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Toughening of polystyrene by natural rubber-based composite particles

Part I *Impact reinforcement by PMMA and PS grafted core-shell particles*

M. SCHNEIDER, T. PITH*, M. LAMBLA†
Ecole d'Application des Hauts Polymères, Institut Charles Sadron (CRM-EAHP),
4, rue Boussingault, Strasbourg, France

This work was focused on the influence of the morphology of composite natural rubber (NR)-based particles on the toughness of polystyrene (PS). Emulsion polymerization processes were used to adjust the microstructure of the latex particles. In order to be suitable for the reinforcement of PS, the NR-based particles were coated with a shell of crosslinked polymethyl methacrylate (PMMA) or PS. Furthermore, PS subinclusions were introduced into the natural core.

A continuous extrusion process was adapted for the incorporation of these natural rubber based impact modifiers into thermoplastics. High deformation speeds (impact testing) were necessary in order to evaluate the mechanical properties of PS blends with a series of the prepared structured latexes. PS could only be toughened by core-shell particles. A PMMA shell proved to be advantageous because it is easier to produce by emulsion polymerization than a hydrophobic PS shell. Pre-vulcanized NR-based particles, which do not cavitate easily, were ineffective. Core-shell particles based on NR-containing PS subinclusions toughened PS more effectively. Solid NR particles caused premature craze and polymer fracture, as the rubber particles break down, debond from the matrix and form large voids at the craze/particle interface. Scanning electron microscopy (SEM) of Izod fracture surfaces showed clearly the cavities of debonded solid rubber particles and demonstrated that subinclusions within the rubber core permitted a larger volume of plastic deformation before failure.

1. Introduction

Most engineering plastics are multiphase materials that contain a dispersed rubber phase in order to improve the impact strength [1–3]. Industrial blends of thermoplastic and elastomeric polymers are usually prepared by a simple mixing process in extruders. Size and shape of the dispersed phase depend on interfacial phenomena and the viscosity of the components. Furthermore, high impact polystyrene (HIPS) which is usually made by a bulk polymerization process contains rubber particles with polystyrene (PS) inclusions. During the early stages of polymerization phase inversion takes place and the size of the rubber particles is established. It is very difficult to determine exactly the influence of factors such as rubber volume content, the morphology of the dispersed rubber particles, the adhesion of the rubber to the matrix and the dynamic mechanical properties of the rubber phase on the fracture toughness of PS. In order to study separately these factors different preformed core-shell particles can be incorporated into PS. A possibility to obtain very fine and well defined morphologies consists of polymer blends with core (rubber)–shell (hard polymer) latex particles of 0.1 to 1 μm which are easily prepared by an emulsion polymerization process [4–6]. This approach to rubber toughening of polymers is not new and is used by industry to toughen poly(methylmethacrylate) (PMMA) and acrylonitrile-butadiene-styrene (ABS). For the toughening of PS rubber particles of 1 μm or larger are required. Only very specialized techniques [7] allow chemists to prepare this particle range which is not easily accessible by conventional emulsion polymerization. However, a natural rubber latex contains particles with a wide range of diameters from 0.01 to 5 μm. Most of the particles are less than 0.5 μm, but most of the mass of the rubber resides in particles greater than 0.6 μm [8]. The particle size distribution is believed not to change

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*Author to whom correspondence should be addressed.
†Deceased.

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from one batch of latex concentrate to another [8]. In order to be suitable for the reinforcement of a PS matrix, NR-based particles were coated with a shell of PMMA or PS. Redox systems were used to control the site of the polymerization and thereby determine the final morphology of the prepared composite NR-based particles. Furthermore, PS subinclusions were introduced into the NR core.

The latex particles act as stress concentrators and produce more extensive matrix deformation by crazing or shear yielding. Depending on the intrinsic brittleness of the matrix polymer, they toughen the matrix by generating multiple crazing as in the case of PS [9] or can change the main fracture mechanism from crazing to shear yielding as in rubber toughened PMMA [10]. This work was focused on the influence of the morphology of composite natural rubber based core-shell particles on the toughness of polystyrene.

In a previous study [11] the suitability of NR-based composite latex particles as a possible impact modifier for thermoplastics had been evaluated. It was shown how the morphology of NR-based composite latex particles affects the impact resistance of poly(methylmethacrylate). Furthermore, some polystyrene model blends were tested. It was possible to compare the effectiveness of identical latex particles for the rubber toughening of two polymers which deform either by crazing (PS) or by shear yielding (PMMA). We found that only core-shell particles toughened PMMA effectively. A crosslinked PMMA shell compatibilized the natural rubber phase with the PMMA matrix. The impact resistance and the Young's modulus of PMMA blends with NR-based core-shell particles was controlled by the NR mass fraction. More complex latex particles containing PS subinclusions within the natural rubber core raised the Young's modulus of the prepared blends, but did not improve significantly the impact resistance of the PMMA blend. On the other hand, PS blends which require at least three times bigger particles for effective reinforcement could only be toughened when PS microdomains were present within the NR core. The few prepared model blends suggested that the very well known "salami" or occluded rubber morphology of high impact polystyrene is also optimal for natural rubber particle toughened PS.

Natural rubber as the core polymer in latex particles has an overall balance of properties which is unmatched by synthetic elastomers. Besides, NR is an alternative to synthetic impact modifiers because of its botanical and hence, renewable origin. First, the NR latex particles had to be modified in order to facilitate the melt mixing and to be effective for rubber toughening. Usually a free flowing powder is employed in continuous extrusion processes for the preparation of polymer blends. However, it was possible to adapt a continuous extrusion process in such a way, that a wet latex could be fed directly into the extruder. This not only avoided degradation of the NR and improved the feeding control, but also made it possible to disperse tacky rubber particles which cannot be incorporated otherwise into thermoplastics. For example pure latex, rubber particles containing PS subinclusions, and latex particles with very thin shells, none of which yield powders suitable for the conventional weight feeders of polymer blending equipment, could be well dispersed into a PS matrix.

A further important feature of this work were electron microscopic observations of the morphology of the prepared blends. Osmium staining techniques [12–15] were used to observe the composite rubber particle and the overall blend morphology by transmission electron microscopy (TEM). In rubber toughened PS, without doubt most of the impact energy is absorbed by the generation and growth of crazes in the matrix [16]. Scanning electron microscopy (SEM) allowed us to demonstrate that subinclusions within the rubber core permitted a larger volume of plastic deformation before failure. Publications of Donald and Kramer [16, 17] deal with the formation of crazes in PS. They analysed the crazing of cast films of PS by TEM at slow deformation speeds and concluded that the optimal particle morphology for HIPS consists of rubber particles with a large number of small PS inclusions. This work shows that fast deformation speeds are particularly important since most of the prepared PS blends containing the different used natural rubber based impact modifiers could be deformed by 50–60% at slow strain rates (ASTM-based tensile testing) but were not equally tough at fast deformation speeds (ASTM-based impact testing).

The purpose of this paper was to apply the data on many different PS blends containing tailor-made rubber particles for a better understanding of structure–properties correlations in this very well known glassy polymer.

2. Experimental procedure

2.1. Materials

The PS matrix Lacqrène 1240 ($M_n = 154\,700$; $M_w = 357\,600$; $M_z = 601\,700$; $T_g = 100\,^\circ\mathrm{C}$) was kindly donated by Elf Atochem. A centrifuged prevulcanized NR latex (Revultex MR) and an uncrosslinked NR latex (Revertex AR) supplied by Revertex Ltd. were used as seed latexes in a sequential emulsion polymerization. The detailed emulsion polymerization technique for the preparation of the toughening composite natural rubber latexes has been described elsewhere [18]. Several initiation systems can be used to control the degree of grafting of the NR phase and the site of polymerization which determines the final morphology of the prepared composite NR-based particles [19]. The extremely polydisperse particle size distribution curves of the two selected natural rubber latexes containing 40 wt% crosslinked PMMA in the shell are plotted in Fig. 1 as obtained by photon correlation spectroscopy performed on a Malvern Autosizer II.

Fig. 2 is a typical SEM photomicrograph of crosslinked NR-based core-shell particles containing 40 wt% crosslinked PMMA in the shell. Polydisperse and isolated particles are clearly visible. Forty wt% of crosslinked PMMA in the particles is sufficient to form a closed shell around the vulcanized NR core in

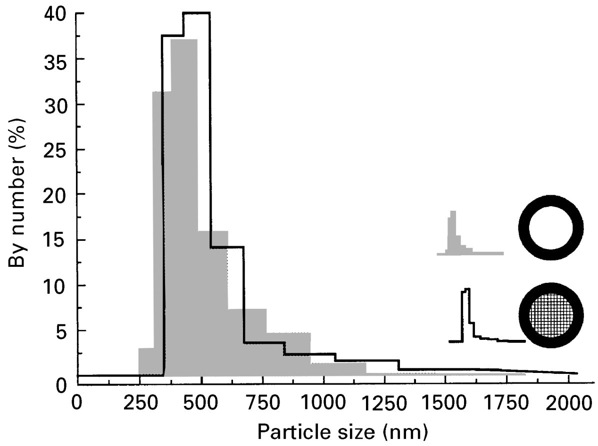


Figure 1 Comparison of the size distribution curve of a crosslinked and not crosslinked natural based latex containing 40 wt% crosslinked PMMA in the shell.

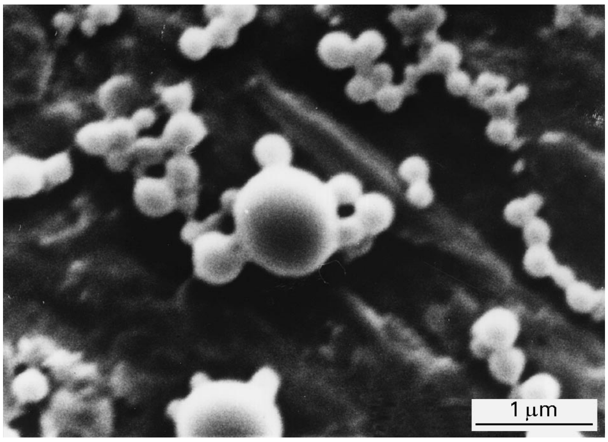


Figure 2 Scanning electron photomicrograph of crosslinked natural based particles containing 40 wt% crosslinked PMMA in the shell.

order to prevent the NR with a glass transition temperature of −60 °C from film forming.

In order to promote a core-shell structure, we used the redox initiator couple t-butyl hydroperoxide/tetraethylene pentamine [20, 21]. In this case, most of the free radicals are produced at the monomer-swollen-particle/water interface, taking into account the fact that the peroxide is soluble in the organic phase, whereas the activator tetraethylene pentamine is water soluble. It is reasonable to assume that the distribution of the secondary polymer (II) within the NR particle is non-uniform with a polymer (II) rich phase at the surface of the latex particle. On the other hand, the formation of crosslinked PS subinclusions inside the NR seed latex results from the initiation induced by azobisisobutyronitrile (AIBN), since the polymerization takes place entirely within the monomer swollen NR latex particles. Fig. 3 shows an example of the morphology of a natural rubber based core-shell particle. It is a TEM photomicrograph of a crosslinked NR based latex particle whose PMMA shell had been stained with phosphotungstic acid. The outer shell is normally not visible if no phosphotungstic acid is applied. The staining is not effective enough to provide a darker shell with a bigger contrast.

The PMMA shell which represents 40% crosslinked PMMA in the particle is clearly visible. Of course only the external region of the shell is formed of pure crosslinked PMMA followed by an intermediate layer of an interpenetrating network of NR and crosslinked PMMA between the NR core and the PMMA shell. A fraction of the PMMA also polymerized in the nucleus of the semi-interpenetrating network (semi-IPN) based seed latex particles. A similar morphology was obtained for non-crosslinked NR-based core-shell particles [18].

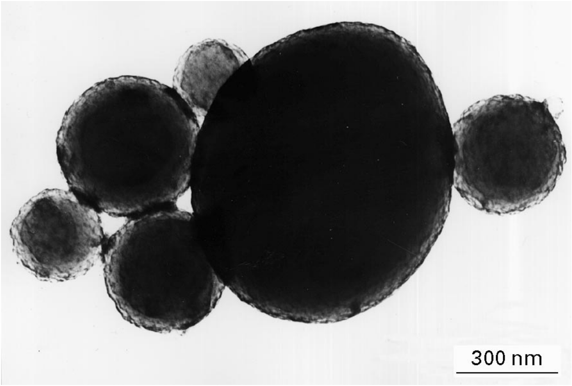


Figure 3 TEM photomicrograph of crosslinked NR based particles containing 40 wt% crosslinked PMMA in the shell. (bipolar redox system).

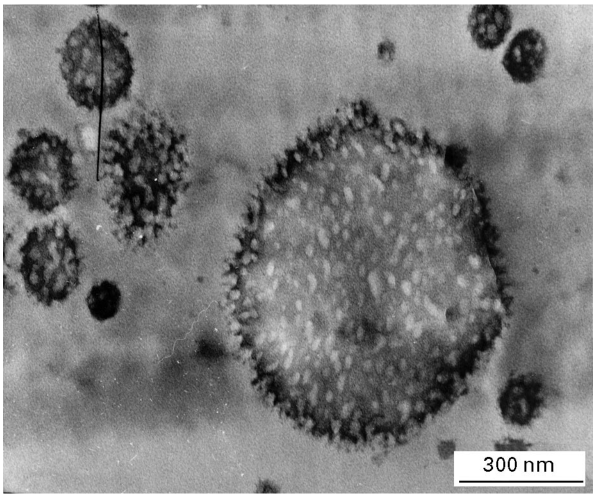


Figure 4 TEM photomicrograph of the ultramicrotome cut of a NR particle containing 40% crosslinked PS in the shell. (bipolar redox system).

The TEM photomicrograph [18] of natural rubber based core-shell particles containing 15 wt% crosslinked PS subinclusions shows clearly that the styrene monomer polymerized in microdomains within the NR seed latex. Most of the secondary polymer resides in 50–100 nm sized domains.

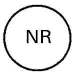
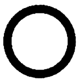
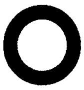
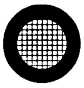
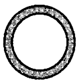
Fig. 4 indicates that a PS shell was much more difficult to produce than a polar PMMA shell when the bipolar redox system and a semicontinuous procedure were used.

Most of the monomer polymerized in very small (30 nm) sized microdomains within the NR core. The subinclusions are two to three times smaller than in the case of AIBN batch synthesis and the diffuse interface of the composite NR particle and the PS matrix indicates an external PS rich layer. Pure NR particles (Fig. 6) or NR/PS latex IPN particles [18] embedded in a PS matrix have a distinctive phase boundary.

In addition to the NR-based latexes, crosslinked poly(*n*-butylacrylate) based core-shell particles were also tested as a possible impact modifier for PS. The synthetic rubber was crosslinked with 0.25 wt% ethylene glycol dimethacrylate. This latex was synthesized in a 50 l pilot plant reactor [22]. The *z*-average particle size, which was obtained by photon correlation spectroscopy, is 180 nm.

Characteristic data on the natural rubber based composite latex particles employed are summarized in Table I. The schematically represented morphology of the particles was verified by TEM observations. All secondary polymers contain 0.25% ethylene glycol dimethacrylate (EGDMA) as crosslinking agent. In the case of the shell synthesis, the bipolar redox initiation system consisting of t-butyl hydroperoxide and tetraethylene pentamine was used for every latex. The PS subinclusions were synthesised by AIBN initiation at 70 °C.

TABLE I Summary of the natural rubber-based composite particle characteristics

Latex	Core composition	Shell composition	Core/shell ratio
	Natural rubber (Revertex AR)	–	–
	Natural rubber	Crosslinked PMMA	75/25
	Natural rubber	Crosslinked PMMA	60/40
	Prevulcanized natural rubber (Revultex MR)	Crosslinked PMMA	60/40
	Natural rubber	Crosslinked PS	60/40
	60% natural rubber/ 40% crosslinked PS	–	–
	80% natural rubber/ 20% crosslinked PS	Crosslinked PMMA	75/25
	Crosslinked poly(*n*-butylacrylate)	Crosslinked PMMA	50/50

2.2. Blend preparation

A continuous extrusion process was adapted for the incorporation of natural rubber based impact modifiers into thermoplastics. An important requirement for rubber toughened polymers is that the rubber phase morphology must not change during the melt fabrication process, i.e. the very sensitive NR based particles should remain unaltered. Fig. 5 shows a schematic of the twin-screw extruder together with weight loss feeder and feeding pump for the wet latex addition.

The extrusion process was performed at a throughput of 5 kg h^{-1}, 150 r.p.m. and 210 °C. Any traces of residual water were taken out of the blend by a vacuum pump just before the last mixing zone. For devolatilization, a heated manifold was attached to a vacuum port onto which one of two liquid nitrogen traps was attached. This made it possible to take samples for a given blend preparation time. The pump could lower the pressure down to about 5 kPa. Monitoring of the liquid nitrogen traps showed that nearly 100% of the introduced water (50% in the latex) had already been evaporated at the introduction point which was open to atmospheric pressure. Different amounts of the wet latexes were fed into the extruder in order to obtain various mass fractions of the composite rubber particles in the PS matrix without changing throughput or processing temperature.

2.3. Mechanical tests

ASTM test samples were moulded on a Billon 150/150 injection moulding machine at 210 °C and left at 23 °C and 50% relative humidity for 1 week.

The Izod impact resistance of V-notched samples (based on ASTM D256) was obtained using a standardized Zwick pendulum impact testing machine. The bar dimensions were 63 × 12.8 × 6 mm. Tensile testing

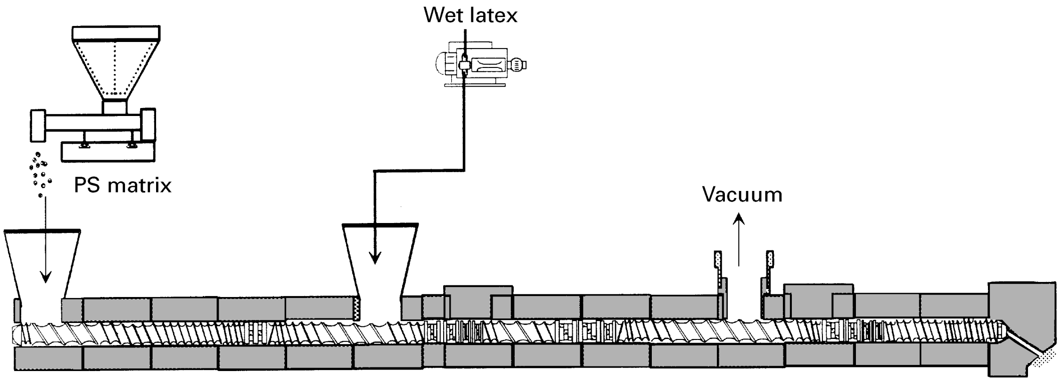


Figure 5 Machine set up for continuous blend preparation.

on dumbbell samples (based on ASTM D638) was performed on a hydraulic Instron 8031 machine at room temperature. The elongation (strain rate $50\,\mathrm{mm\,min^{-1}}$) was measured directly on the sample by a tensometer.

2.4. Electron microscopy

A Cambridge Instruments Stereoscan 120 scanning electron microscope was used for the examination of the latex sample in Fig. 2 which was prepared in the following way. A diluted drop of latex was put onto an aluminium support and subsequently put into liquid nitrogen. Then a gold layer was deposited on the still frozen support with a Cambridge Instruments sputter coater. Izod fracture surfaces of the prepared blends were coated by gold vapour deposition before viewing.

A Philips EM 300 transmission electron microscope was used in order to observe ultramicrotome sections of PS blends which were prepared in the following way. First a smooth surface of a PS blend was exposed to osmium tetroxide vapours during 48 h in order to stain the NR phase [12–14, 23]. The staining not only enhanced the contrast for the microscopic viewing of the blend morphology but also hardened the rubber phase. In this way ultramicrotome sections could be prepared without altering the particle morphology of the no longer soft natural rubber particles.

3. Results and discussion

3.1. Blend preparation

The main purpose of this research project is to provide a set of information on the influence of the morphology and the physical properties of natural rubber particles on the mechanical properties of a standard PS material. Before talking about the influence of the chemical and morphological composition of the particles, it is necessary to check that the natural rubber based particle morphology does not change during the blending process. In order to meet this need all prepared NR based latexes were fed as a wet latex into a ZSK 30 Werner & Pfleiderer twin-screw extruder. The introduction of the wet latex directly into the melt not only protected the NR from oxidation, but also improved the dispersion of the particles within the matrix. For examples, even pure NR particles could be well dispersed in thermoplastics, as shown by the transmission electron photomicrograph in Fig. 6 which confirms the integrity of the NR particles after mixing. This fact also implies that the unmodified natural rubber latex used must have been slightly crosslinked since the particles did not disintegrate in the shear fields of the twin-screw extruder.

TEM observations of the other prepared blends containing core-shell particles showed well dispersed particles within the PS matrix. It is easier to distribute hard particles within a polymer since they do not stick together. Especially at high particle mass fractions in the blend, particle collisions can lead to particle agglomeration. Of course, hard particles can also be fed as a free flowing powder as in conventional blend preparation processes [11].

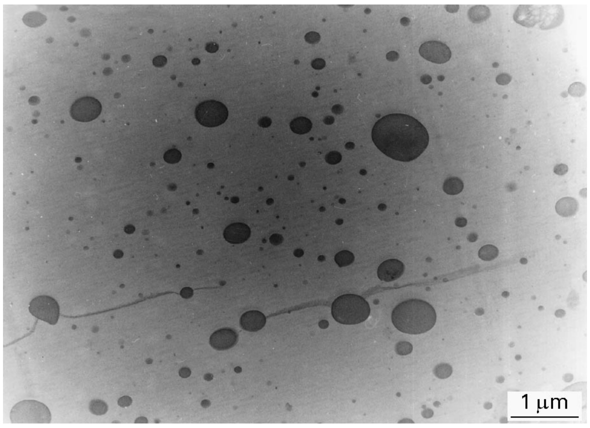


Figure 6 TEM photomicrograph of a PS blend containing 10 wt% pure natural rubber particles.

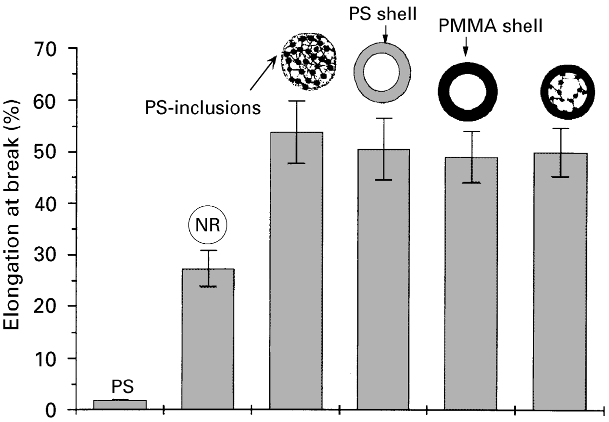


Figure 7 Comparison of the elongation at break of PS blends containing 20 wt% different NR-based composite latex particles. (natural rubber/secondary polymer ratio 60/40).

3.2. Tensile testing

Fig. 7 shows that nearly all the prepared PS blends containing 20 wt% of different composite latex particles could be deformed to 50–60% before breaking. The incorporated composite particles which always contained 40 wt% of secondary polymers are represented schematically above the corresponding bar graphs.

Even pure natural rubber particles allowed the PS matrix to be elongated to more than 25%. No clear differentiation was possible between the other four blends. High deformation speeds (impact testing) were necessary in order to evaluate the mechanical properties of PS blends with a series of the prepared structured latexes.

3.3. Impact resistance of PS blends containing core-shell particles

Fast deformation speeds during impact testing indicated that PS could only be toughened by core-shell particles. In general rubber particles need to adhere to the matrix polymer. Satisfactory adhesion is often obtained by the formation of chemical bonds between the matrix and the rubber phase. A PMMA shell which

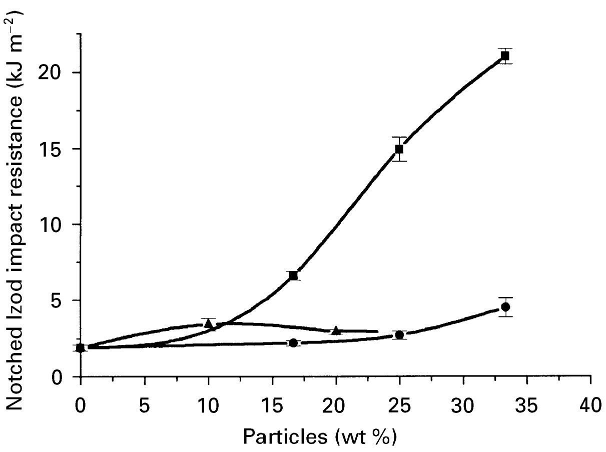


Figure 8 Impact energy of PS blends containing different amounts of pure NR or core-shell particles (core/shell ratio 60/40). (■) PMMA shell; (●) PS shell; (▲) NR.

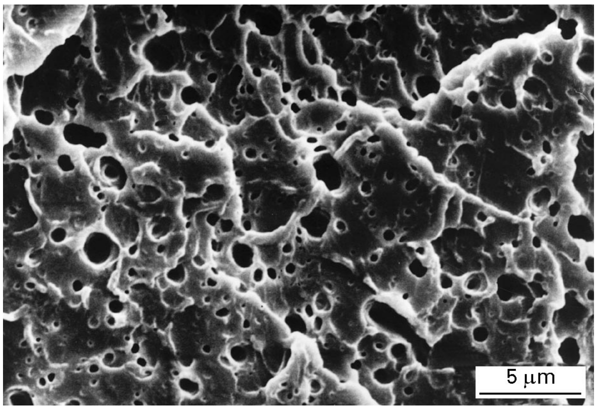


Figure 9 Scanning electron micrograph of the Izod fracture surface of a PS blend containing 10 wt% pure NR particles.

is incompatible with the PS matrix should render the rubber toughener ineffective compared to a PS shell. In fact, Rudin and co-workers [24] found that poly(*n*-butyl acrylate) rubber-based core-shell particles must have a PS shell in order to provide a strong bond between the rubber core and the matrix. However, Fig. 8 indicates that a crosslinked PMMA shell ensured the development of massive crazing and controlled craze breakdown in order to avoid premature fracture at fast deformation speeds. The incorporated composite particles are represented schematically beside the corresponding graph of the impact resistance.

Pure natural rubber particles did not reinforce PS. TEM studies of cast films [17], which were deformed at slow speeds, showed that homogeneous rubber particles extend in the tensile direction and contract along a direction normal to the tensile axis until the particles debond from the matrix polymer. The authors of reference 17 found that large voids are formed between the dispersed rubber core and the outer grafted PS layer resulting in a premature failure of the craze, and polymer fracture. Examination of Izod fracture surfaces of the prepared PS blends confirmed these findings.

The SEM photomicrograph of an Izod fracture surface in Fig. 9 shows clearly the cavities of debonded solid rubber particles. Furthermore, it confirms that the applied blend preparation method permitted even tacky pure rubber particles to disperse uniformly into the PS matrix as is already shown by the TEM photo in Fig. 6.

In order to understand why PS-coated natural rubber particles also did not toughen PS it is necessary to take into account how these particles were synthesized. It is known [25, 26] that the bipolar initiation system used for the particle synthesis grafts natural rubber. Fig. 4 shows clearly that the particles contained the crosslinked secondary polymer both in very small PS subinclusions within the rubber core and in an outer layer. This means that the modulus of the incorporated PS-coated natural rubber particles had been increased, and the rubber particles initiate crazes less effectively [27]. Furthermore, the minimum particle size for craze nucleation is raised [27] and the small particles of the used very polydisperse NR latex, whose particle size distribution curve is plotted in Fig. 1, were ineffective. Hence, more particles had to be incorporated before the impact resistance began to rise. Fig. 8 indicates that composite PS-grafted toughening particles began to reinforce PS at particle mass fractions exceeding 25 wt%. Another explanation for the inferior toughening capacity of the PS-grafted NR-based core-shell particles is the restricted cavitation facility of high modulus particles, since cavitation within the rubber core precedes the crazing process of the PS matrix [28]. The few nucleated crazes failed and premature matrix fracture was caused. A polar PMMA shell was much easier to produce during emulsion polymerization and most of the secondary polymer was concentrated in the exterior region of the composite particle, as shown in Fig. 3. A steep rise of the impact resistance at 18 wt% particles in the blend can be observed in Fig. 8. It is clear that below a critical particle content in the blend the matrix is not toughened as the initiated crazes grow unhindered up to the initiation of catastrophic crack growth. At higher particle fractions in the blend the distance between rubber particles drops to values below the critical craze length and premature polymer fracture is prevented.

3.4. Effect of deformation rate

The tensile testing results in Fig. 10 indicate that by decreasing the deformation rate the modulus of the particles decreases, too, enabling the PS-grafted rubber particles to be as effective as PMMA-coated particles. The incorporated NR-based particles contained 40 wt% crosslinked PMMA or PS in the shell.

The elongation at break rose at a particle content of more than 10 wt% in the blend and reached a level of 60% for more than 30 wt% particles. The results in Fig. 10 imply that a PS shell renders the rubber particles more effective at low particle concentrations in the blend since the PS shell increased the adhesion between the rubber core and the PS matrix. This is in accordance with results of Cook *et al.* [24] about PS and PMMA grafted poly(*n*-butylacrylate)-based core-shell particle-toughened PS.

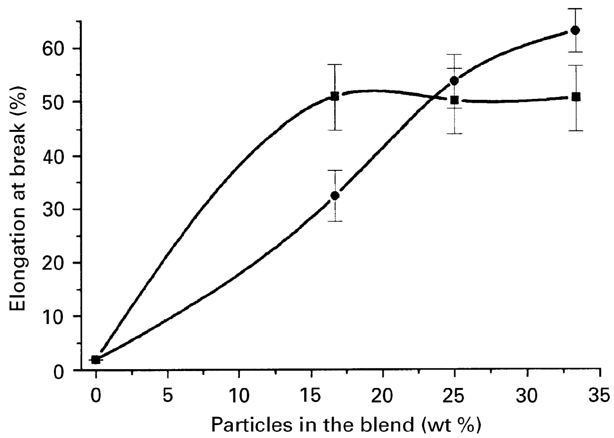


Figure 10 Elongation at break of PS blends with NR based particles containing 40 wt% crosslinked PMMA (●) or PS (■) in the shell.

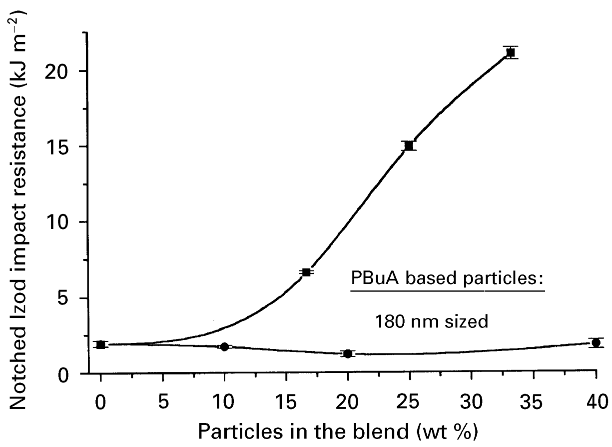


Figure 11 Comparison of the impact energy of PS blends containing either natural rubber (■) or small, 180 nm sized poly(*n*-butylacrylate) (●) based core-shell latexes (core-shell ratios: NR/PMMA 60/40, PBuA/PMMA 50/50).

3.5. Effect of the type and the size of the incorporated rubber particles

The used NR latexes, whose particle size distribution curves are plotted in Fig. 1, contained many small rubber particles. In order to demonstrate that small particles alone cannot toughen PS monodisperse 180 nm synthetic poly(*n*-butylacrylate)-based core-shell particles were incorporated into PS without changing the blend preparation and testing procedures. A separation of large sized NR particles from small sized particles by centrifugation techniques is possible but was not done because a large amount of concentrated rubber latex is needed for continuous blend preparation. The impact resistance of PS blends containing different mass fractions of small PBuA-based particle was tested. The PBuA-based latex particles contained 50 wt% crosslinked PMMA in the shell.

Fig. 11 shows that small, 180 nm sized crosslinked PBuA-based latex particles did not reinforce PS even at a weight fraction of 40% particles in the blend. They are too small for effective rubber toughening of PS which requires micrometre sized particles.

TABLE II Comparison of the tensile properties of a PS blend containing 20 wt% small polybutylacrylate based core-shell particles and unmodified PS

Particle content (wt%)	*E*-modulus (MPa)	Elongation at break (%)	Yield stress (MPa)
0	3275 ± 55	1.9 ± 0.1	49 ± 3
20	2805 ± 60	2.3 ± 0.2	44 ± 1

In order to verify whether small PBuA-based core-shell particles toughen PS at slow deformation speeds, tensile testing was also performed on PS blends containing these particles. Table II compares the tensile properties (slow deformation speeds) of the PS matrix with a PS blend containing 20 wt% poly(*n*-butylacrylate)-based core-shell particles.

The results indicate that besides lowering *E*-modulus and yield-stress, small PBuA-based core-shell particles did not generate and control the growth of crazes at slow deformation speeds either. The elongation at break of the blend could not be increased. The deformation rate (50 mm min^{-1}) was not sufficiently low in order to stabilize the nucleated crazes as in the case of all other types of NR-based latex particles.

The Goodier equations [29] predict that stress enhancement at the rubber particle/matrix interface is independent of particle diameter and recent publications [30, 31] suggest that submicrometre particles can toughen PS. However, whether small sized particles toughen PS is controversial. The data presented in Fig. 11 are in accordance with results on latex-rubber modified PS published by Cook *et al.* [32] who determined an optimal particle size of 2–3 μm for PS-coated crosslinked PBuA-based particles. They found that submicrometre PBuA-based particles were ineffective. PS can be toughened only by particles whose size is near to or exceeds the craze thickness of the matrix polymer [33]. Since the craze thickness of PS is about 1–2 μm [34] the 180 nm sized PBuA-based core-shell particles cannot toughen PS. However, they proved to be efficient for the reinforcement of PMMA [22], whose optimal rubber-toughening particle diameter is about 300 nm [35]. Very polydisperse PMMA-grafted natural rubber particles, whose particle size distribution curve is presented in Fig. 1, toughened both PMMA [11] and PS matrixes. It was shown that in a mixture of natural rubber [36] or polybutadiene-based [30] small and large sized particles, first large particles nucleate crazes which grow in the direction of small particles. Finite element analysis of such blends showed that the stress is highly concentrated at the surfaces of both a large particle and a small particle close to the large particle [30].

The polydisperse particle size distribution of the incorporated impact modifier plotted in Fig. 1 is beneficial for the rubber toughening of PS. Literature [30, 37] reported optimum mechanical properties for a bimodal HIPS with a minimum number of large particles and a maximum number of small particles. Most of the particles of the very polydisperse natural rubber latex are below 500 nm and the attained interparticle distance was smaller compared to HIPS containing only 2 or 3 μm sized particles. Wu [38] derived that the ligament thickness or distance between two rubber particle surfaces τ in monomodal HIPS with the rubber volume fraction Φ_r is proportional to the rubber particle size D

$$\tau = D[(\pi/6\Phi_r)^{1/3} - 1] \qquad (1)$$

Hence, the large number of small particles in the polydisperse NR latex resulted in a thin ligament thickness.

3.6. Effect of natural rubber crosslinking

In order to understand how the degree of crosslinking of the rubber phase affects the mechanical properties of PS blends, prevulcanized NR latex particles with a crosslinked PMMA shell were also tested. Fig. 1 shows that both types of NR-based core-shell particles, which contained the same amount of crosslinked PMMA in the shell, have very similar particle size distribution curves. The prepared PS blends containing these two types of particles can be compared. Fig. 12 compares the effectiveness of crosslinked and uncrosslinked NR-based particles containing 40 wt% crosslinked PMMA in the shell.

It is known that cavitation of toughening particles precedes the crazing of a PS matrix in impact [39]. The void provides a free surface from which a craze can grow through the Argon–Salama meniscus instability mechanism [40]. Literature [39] suggests that crosslinked rubber particles do not cavitate if the strain energy released during cavitation is lower than the energy to form a void. Hence, no free surface is provided from which crazes can be nucleated. This finding could explain why the prevulcanized NR particles did not act as an efficient toughening agent. Experiments in which the rubber was crosslinked by γ-irradiation showed that crosslinked rubber is harder to cavitate [41]. Considering particle sizes clarifies further the inferior ability of prevulcanized NR-based latexes to toughen PS. The minimum particle size for craze initiation is smaller for uncrosslinked than for prevulcanized high modulus rubber particles [42] and more particles have to be incorporated before the impact resistance rises. A model of Bucknall and coworkers [28, 43] describing rubber particle cavitation leads to the same conclusion. The model requires the volumetric strain energy to be greater than the energy to form a void. The void within a rubber particle of radius R, shear modulus G_r and bulk modulus K_r is regarded as a sphere of radius r which is formed in response to an imposed volume strain ΔV_R. The strain energy $U_r(r)$ is given by

$$U_r(r) = 2/3\pi R^3 K_r(\Delta V_R - r^3/R^3)^2 + 4\pi r^2\Gamma + 2\pi r^3 G_r F(\lambda_f) \qquad (2)$$

where $4\pi r^2\Gamma$ is the surface energy of the void and λ_f is the maximal extension ratio of the rubber. The third paper of this series [36] shows that this model describes composite natural rubber toughened PS very well as indeed rubber cavitation in the centre of the core-shell particles could be observed by TEM studies.

The effect of crosslinking the rubber phase on the Izod fracture surface morphology is evident by comparing Figs 13 and 14. The pictures are SEM photomicrographs of PS blends containing the same amount of crosslinked and uncrosslinked rubber-based core-shell particles.

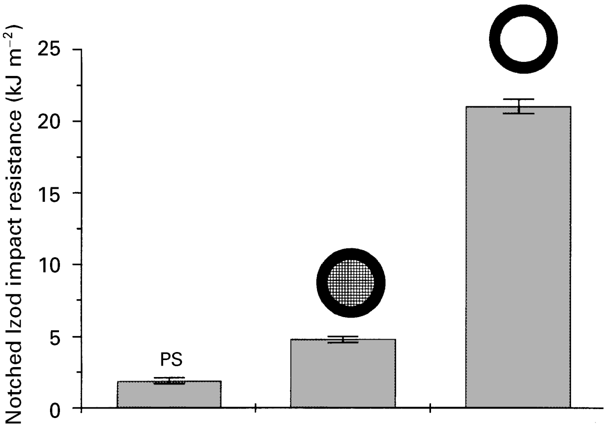


Figure 12 Impact energy of PS blends containing 33 wt% crosslinked or not crosslinked natural rubber based particles with 40 wt% crosslinked PMMA in the shell.

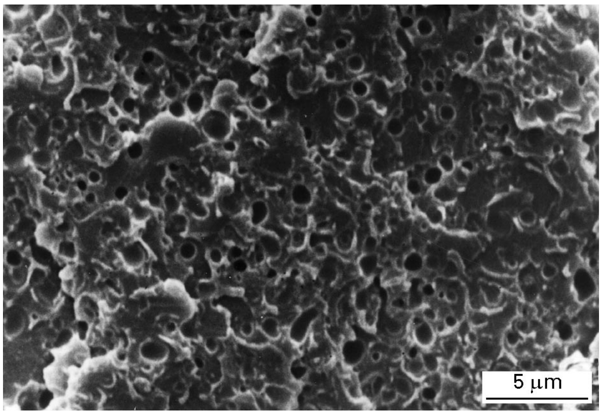


Figure 13 SEM photomicrograph of the Izod fracture surface of a PS blend containing 33 wt% core (crosslinked natural rubber)-shell (crosslinked PMMA particles) (core/shell ratio: 60/40).

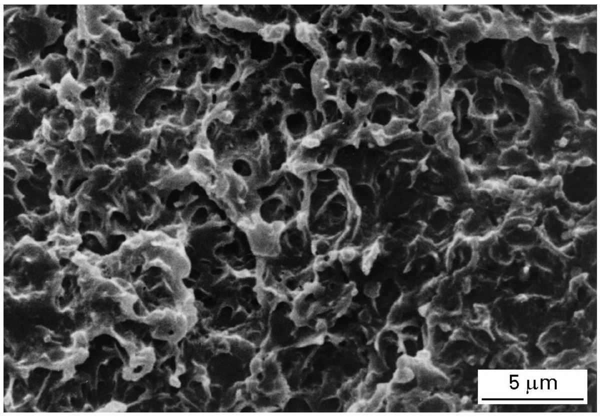


Figure 14 SEM photomicrograph of the Izod fracture surface of a PS blend containing 33 wt% core (natural rubber)-shell (crosslinked PMMA particles) (core/shell ratio: 60/40).

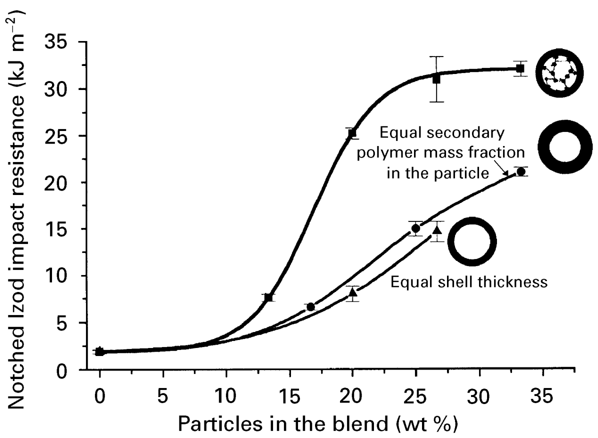


Figure 15 Comparison of the toughening effectiveness of NR-based core-shell particles containing 15 wt% crosslinked PS subinclusions in the rubber core and 25 wt% crosslinked PMMA in the shell with unoccluded NR particles containing 25 or 40 wt% crosslinked PMMA in the shell.

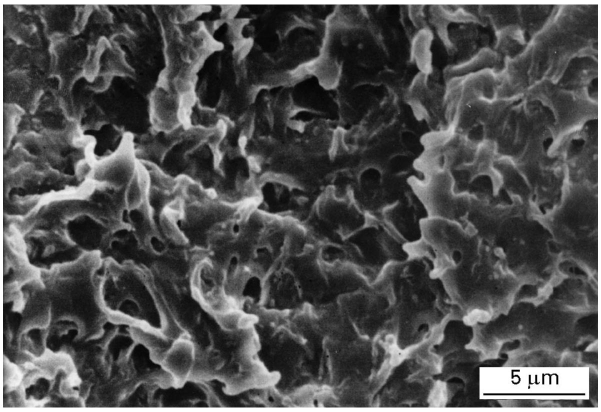


Figure 16 SEM photomicrograph of the Izod fracture surface of a PS blend containing 27 wt% PMMA coated 80% NR/20% crosslinked PS-based latex particles (core/shell ratio: 75/25).

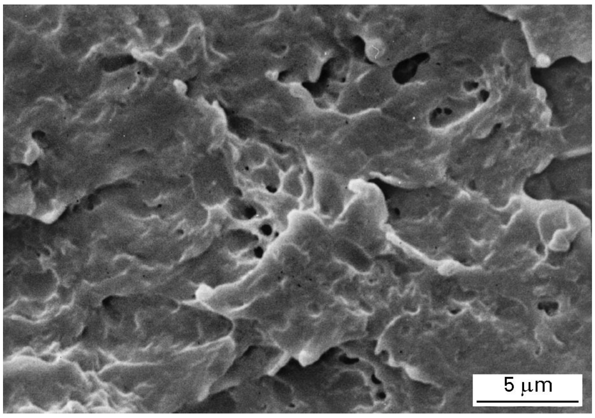


Figure 17 SEM photomicrograph of the Izod fracture surface of a PS blend containing 27 wt% PMMA coated NR-based latex particles (core/shell ratio: 75/25).

Nearly all the incorporated particles have debonded from the matrix when the NR phase was crosslinked. Crosslinked rubber particles did not cavitate and the crack went around the particle. On the other hand, most of the uncrosslinked particles ruptured and the crack propagated through the NR core. Uncrosslinked NR-based latex particles were well integrated in the crazed matrix.

3.7. Internal structure of the incorporated core-shell particles

Fig. 15 indicates clearly that core-shell particles based on NR-containing PS subinclusions toughened PS more effectively. To provide a comparison to complex core-shell (75/25) particles containing 15 wt% PS subinclusions in the core, simple core-shell particles with either an equal amount of secondary polymer (core/shell ratio: 60/40) or an equal amount of the shell forming polymer (core/shell ratio: 75/25) were also incorporated into blends.

Thicker crosslinked PMMA shells around a NR core without subinclusions were no more effective in conferring toughness to PS blends. The graphs of the impact resistance versus particle content in Fig. 15 are nearly superimposed in the case of simple core-shell particles containing different amounts of PMMA in the shell. This means that the rubber volume content (NR and PMMA phase) controls the impact resistance of PS blends with the same type of particles. The morphology actually obtained in the core-shell particles is in accordance with this result. The PMMA phase meandered into the core and also formed very small occlusions within the rubber core. The volume of the rubber phase was thereby increased, which means that more effective use was made of the NR. A possibility to nearly double the efficiency of the toughening agent consists of the use of core-shell particles which contain hard PS subinclusions within the rubber core. It has been demonstrated [16, 17] that rigid occlusions in rubber particles, as in a typical HIPS, constrain the rubber that separates them. As an occluded particle is extended in the tensile direction, the rubber is broken up into fibrils which accommodates the displacement of the surrounding craze and no large voids are formed. Fracture mechanics indicate the damaging effects of large voids in comparison to small ones. Pure NR particles led to premature craze and polymer fracture, as shown in Fig. 8. Simple core-shell rubber particles were effective in generating and growing crazes because a crosslinked PMMA shell ensured a satisfactory stress transfer at fast deformation speeds and some PMMA subinclusions which could not be avoided during the shell synthesis helped to fibrillate the rubber phase at impact. In a further step, subinclusions were purposely introduced within the rubber core. The impact data of Fig. 15, which correlates the particle content and not the rubber mass fraction in the blends with the impact resistance, implies that subinclusions increase the crazing efficiency of rubber particles and do not simply increase their effective rubber volume fraction.

Examination of the Izod fracture surfaces in Figs 16 and 17 of PS blends containing either occluded core-shell particles or simple PMMA coated particles with the same amount of the shell-forming polymer confirmed these findings.

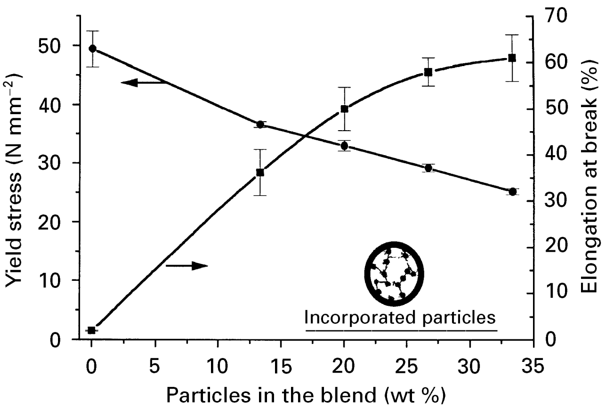


Figure 18 Yield stress and elongation at break of PS blends with 80 wt% NR/20 wt% crosslinked PS based particles containing 25 wt% crosslinked PMMA in the shell.

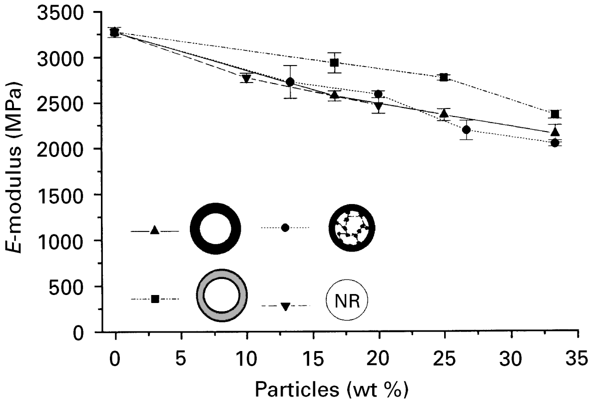


Figure 19 Correlation of the *E*-modulus of different PS blends with the particle mass fraction in the blend (40 wt% secondary polymers in the particles).

It can be seen that both types of natural rubber-based particles promote massive crazing in the polystyrene matrix. However, the SEM photos demonstrate that subinclusions within the rubber core permitted a larger volume of plastic deformation before failure.

3.8. Tensile behaviour of composite NR particle-toughened PS blends

In Fig. 18 the values of yield stress and elongation at break of PS blends are plotted versus the particle mass fraction in the blends. Different amounts of core-shell particles containing 15 wt% subinclusions in the core were incorporated in the PS matrix.

The yield stress is a linear function of the particle mass fraction in the blends whereas the elongation at break rose first linearly with the particle content and then levelled out. At higher particle mass fractions in the blend the distance between rubber particles drops to smaller values and their stress fields begin to overlap. Hence, the yield stress was lowered and the tensile samples could be strained further.

A direct comparison of the dependence of the *E*-modulus on the rubber weight fraction of PS blends containing different composite latex particles is illustrated in Fig. 19. The composite rubber particles contained always the same amount of secondary polymers.

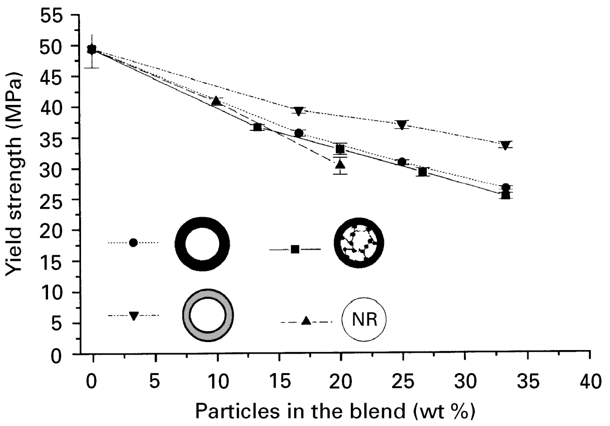


Figure 20 Correlation of the yield strength of different PS blends with the particle weight fraction in the blend (40 wt% secondary polymers in the particle).

In the case of all blends, which contained four different kinds of rubber particles, a linear dependence of the modulus and the incorporated particle weight fraction was found. PS-grafted particles increased the modulus of the blend. The graphs of PS blends containing composite particles with or without PS subinclusions are superimposed since the particles contained the same amount of rubber. The *E*-modulus of PS blends containing pure NR particles is only marginally decreased compared to PS blends containing core-shell particles.

The yield strengths of different PS blends containing composite NR-based particles with the same mass fraction of secondary polymers and pure natural rubber are compared in Fig. 20.

The yielded material of the different blends includes craze matter and portions of the incorporated composite rubber particles which are connecting craze surfaces. The three obtained graphs, representing the dependence of the yield stress on the particle mass fraction of pure NR particles and PMMA coated particles with and without PS subinclusions, are superimposed. This means that all three types of particles are equally effective in decreasing the yield stress of the matrix polymer at slow deformation speeds. The PS-coated high modulus particles increased the yield strength of the blend. As the modulus of the particles is increased the resistance to rubber cavitation increases and the rubber cavitation which precedes the crazing process is retarded. Hence, the tensile stress needed for matrix deformation was higher.

3.9. Evaluation of the mechanical performance of NR-toughened PS blends

Two characteristic properties determine principally the mechanical performance of a material. One describes the stiffness (e.g. *E*-modulus) and the other toughness (e.g. Izod impact resistance). It is possible to evaluate the prepared PS blends containing different

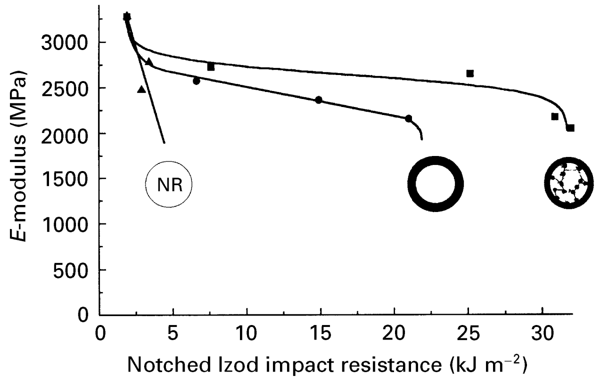


Figure 21 Correlation of the *E*-modulus and the notched Izod impact resistance of different PS blends containing pure NR and core-shell particles with or without PS subinclusions (40 wt% secondary polymers in the particles).

kinds of rubber particles when these two characteristics are plotted against each other [44]. Fig. 21 compares the performance of PS blends containing pure natural rubber and PMMA coated particles with or without PS subinclusions. The composite particles contained the same mass fraction of secondary polymers.

High impact resistance and modulus which generally are the desired properties of a polymer blend can be found in the right-hand corner of the diagram. It is obvious that pure natural particles only decreased the *E*-modulus without any improvement of the mechanical properties of the blends. The use of particles containing PS subinclusions in the rubber core, which was further studied [36, 45], significantly shifted the mechanical properties in the desired upper right-hand corner of the diagram. On the one hand the *E*-modulus was increased and on the other hand occluded particles yielded PS blends which were more effectively toughened. Comparing the occluded particles with latexes containing the same amount of hard polymer and rubber suggests that the deformation mode of the matrix polymer had been changed.

4. Conclusions

In this study of composite NR latex-toughened polystyrene, the influence of factors like the morphology of the dispersed rubber particles, the nature and thickness of the shell-forming polymer, the particle content and the properties of the rubber phase on the fracture toughness of PS were examined. Furthermore, a novel continuous blend preparation method was used for the incorporation of wet latexes directly into a twin-screw extruder. The data on many different PS blends containing tailor-made rubber particles helped to come to a better understanding of structure–properties correlations of this very well known glassy polymer.

1. The incorporation of a wet latex directly into the extruder improved the dispersion of the particles within the matrix and allowed even tacky rubber particles to disperse which by conventional blend preparation procedures cannot be incorporated into PS.
2. High deformation speeds (impact testing) were necessary for the evaluation of the different impact modifiers for PS. Tensile testing could not differentiate between the different composite NR latexes because all particles yielded PS blends which could be equally well deformed. Even pure NR particles allowed PS blends to be elongated to 30%.
3. Impact testing showed that PS could only be toughened by core-shell particles. Interfacial adhesion was not essential since a PMMA shell which is less incompatible with PS proved to be effective. The shell must only provide adequate stress transfer and the absolute interface adhesion beyond this point had no influence. It was found that the particle shell thickness had little effect on the impact toughness. However, more effective use could be made of the NR because part of it could be substituted by an increased PMMA fraction in the particle. A compatible PS shell did not render an effective toughening agent since grafting increased the particle modulus too much.
4. The rubber particle must fracture in preference to particle/matrix separation at impact. Scanning electron microscopy (SEM) showed that the introduction of hard PS subinclusions within the soft rubber core improved rubber fibrillation at impact, which prevented a particle matrix separation. Thus, a larger volume of plastic deformation was permitted before failure. SEM observation of fracture surfaces of PS blends containing pure natural rubber latex particles proved that solid rubber particles debond from the matrix and do not offer any impact improvement to PS.
5. More than 18 wt% of core-shell particles had to be incorporated into PS before the impact strength began to rise steeply. Incorporating more particles did not increase toughness and elongation at break of the prepared PS blends anymore. The modulus of the blends depended linearly on the particle mass fraction.
6. It was established that precrosslinked NR-based latex particles which do not cavitate at impact were not suited for the reinforcement of PS. Polybutylacrylate-based core-shell latexes (180 nm) were too small for the reinforcement of PS.

The results suggest that core-shell particles containing PS subinclusions in the rubber core are well suited for the toughening of PS. The hard shell assures adequate stress transfer at fast deformation speeds and the rigid subinclusions render the rubber particles capable of stabilizing a generated craze since the incorporated rubber particle do not debond from the matrix.

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