymers are listed. The molecular weight of the polybutadiene blocks is the same for all block copolymers, since this is predetermined in their synthesis. The most important difference between these block copolymers is the acrylonitrile content of their SAN blocks, because this will determine their miscibility with the PVC phase.

Table 1 Characteristics of segmented EB(SAN-*block*-EB)$_n$ block copolymers used in this study

Code	F_{AN} in SAN (mol%)	F_{AN} in SAN (wt%)	M_n block copolymer ($\times 10^{-4}$)	Average number of alternating blocks in copolymer	%SAN in block copolymer	PB block length ($\times 10^{-4}$)	SAN block length ($\times 10^{-4}$)
EBSAN-5	9.4	5.0	17.7	4.8	82	1.1	6.6
EBSAN-11	19.5	11.0	15.5	7.0	80	1.1	5.5
EBSAN-17	28.5	16.9	15.9	6.1	77	1.1	4.8
EBSAN-20	33.3	20.3	21.1	7.2	74	1.1	3.8

Table 2 Mechanical properties of materials used in this study

Material	Trade name	E_{young} (GPa)	σ_{yield} (MPa)	σ_{break} (MPa)	ϵ_{yield} (%)	ϵ_{break} (%)	Toughness (MPa)
PVC	PVC-LOX	1.7	55.0	28.2	6.5	32	13.7
	Lucovyl RB 8010	1.6	54.0	36.7	6.2	37.1	14.9
LDPE	Stamylan LD 1808 A/ LD 2100 TN00	0.1	9.4	11.6	16	450	47.0

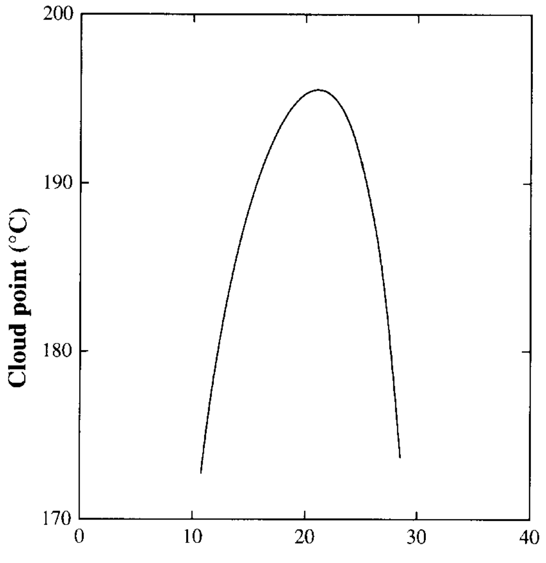


Figure 1 Miscibility window for 40/60 PVC/SAN blend (from ref. 16)

In *Figure 1* the miscibility behaviour of a 40/60 SAN/PVC blend is schematically indicated as a function of acrylonitrile content. It is based on miscibility studies by Kim *et al.*[16]. They showed, that SAN copolymers form miscible blends with PVC for 11.5–26 wt% AN. *Figure 1* shows that an optimum in miscibility between SAN and PVC exists when the SAN copolymer contains approximately 20 wt% acrylonitrile. So, for the hydrogenated segmented EB(SAN-*block*-EB)$_n$ block copolymers, we expect the block copolymer with 20 wt% acrylonitrile in the SAN blocks to give the best results. *Figure 1* in fact only shows the cloud point curve for a specific (i.e. 40/60 w/w%) blend. The cloud points of blends, containing a small amount of either PVC or SAN, are considerably higher. Since in our case, we use only small concentrations of the EB(SAN-*block*-EB)$_n$ block copolymers with respect to the PVC, we assume that the melt processing temperatures used by us are well below the cloud points for the PVC and the SAN blocks of the block copolymers (provided that the composition of the SAN blocks is well within the limits of the miscibility window).

(10/90) LDPE/PVC blends processed in a micro-extruder

For the blends, which were processed in a co-rotating twin-screw micro-extruder, we used PVC-LOX (Wavin KLS Hardenberg, The Netherlands), which is a commercial PVC. No stabilizing agent was added to this material. The LDPE used was Stamylan LD 2100 TN00 (DSM Geleen, The Netherlands, meltflow index 0.3 dg min^{-1}). The processing temperature was 200°C for every blend, while the compression moulding temperature was 180 or 190°C. The properties and trade names of all polymers used are listed in *Table 2*.

Table 3 shows the mechanical properties of the (10/90) LFPE/PVC blends, compatibilized with various segmented EB(SAN-*block*-EB)$_n$ block copolymers, added in amounts varying from 0.2 to 10 wt%. The (10/90) PE/PVC blend exhibited poor properties compared to those of the pure polymers, especially regarding elongation at break of the material. First of all, it is apparent from *Table 3* that, apart from blending conditions, the compression moulding temperature has a substantial effect on the mechanical properties of the blends. The best results were obtained with specimens compression moulded at 190°C. Apparently a compression moulding temperature of 180°C is too low to ensure a good melt flow of the material. Therefore we will discuss from here on only blends which were compression moulded at 190°C.

The mechanical properties of the materials, which were compression moulded at 190°C, demonstrate very clearly the effect of the acrylonitrile content of the SAN blocks in the block copolymers on their compatibilizing effectivity. While addition of EBSAN-5 (block copolymer with 5 wt% acrylonitrile in the SAN blocks) to the LDPE/PVC blend only leads to deterioration of its mechanical properties, addition of EBSAN-11 already gives approximately the same properties as obtained for the uncompatibilized blend. However, there is a remarkable improvement in properties of the LDPE/PVC blend when a small amount of EBSAN-17 or EBSAN-20 is added. These results are consistent with the earlier mentioned publication of Kim *et al.* on the miscibility behaviour of SAN copolymers with PVC[16], which show that there is an optimum in miscibility between these polymers when the SAN copolymer contains 20 wt% acrylonitrile (see *Figure 1*). As can be seen in *Table 3*, addition of EBSAN-5 block copolymer to the LDPE/PVC blend only worsens the blend properties. Presumably a large part of the EBSAN-5 block copolymer is lost in the PVC bulk phase, because both the polybutadiene blocks and the SAN blocks containing 5% acrylonitrile are immiscible with PVC. The part of the block copolymer which reaches the interface will not have any favourable effect on the interfacial adhesion because of immiscibility of the SAN-5 blocks of the block copolymer with the PVC. Since SAN-11 is also just outside the limit of the miscibility window, addition of EBSAN-11 does not improve the mechanical properties of the blend as well. However, EBSAN-17 and especially EBSAN-20, which possess SAN blocks of the proper

Table 3 Influence of addition of segmented EB(SAN-*block*-EB)$_n$ block copolymers on mechanical properties of a LDPE/PVC^a (10/90) blend, mixed in a micro-extruder at 200°C for 5 min

Compatibilizer	Compatibilizer content (%)	Compression moulding temperature (°C)	E_{young} (GPa)	σ_{yield} (MPa)	σ_{break} (MPa)	ϵ_{yield} (%)	ϵ_{break} (%)	Toughness (MPa)
–	–	180	1.5	–	33.1	–	3.8	0.8
EBSAN-17	0.2	180	1.4	44.8	41.5	6.8	7.7	2.5
EBSAN-17	0.5	180	1.5	–	46.3	–	5.7	1.7
EBSAN-17	1.0	180	1.7	46.2	32.1	6.8	12.7	4.5
EBSAN-17	5.0	180	1.4	41.1	32.3	5.7	8.9	2.9
EBSAN-20	0.2	180	1.5	–	43.4	–	6.1	1.5
EBSAN-20	0.5	180	1.3	–	37.1	–	7.4	1.8
EBSAN-20	1.0	180	1.2	–	40.0	–	4.6	1.6
EBSAN-20	5.0	180	1.4	–	30.2	–	3.4	0.7
–	–	190	1.3	–	40.3	–	5.5	1.5
EBSAN-5	5.0	190	1.2	–	26.4	–	3.0	0.5
EBSAN-5	10.0	190	1.2	–	20.9	–	1.8	0.2
EBSAN-11	5.0	190	1.2	–	32.1	–	5.0	1.1
EBSAN-11	10.0	190	1.2	–	38.2	–	6.3	1.5
EBSAN-17	0.2	190	1.4	44.8	28.8	5.6	11.5	3.7
EBSAN-17	0.5	190	1.5	44.2	35.7	5.0	16.0	5.7
EBSAN-17	1.0	190	1.3	43.3	30.9	6.4	20.7	6.8
EBSAN-17	5.0	190	1.4	44.1	33.7	5.8	22.0	7.8
EBSAN-20	0.2	190	1.4	45.8	28.6	5.9	12.2	4.9
EBSAN-20	1.0	190	1.4	46.8	35.9	5.8	29.1	10.7

^{a} LDPE: Stamylan 2100 TN00; PVC: PVC-LOX (Wavin KLS Hardenberg, The Netherlands)

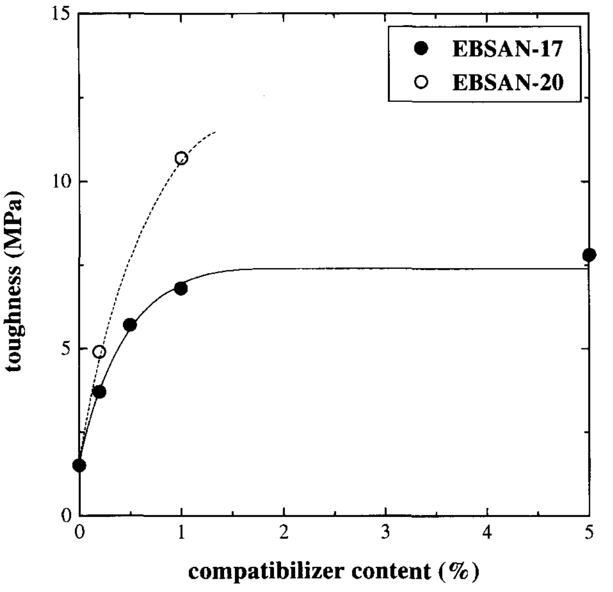


Figure 2 Dependence of toughness of 10/90 LDPE/PVC blend on compatibilizer concentration for EBSAN-17 and EBSAN-20

composition to ensure miscibility with the PVC phase, prove to be very efficient compatibilizers for these LDPE/PVC blends.

Figure 2 shows the dependence of the blend toughness on the content of added block copolymer EBSAN-17 and EBSAN-20 in the blend. It is obvious that the toughness of the blend reaches a constant level at a relatively low concentration of EBSAN-17 (between 1 and 2 wt%). A possible explanation is that addition of approximately 1 wt% of block copolymer already saturates the interface, and addition of more block copolymer has no additional compatibilizing effect. Whether this 'excess' amount of block copolymer will form micelles or mesophases at the interface, and what effect this will have on the blend properties, is hard to predict. However, since 1% or less of the segmented block copolymer is enough to achieve a significant improvement in blend toughness, it is reasonable to assume that only a small part of the block copolymer is lost in bulk phases and the majority migrates to the PE–PVC interface.

Furthermore, in a theoretical analysis by Noolandi[28], it is argued that, because of its structure, less multiblock copolymer than diblock copolymer is lost in bulk phases as micelles and mesophases. Also, he argues that a diblock copolymer is oriented perpendicularly to the interface plane, while a multiblock copolymer will lie in the plane of the interface. Therefore, a multiblock copolymer molecule covers a larger part of the interfacial surface than a diblock copolymer. These arguments are in line with the surprisingly small amount of segmented block copolymer that is needed to compatibilize the 10/90 LDPE/PVC blend.

As mentioned above, the most effective block copolymer for this blend is EBSAN-20. In *Figure 3* the stress–strain behaviour of the pure PVC, a 10/90 LDPE/PVC blend and a 10/90 LDPE/PVC blend, compatibilized by 1% EBSAN-20 is shown. The compatibilized blend has a stress–strain behaviour comparable to the pure PVC, only with a slightly lower tensile stress, which of course is inevitable because of the very much lower tensile stress of PE, compared to PVC. Addition of 1% of block copolymer EBSAN-20 leads to an increase of the

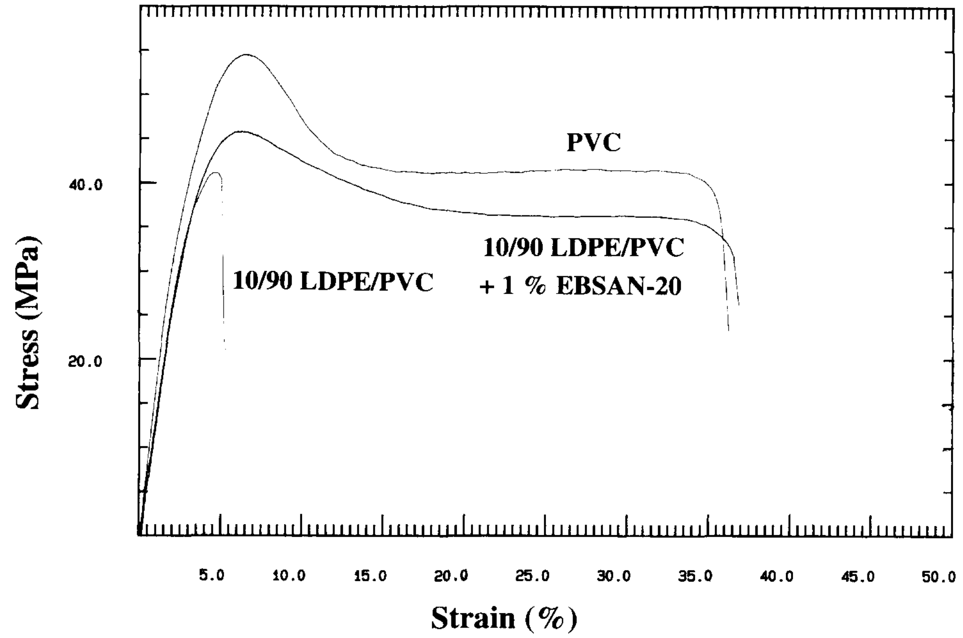


Figure 3 Influence of addition of 1% EBSAN-20 on stress–strain behaviour of a 10/90 LDPE/PVC blend

elongation at break of the blend from 5.5% for the virgin blend to approximately 30% for the compatibilized blend. Furthermore, the toughness of the compatibilized blend, which is obtained from the area under the stress–strain curve and thus is a measure for the total amount of energy dissipated during deformation, is improved dramatically to 10.7 MPa, which is more than seven times as much as the blend toughness without block copolymer.

Moreover, all of the blends (compression moulded at 190°C) which were compatibilized by EBSAN-17 or EBSAN-20, did not break before the yield point was reached. This means that there must be energy dissipation due to micromechanical mechanisms like crazing and shear yielding in the blend. Macroscopically, these mechanisms were indicated by a stress whitening of the fracture surface. Because the compatibilized blends yield, their maximum tensile strength is also slightly improved.

To study the particle sizes in the compatibilized blends, scanning electron micrography was performed. SEMs (see *Figures 4–8*) of cryo-fractured specimens after compression moulding at 190°C clearly show a much finer morphology of the blend after addition of block copolymer EBSAN-17. Here the dispersed phase consists of LDPE, while the matrix is formed by PVC. *Figures 4–7* show the development of the blend morphology as a result of an increasing concentration of added block copolymer EBSAN-17. The micrograph of the uncompatibilized 10/90 LDPE/PVC blend (*Figure 4*) shows rather large PE lumps, while there is an enormous variation in particle size and shape. Clearly, the PE particle size is reduced significantly by the addition of small amounts of block copolymer EBSAN-17 and there is a much smaller distribution in PE particle size. Even the addition of 0.2 wt% of EBSAN-17 already disperses the morphology into somewhat smaller domains with significantly smaller particle size distribution (*Figure 5*). The dispersion of the morphology continues with addition of more block copolymer EBSAN-17. The dispersion of the blend morphology is even more pronounced, when 1 wt% of EBSAN-20 is added to the blend (*Figure 8*). In this compatibilized blend the average polyethylene particle diameter is as small as 0.5 μm,

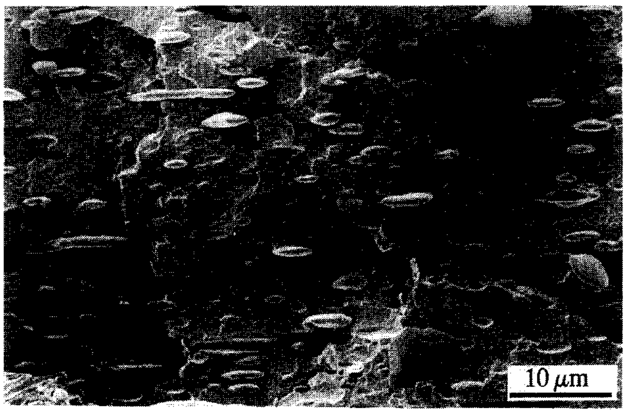


Figure 4 SEM of a cryo-fractured 10/90 LDPE/PVC blend (processed in a micro-extruder)

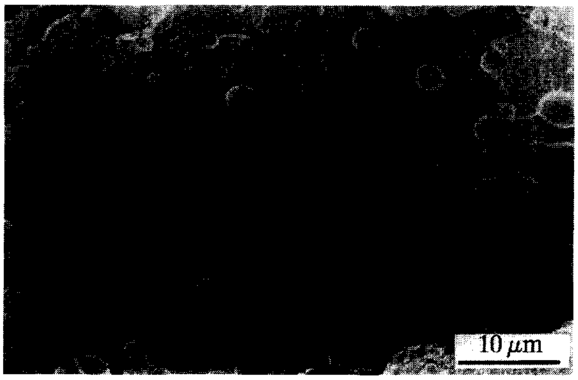


Figure 5 SEM of a cryo-fractured 10/90 LDPE/PVC blend, compatibilized by 0.2 wt% of EBSAN-17 (processed in a micro-extruder)

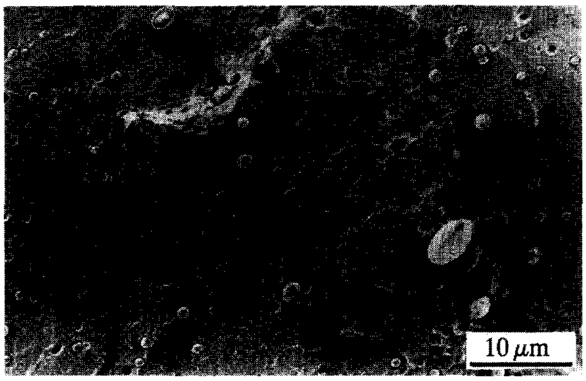


Figure 6 SEM of a cryo-fractured 10/90 LDPE/PVC blend, compatibilized by 0.5 wt% of EBSAN-17 (processed in a micro-extruder)

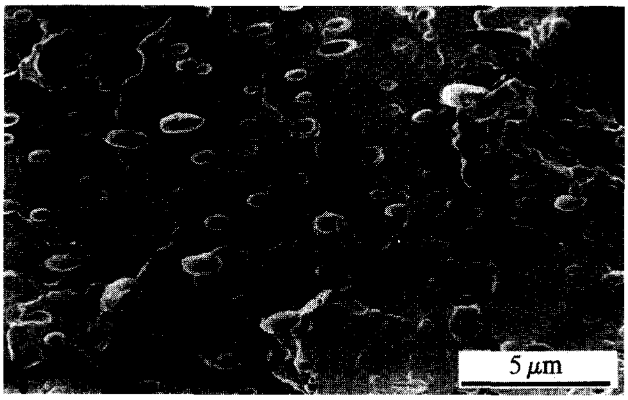


Figure 7 SEM of a cryo-fractured 10/90 LDPE/PVC blend, compatibilized by 1.0 wt% of EBSAN-17 (processed in a micro-extruder)

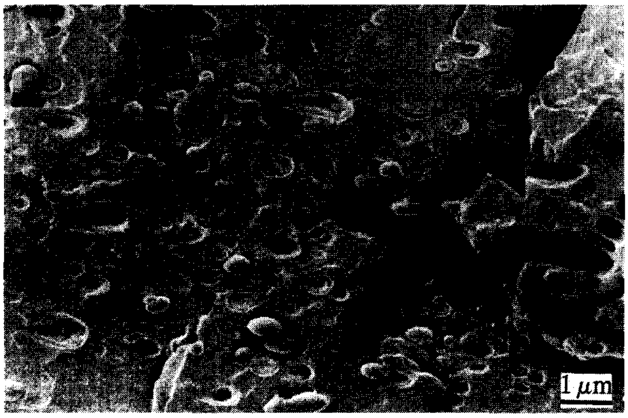


Figure 8 SEM of a cryo-fractured 10/90 LDPE/PVC blend, compatibilized by 1.0 wt% of EBSAN-20 (processed in a micro-extruder)

Table 4 Estimated average PE particle diameters of (10/90) LDPE/PVC blends, compatibilized by various concentrations of block copolymers EBSAN-17 and EBSAN-20

Added block copolymer	Block copolymer concentration (wt%)	Average PE particle diameter (μm)
–	0	2.5
EBSAN-17	0.2	2.4
EBSAN-17	0.5	1.7
EBSAN-17	1.0	0.9
EBSAN-20	1.0	0.5

while the particle size distribution is very small. These results are consistent with the considerable improvement in polymer blend properties after addition of EBSAN-20. In *Table 4* the estimated average PE particle diameters are listed for the compatibilized 10/90 LDPE/PVC blends. In the case of the uncompatibilized (10/90) LDPE/PVC blend, which shows elongated PE particles, the average particle volume was determined, after which the average PE particle diameter for a symmetrical sphere was calculated.

(10/90) LDPE/PVC blends processed in a Brabender Plasticorder

Because it is obvious from the experiments performed in the microextruder that addition of more than 1% block copolymer hardly gives a further improvement of mechanical properties of the (10/90) LDPE/PVC blend, further blending experiments in a Brabender Plasticorder were performed with blends compatibilized by 1% of segmented EB(SAN-*block*-EB)$_n$ block copolymer at different processing conditions. The PVC (Lucovyl RB 8010; $M_n = 36\,000$, $M_w = 75\,000$) is of a different type than the one used in the previous experiments in the micro-extruder, but has similar mechanical properties (see *Table 2*). The LDPE in this case was Stamylan LD 1808A (meltflow index 7.5 dg min^{-1}). Stabilizer (2.5 wt%) was added to the PVC to avoid thermal degradation of the polymer.

In *Table 5* the results of compatibilized 10/90 LDPE/PVC blends, mixed at 180 and 200°C in a Brabender Plasticorder are shown. Because, as mentioned before, blends compression moulded at 190°C show much better properties than those compression moulded at 180°C, a compression moulding temperature of 190°C was used for all blends.

The uncompatibilized 10/90 LDPE/PVC blend, which was processed in a Brabender Plasticorder, showed better properties than the corresponding blend processed in a micro-extruder. This is not believed to be the result of an improved mixing process, but rather due to an improved matching of the blend component viscosities in this material.

Blends which were processed at 180°C had slightly better mechanical properties than those processed at 200°C. Furthermore, the same trends are observed (*Table 5*) as previously for the experiments performed in a micro-extruder. As observed for the blends processed in a micro-extruder, the addition of EBSAN-5 or EBSAN-11 (1 wt%) only gave a deterioration of the blend properties, while the addition of 1 wt% EBSAN-17 or EBSAN-20 to the 10/90 LDPE/PVC improved the mechanical properties significantly. The elongation at break of the blend, processed at 180°C and compatibilized by 1% of EBSAN-20, was found to be even higher than observed for the virgin PVC. These compatibilized blends showed a significant stress whitening at the entire surface of the tensile specimens.

To investigate the difference in deformation mechanisms between an uncompatibilized 10/90 LDPE/PVC blend and a blend compatibilized by 1 wt% EBSAN-20, SEM was performed on the fracture surface of selected tensile specimens (*Figures 9* and *10*). The SEM of the uncompatibilized blend (*Figure 9*) clearly shows that no deformation of the PE phase has taken place. Only the PVC phase is deformed, while the undeformed PE

Table 5 Influence of segmented EB(SAN-*block*-EB)$_n$ block copolymers on the mechanical properties of LDPE/PVC[a] (10/90) blend, mixed in a Brabender Plasticorder for 5 min and compression moulded at 190°C

Compatibilizer	Compatibilizer content	Blending temperature (°C)	E_{young} (GPa)	σ_{yield} (MPa)	σ_{break} (MPa)	ϵ_{yield} (%)	ϵ_{break} (%)	Toughness (MPa)
-	0	180	1.3	37.8	29.9	5.9	16.4	5.0
EBSAN-5	1.0	180	1.3	39.0	28.7	6.1	12.7	3.8
EBSAN-11	1.0	180	1.2	36.9	27.8	5.7	13.5	3.7
EBSAN-17	1.0	180	1.3	39.9	33.1	5.9	22.0	7.2
EBSAN-20	1.0	180	1.4	46.4	35.7	6.3	43.6	14.6
–	0	200	1.3	36.2	21.3	5.0	13.4	4.5
EBSAN-17	1.0	200	1.3	39.0	32.5	6.3	24.5	6.2
EBSAN-20	1.0	200	1.2	41.7	34.1	7.2	20.2	6.6

[a] LDPE: Stamylan 1808A; PVC: Lucovyl RB 8010 (2.5% Irgastab was added as a stabilizer)

Figure 9 SEM of fracture surface of a 10/90 LDPE/PVC blend (processed in a Brabender Plasticorder) after tensile test

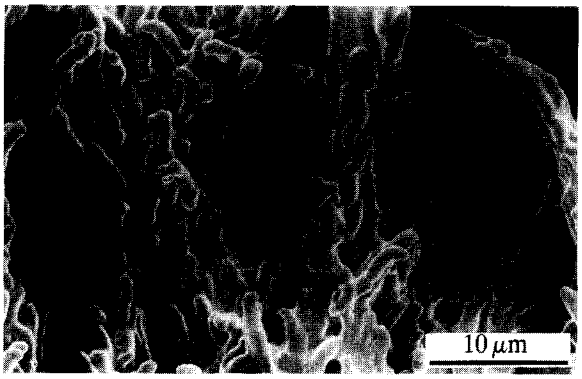


Figure 10 SEM of fracture surface of a 10/90 LDPE/PVC blend (processed in a Brabender Plasticorder), compatibilized by 1.0 wt% of EBSAN-20, after tensile test

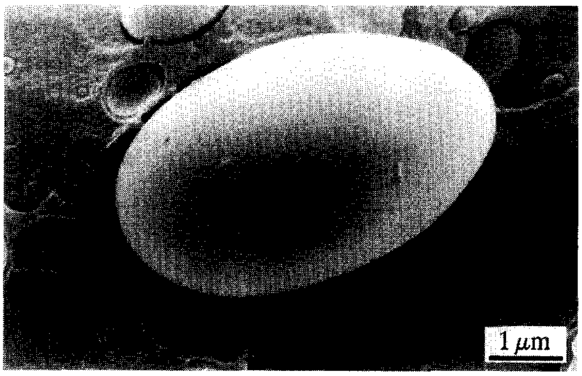


Figure 11 SEM of a PE particle in a 10/90 LDPE/PVC blend (processed in a Brabender Plasticorder)

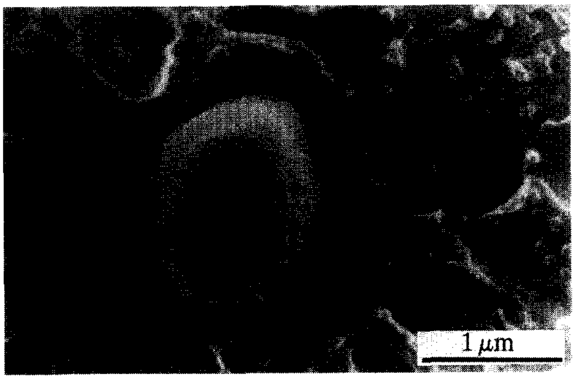


Figure 12 SEM of a PE particle in a 10/90 LDPE/PVC blend, compatibilized by 1.0 wt% EBSAN-20 (processed in a Brabender Plasticorder), showing adhesion between the two phases

particles are still present or have been pulled out of the matrix during breaking of the specimen. A totally different situation is shown in *Figure 10*. In this micrograph no separate PE phase can be detected anymore, while the structure of the material shows that a lot of plastic deformation has occurred during deformation. So there must have been a deformation of the entire material, including the dispersed PE phase. This is clearly an indication for good adhesion between the two phases due to compatibilization.

Furthermore, as expected, SEMs again showed a distinct dispersion of the morphology after compatibilization of the blend by both EBSAN-17 and EBSAN-20. Because we wanted to look at the interfacial area itself, electron micrographs were taken of the PE particles at a higher magnification. *Figure 11* shows a PE particle in an uncompatibilized 10/90 LDPE/PVC blend. The surface of the particle appears to be very smooth, while there is no indication of any adhesion between the PE particle and the PVC matrix. This was seen throughout the material, so it can be concluded that there is no adhesion between the two phases in the uncompatibilized blend. The SEM of a typical PE particle in a 10/90 LDPE/PVC blend, compatibilized by 1 wt% EBSAN-20, reveals a totally different structure (*Figure 12*). Apart from the significant decrease in size of the dispersed particle compared to *Figure 11*, the surface of the PE particle is clearly much rougher and there apparently is a good adhesion between the particle and the matrix. Probably because of shrinkage of the PE phase during cooling after compression moulding due to crystallization, the PVC material, which is attached to the PE particle, has been drawn into fibres at some places. These micrographs clearly demonstrate that, apart from dispersing the blend into a much finer morphology, the segmented EB(SAN-*block*-EB)$_n$ block copolymers are also effective agents for the improvement of the adhesion between the dispersed PE phase and the PVC matrix.

*Effect of SAN block composition on miscibility behaviour of blends of segmented EB(SAN-*block*-EB)$_n$ block copolymers and PVC*

The results of the blending experiments described above indicate a very distinct influence of the composition of the SAN blocks in the block copolymers on their miscibility with the PVC. To study their miscibility behaviour more elaborately, we prepared solutions containing 2.5% of a mixture of the block copolymer and the PVC, using THF as the solvent. In all mixtures the SAN/PVC ratio was kept at 50/50. The block copolymers used here are non-hydrogenated, because the hydrogenated block copolymers are insoluble in THF at room temperature.

Simple solvent casting of a blend of two polymers which are indeed miscible often leads to phase-separated mixtures. Therefore we precipitated the solutions into methanol (ten times the volume of the solution), which circumvents this difficulty[16]. The polymer material was collected and was dried in a vacuum oven at 50°C for three days. *Figures 13–15* show the thermograms of the prepared mixtures. In all cases the material was first heated to 130°C and then quenched to −110°C. The second scan was used to study the miscibility of the SAN blocks and the PVC. This procedure ensures that the blend has reached thermodynamical equilibrium. For all blends, a separate glass transition temperature (T_g) for the PB blocks of the block copolymers was observed at −75 to −80°C.

In *Figure 13* a thermogram of a PBSAN-5/PVC blend is shown together with those of the pure blend components. This blend clearly shows phase-separation between the SAN blocks and the PVC, since two distinct T_gs can be seen, one T_g of the SAN-5 blocks of the block copolymer at 107°C and one T_g of the PVC at 87°C. Contrarily, the blends of PBSAN-17 and PBSAN-20 show one mixing T_g in this area (*Figures 14* and *15*), which proves miscibility of the SAN blocks with PVC. However, the mixing T_g for the PBSAN-17/PVC blend is rather broad, compared to the mixing T_g observed for the PBSAN-20/PVC blend. This observation is consistent with the expected higher miscibility for a SAN-20/PVC blend. Furthermore, it can be seen from these figures that a higher acrylonitrile content of the SAN blocks highers the T_g.

These results demonstrate once more that the acrylonitrile content of the SAN blocks of the block copolymer is indeed a key factor in the miscibility behaviour with the PVC, and thus in the compatibilizing effectiveness of the block copolymer for PE/PVC blends.

CONCLUSION

The synthesized hydrogenated segmented block copolymers of PB and poly(styrene-*co*-acrylonitrile) are effective agents for the dispersion and stabilization of the morphology of (10/90) blends of LDPE and PVC, provided that the

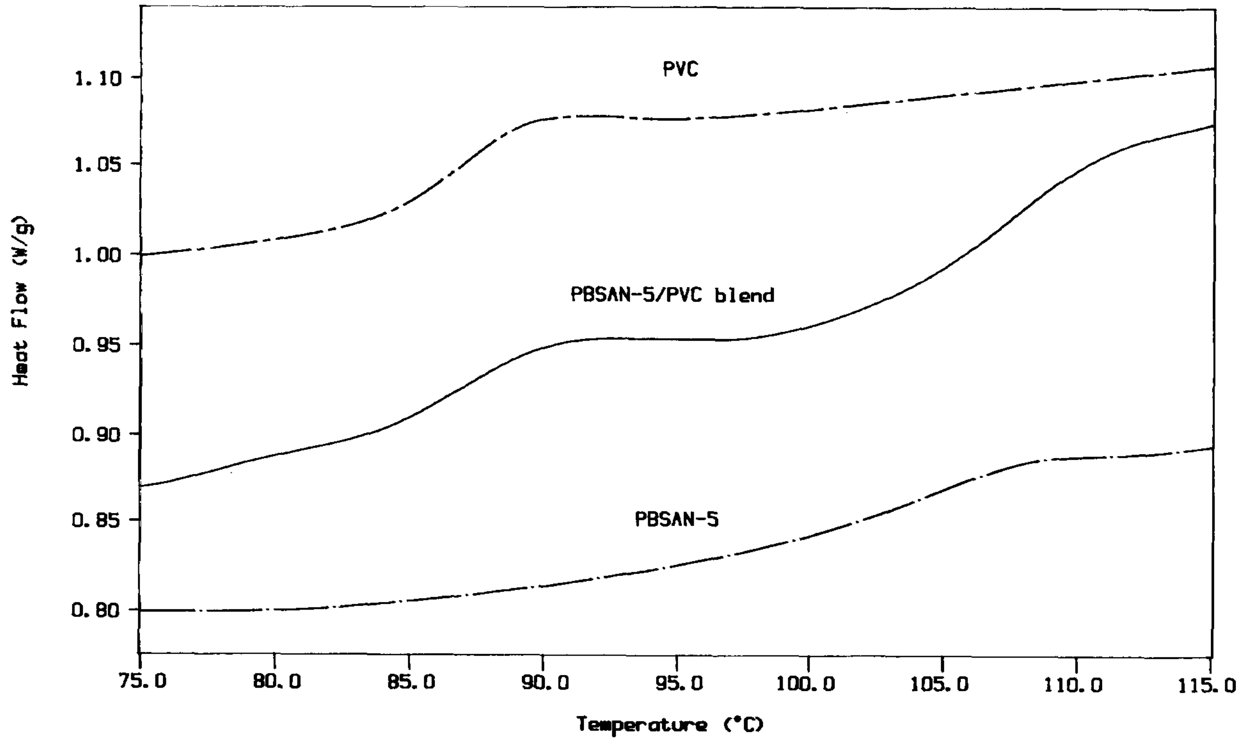


Figure 13 D.s.c. thermogram for PVC/EBSAN-5 blend prepared by precipitation from THF solution into methanol

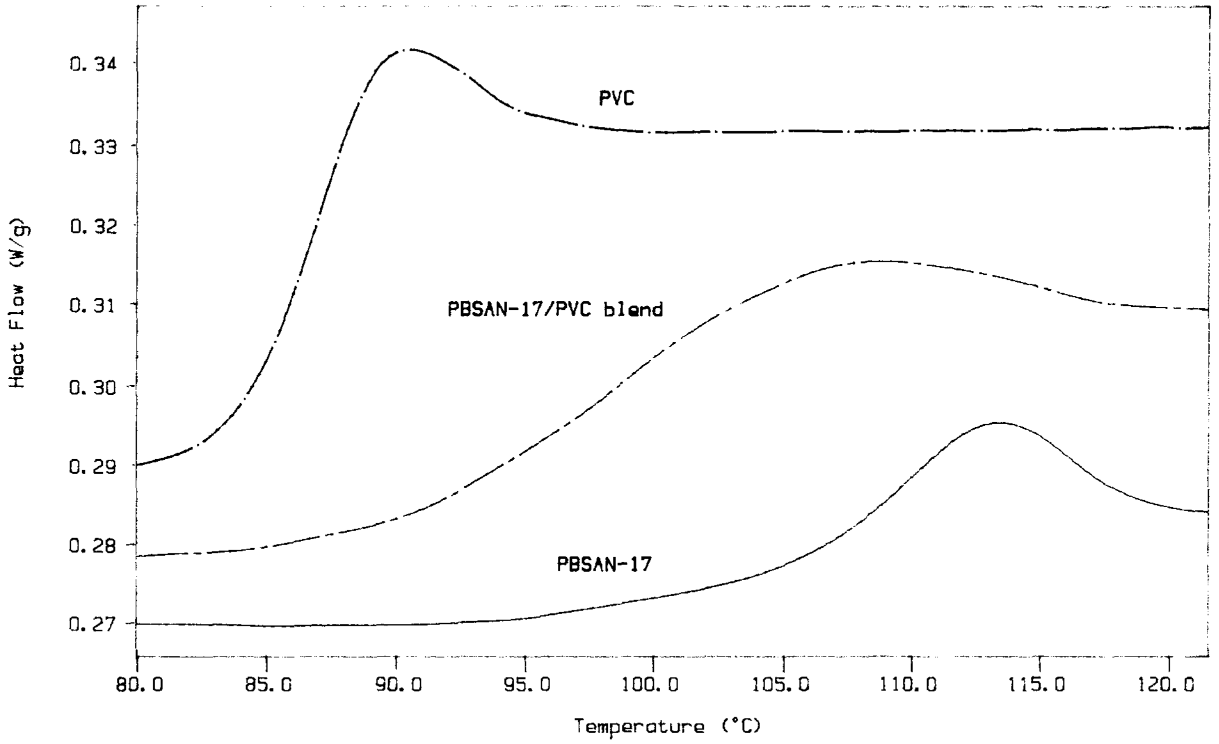


Figure 14 D.s.c. thermogram for PVC/EBSAN-17 blend prepared by precipitation from THF solution into methanol

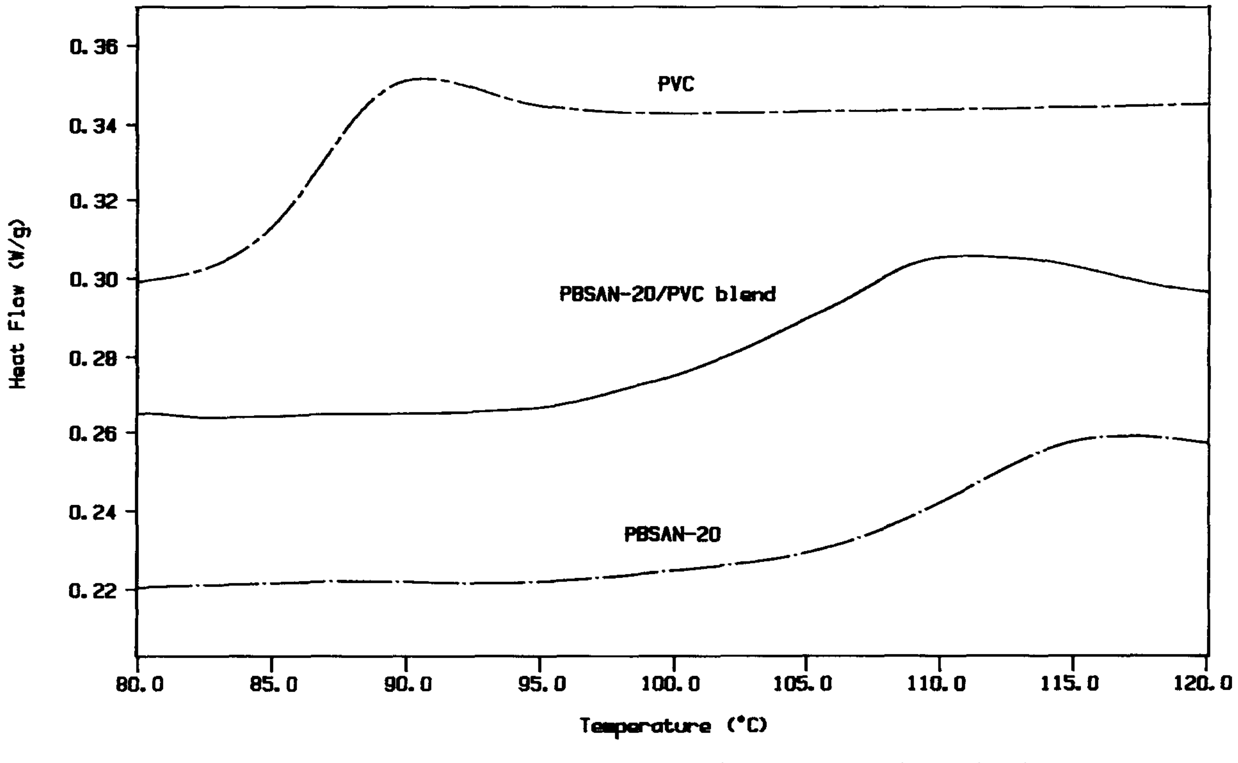


Figure 15 D.s.c. thermogram for PVC/EBSAN-20 blend prepared by precipitation from THF solution into methanol

SAN blocks have an acrylonitrile content close to 20 wt%. The mechanical properties of the blend can be improved significantly by the addition of a small amount of block copolymer ($\leqslant 1$ wt%). We succeeded in preparing a (10/90) LDPE/PVC blend, showing a toughness and elongation at break comparable to those of the virgin PVC, by adding 1% of a segmented EB((SAN-20)-*block*-EB)$_n$ block copolymer to the mixture. SEMs proved that the block copolymers are not only effective in dispersing the morphology, but also in improving the adhesion between the dispersed PE phase and the PVC matrix.

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