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# **POLYBLEND '97 SPE RETEC**

***International Symposium  
on Polymer Blends, Alloys  
and Filled Systems***

October 9-10, 1997  
Industrial Materials Institute  
National Research Council Canada  
Boucherville, Qc, Canada

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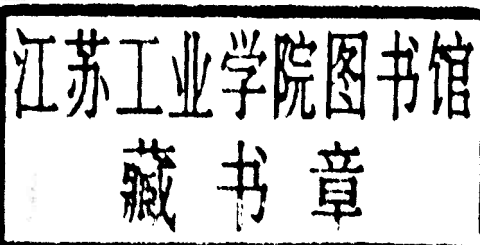
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## **Recent Studies in Immiscible Blends Compatibilization**

B. Brown

General Electric Company  
Schenectady, NY, USA

For more information please communicate directly with the author.



## ***Has the reaction kinetics an effect on the phase morphology and mechanical properties of blends prepared by reactive processing?***

**Pagnouille C., Jérôme R.**

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University of Liège, Institute of Chemistry, B6, Sart-Tilman, 4000 Liège Belgium***

*The reactive blending of SAN with EPR has been studied as a straightforward way of toughening the otherwise fragile thermoplastic. For this purpose, SAN (or part of SAN) has been modified by various amounts of primary amines or carbamate groups (which are nothing but primary amine precursors) and used in conjunction with commercially available EPR-g-maleic anhydride (EPR-g-MA) preblended with EPDM. A SAN-g-EPR is expected to be formed at the interface through an imide bonding. It is clear that the molecular architecture and the residence of this copolymer at the interface depends on the reaction kinetics in a close dependency on the type and concentration of the reactive groups attached to SAN, the content of reactive SAN in the SAN phase, the addition order of the constitutive components of quaternary blends (reactive SAN+SAN+EPR-g-MA-EPDM) of a constant composition. Dependence of the impact properties, the phase structures and the interfacial adhesion on these experimental parameters will be discussed, and conditions for a 10 fold increase in the impact energy as well.*

Toughening of SAN by EPR has been studied by reactive processing of EPDM containing EP-g-maleic anhydride (50 wt %) and SAN added with various amounts of reactive SAN: SAN-NH<sub>2</sub> and SAN-Carbamate (precursor of SAN-NH<sub>2</sub> at the processing temperature) with various contents of reactive groups. The general SAN/EP composition is systematically 75/25. The main conclusions may be summarised as follows:

### ***1. Effect of the type of the reactive groups attached onto SAN (NH<sub>2</sub> or carbamate).***

In this study, a special attention has been paid to the effect of the intrinsic reactivity of the groups attached to SAN on the impact resistance of SAN/EPR reactive blends. For this purpose, neat SAN has been added with SAN chains that contain 0.028 mol/wt % either carbamate (SAN-Carb) or NH<sub>2</sub> groups (SAN-NH<sub>2</sub>) able to react with the EP-g-MA rubber, so as to form a graft copolymer.

In order to estimate the extent of the compatibilization, polyblends have been extracted by refluxing acetone, which is a selective solvent for SAN. The unreacted SAN has been accordingly separated from the original mixture of insoluble EP-g-SAN graft copolymer, unreacted EP-g-MA and EPDM. The percentage of SAN grafted to the rubber phase has been calculated from the FTIR spectrum of the insoluble material (by using a calibration curve). The compatibilization efficiency (Charpy impact strength, phase structure) of SAN bearing carbamate and primary amine, respectively, have been compared at constant weight contents of SAN grafted to the rubber phase.

#### ***Dependence of impact properties on the amount of SAN grafted to the rubber phase.***

The Charpy impact strength is reported in Figure 1 versus the amount of reactive SAN grafted to the rubber phase. The increase of the impact strength with the amount of grafted SAN-NH<sub>2</sub> is initially much more rapid compared to that one of the SAN-Carbamate, and then levels off beyond 5 wt % of bound SAN. In case of SAN-Carbamate, the impact resistance

does not level off, but continuously increases with the extent of the grafting reaction. Only 4.5 wt % bound SAN-NH<sub>2</sub> (which corresponds to 13 wt % of reactive SAN added to the SAN phase) is required to reach the brittle-tough transition (i.e. 30 kJ/m<sup>2</sup>), compared to 10.1 wt % (or 40 wt % of reactive SAN in the SAN matrix) in case of SAN-Carbamate. It is worth noting that the plateau value of impact strength observed in case of SAN-NH<sub>2</sub> (i.e. 35 kJ/m<sup>2</sup> for 5 wt % bound SAN) is slightly smaller than the highest value reached with SAN-Carbamate (i.e. 38 kJ/m<sup>2</sup> for 12.5 wt % grafted SAN).

#### *Phase structure-property relationship.*

In order to establish some relationships between the morphology of the reactive blends (i.e. the size of the dispersed phase and the conformation of the copolymer at the interface) and the course of the grafting reaction (kinetics and completeness), polyblends modified by increasing amounts of reactive SAN containing either NH<sub>2</sub> or carbamate groups have been analyzed by transmission electron microscopy after staining of the SAN phase with RuO<sub>4</sub>. When the SAN-Carb is considered, a quasi linear dependence of the average cross-sectional (or diameter) of the dispersed rubber phase on the amount of SAN grafted is observed beyond 3 weight percent of bound SAN (Figure 2). In case of SAN-NH<sub>2</sub>, this area decreases much more rapidly with the amount of grafted SAN and then tends to level off beyond 5 wt % of bound SAN, at a value (0.10-0.11 μ<sup>2</sup>) slightly higher than in case of SAN-Carb (0.07 μ<sup>2</sup>).

*There is an interesting parallelism between the dependence of the impact resistance on the SAN grafting and that one of the rubber particle size, such that the decrease in the rubber particle diameter appears to have a major effect on the improvement of SAN toughness.*

Assuming that the SAN-g-EP copolymer formed by reactive processing remains at the interface, the average interfacial area stabilized per bound SAN molecule can be estimated from the rubber particle size and the amount of SAN grafted to the rubber phase. In case of SAN-Carb, this interfacial area is 12 nm<sup>2</sup> independently of the amount of grafted SAN, whereas this value is 1.70 times larger (19-21 nm<sup>2</sup>) in case of SAN-NH<sub>2</sub>, until a SAN grafting of 5 wt % followed by a decrease (12 nm<sup>2</sup>) when the grafting is more important. According to Tang and Huang<sup>1</sup>, this decrease in the interfacial area occupied per bound SAN-NH<sub>2</sub> molecule beyond a critical value of grafting would indicate a change in the conformation of the grafted chains, from a "flat conformation" on the rubber phase to a conformation more extended into the continuous SAN phase.

Kinetics of the interfacial reaction can explain the differences observed between the two types of reactive groups attached to SAN. In case of SAN-Carb, the formation of SAN-g-EP graft copolymer at the interface is thought to be controlled by the carbamate-maleic anhydride reaction, which is slower than the chain migration, whereas in case of SAN-NH<sub>2</sub>, the grafting reaction is much faster than the migration of the reactive chains to the interface. Once a SAN-NH<sub>2</sub> molecule comes in contact with a rubber particle, the probability that several amine groups of this chain react is higher than the reaction of an amine of a not yet grafted chain<sup>2,3</sup>. As result, the high functional SAN-NH<sub>2</sub> molecule is expected to be more extensively spread on the interface, leading to a larger interfacial surface area stabilized per bound SAN-NH<sub>2</sub> molecule (19-21 nm<sup>2</sup>) compared to the SAN-Carb counterpart (11.9-12 nm<sup>2</sup>), of which grafted chains would more deeply penetrate the SAN phase. Thus, a lower amount of bound SAN-NH<sub>2</sub> is required to cover the interface, to stabilize finer dispersion of the rubber phase and to improve impact properties.

Nevertheless, it can be easily imagined that, at a high content of reactive SAN chains in the SAN phase, the probability that several chains react is higher than the reaction of a single molecule through multiple bonding. This hypothesis might explain why beyond a critical value of grafting the interfacial area stabilized per bound SAN-NH<sub>2</sub> molecule decreases and tends to reach the value observed with SAN-Carb.

### ***Interfacial adhesion.***

In addition to the decrease of the rubber particle size and the improvement of the impact resistance, the graft copolymer formed could also improve the interfacial adhesion<sup>4</sup>. In order to clear up that point, the interfacial adhesion between immiscible SAN and PP-g-MA (0.7 wt % maleic anhydride) has been measured by the asymmetric double cantilever beam technique. The reactive SAN (SAN-NH<sub>2</sub> or SAN-Carb) has been added to the sandwich assembly in different ways (spin casting of reactive SAN onto either PP-g-MA or SAN sheet, preannealing of the phase supporting the reactive SAN layer or not). PP-g-MA was used instead of EP-g-MA because of a higher elastic modulus, leading to more reliable measurements. Preliminary experiments have shown that:

- The diffusion of reactive SAN chains into neat SAN (preannealing of the SAN strip supporting the reactive SAN layer) is required to provide the SAN/PP-g-MA interface with high adhesion.
- The adhesion energies measured with SAN-Carb are much higher than the energies imparted by the SAN-NH<sub>2</sub> counterpart.

Thus, SAN-NH<sub>2</sub> is not as effective as SAN-Carb in toughening the SAN/PP-g-MA interface. This observation is consistent with the conformation of the grafted SAN chains at the interface proposed earlier. The grafted SAN chains appear to be more extensively spread on the interface (by multiple bonding), when the reactive groups are NH<sub>2</sub> rather than carbamate (see interfacial surface areas stabilized per bound SAN molecule reported above, SAN-Carb: 12 nm<sup>2</sup> and SAN-NH<sub>2</sub>: 19-21 nm<sup>2</sup>). The grafted SAN-NH<sub>2</sub> chains would thus form smaller size loops less efficiently entangled with bulk SAN compared to the grafted SAN-Carb chains

### ***Conclusions***

According to the results of interfacial adhesion, it appears that this property is less critical than the size of the rubber particles for providing the polyblends with high impact performances. For a constant amount of SAN grafted to the rubber phase (i.e. constant concentration of SAN-g-EP graft copolymer at the interface), SAN-NH<sub>2</sub> stabilizes, by multiple bonding to the rubber, a larger interfacial surface area and thus provides a finer rubber dispersion compared to SAN-Carb. A larger amount of grafted SAN-Carb is accordingly required to reach comparable rubber particle size and impact resistance.

## ***2. Effect of the number of reactive groups attached onto SAN.***

The reactive groups contents of SAN, i.e. SAN-NH<sub>2</sub> or SAN-Carb, is also of a prime importance. In this study, the impact properties of the reactive blends have been compared at a constant content of reactive SAN (SAN-NH<sub>2</sub> or SAN-Carb) in the SAN phase (33.33 wt %), while changing the content of reactive groups per chain (0.004, 0.028, 0.049, 0.078 mol/wt % reactive groups). The Charpy impact strength is reported in Figure 3 versus the amount of reactive groups attached onto the reactive SAN chain. A bell-shaped curve is observed for the dependence of the impact properties on the SAN reactive groups content. The initial improvement in the impact strength observed for both SAN-NH<sub>2</sub> and SAN-Carb is the signature of the beneficial effect of increasing probability of grafting at the interface. However, when the NH<sub>2</sub> content of SAN-NH<sub>2</sub> exceeds 0.028 mol/wt % (i.e. 0.049 and 0.078 mol/wt %), a sharp drop in the impact properties is observed. A too high content of NH<sub>2</sub> groups attached onto SAN does not impart anymore ductility to the polyblend. This observation could result from an excess of grafting at the interface.

In order to check this hypothesis, a fast interfacial reaction able to consume part of the NH<sub>2</sub> groups has been considered. For this purpose, the reactive blend containing 20 wt %

SAN-NH<sub>2</sub> (0.049 mol/wt %) in the SAN phase has been modified by various amounts of phthalic anhydride in the rubber phase <sup>6</sup>. The Charpy impact strength appears to increase continuously with the phthalic anhydride content (see results reported in Table 1). This indicates that this small organic molecule competes with the EP-g-MA for reacting with SAN-NH<sub>2</sub> which limits the extension of the grafting reaction.

Moreover, a shift towards higher contents of carbamate groups in reactive SAN is clearly observed compared to SAN-NH<sub>2</sub>. The best improvement in the impact resistance is indeed observed for SAN-Carb containing 0.049 mol/wt % carbamate, compared to 0.028 mol/wt % NH<sub>2</sub> in case of SAN-NH<sub>2</sub>. Once again, the kinetics of the interfacial reaction might explain these observations.

### *3. Effect of the mixing sequence.*

In the case of reactive compatibilization, the mixing sequence, i.e. the addition order of the constitutive components of quaternary blends (reactive SAN+SAN+EP-g-MA+EPDM), has a major effect on the final blend properties. Two main blending routes have been considered.

In a first approach, samples have been melt blended according to a non reactive two-step procedure. A homogeneous mixture of EPDM and EP-g-MA has been first prepared by melt blending 50 wt % EP-g-MA and EPDM, respectively. In a second step, the reactive SAN has been melt blended with SAN, followed by the addition of the (EPDM/EP-g-MA 1/1) preblend. It is worth noting that all the results reported above have been obtained by using this "in situ compatibilization".

In an alternative procedure, the SAN-g-EP graft copolymer has been preformed by melt blending the reactive SAN with the (EPDM/EP-g-MA 1/1) preblend in various ratios. This premade "compatibilizer" has been then compounded with the neat SAN matrix in order to comply with the final SAN/rubber 75/25 wt composition.

In the "in situ compatibilization", the two reactive components, i.e. EP-g-MA and reactive SAN, are uniformly distributed in their host polymer phase before reaction. Thus, they have to migrate to the interface, where the SAN-g-EP graft copolymer is expected to be formed. This explains why, as observed earlier (see § 1), the Charpy impact resistance and the rubber dispersion are continuously improved with the amount of bound SAN until a critical value of grafting.

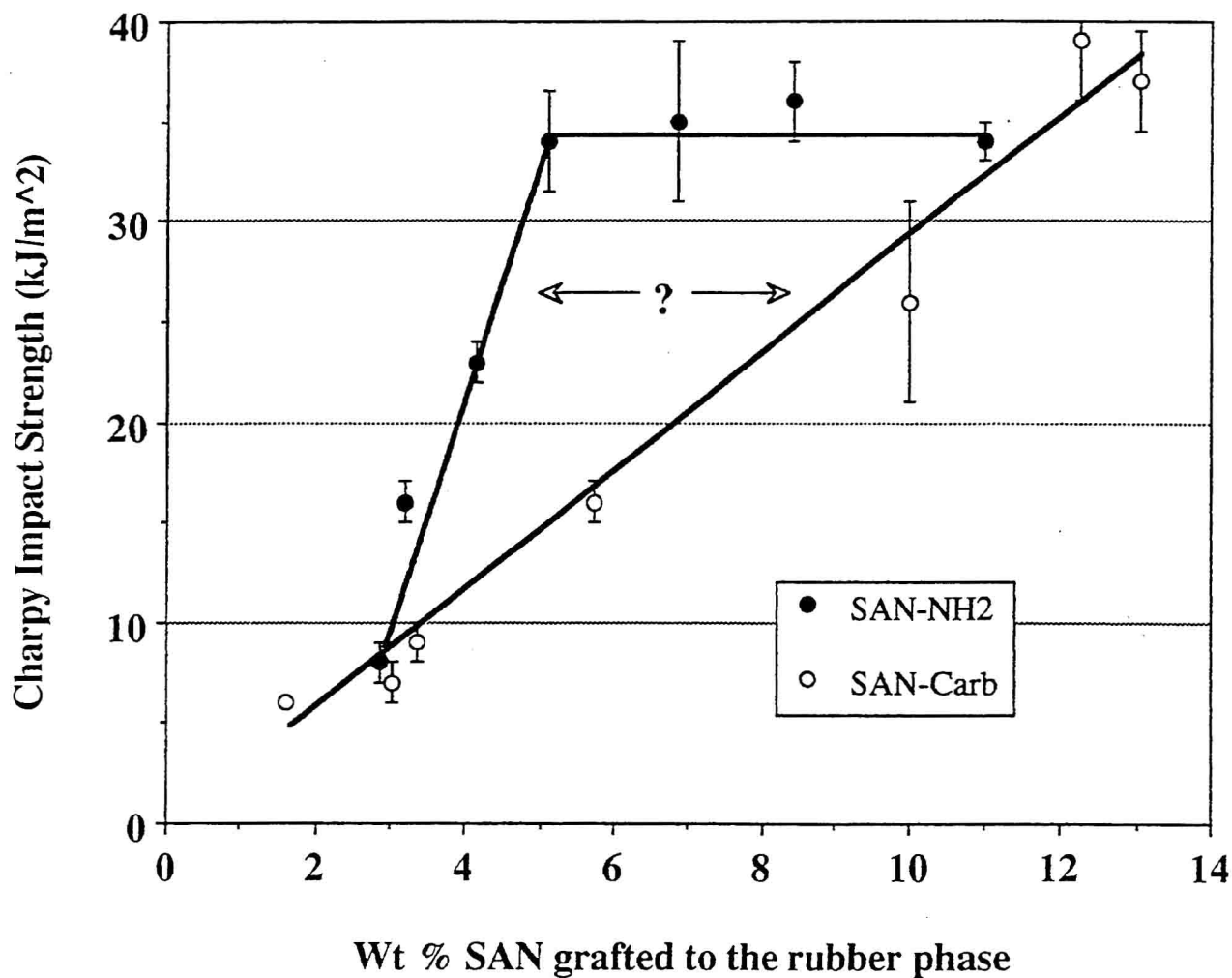
In sharp contrast, when a premade compatibilizer is used, the dependency of the impact strength on the reactive SAN content of the final blend is sigmoidal. It has been observed that at least part of reactive SAN is maintained as sub-inclusions in the rubber phase generating a composite structure for the dispersed rubber phase <sup>7</sup>, as illustrated in Figures 4 c and d. The amount of these sub-inclusions within the dispersed rubber particles has appeared to be affected by the reaction kinetics, i.e. the type of reactive groups attached to SAN, in a close dependency on the SAN/EP composition of the preblend. It is worth noting that only a few sub-inclusions in the rubber have been observed when the constitutive components of polyblends are mixed according to the "in situ compatibilization" (see Figures 4 a and b). In that case, the formed SAN-g-EP graft copolymer resides at the interface between the SAN matrix and the rubber particles rather than being trapped within the rubber phase. This might explain why the "in situ compatibilization" is much more efficient than the alternative method based on a reactive premade compatibilizer in order to provide polyblends with high toughness at least for low concentrations of reactive SAN in the final polyblend.

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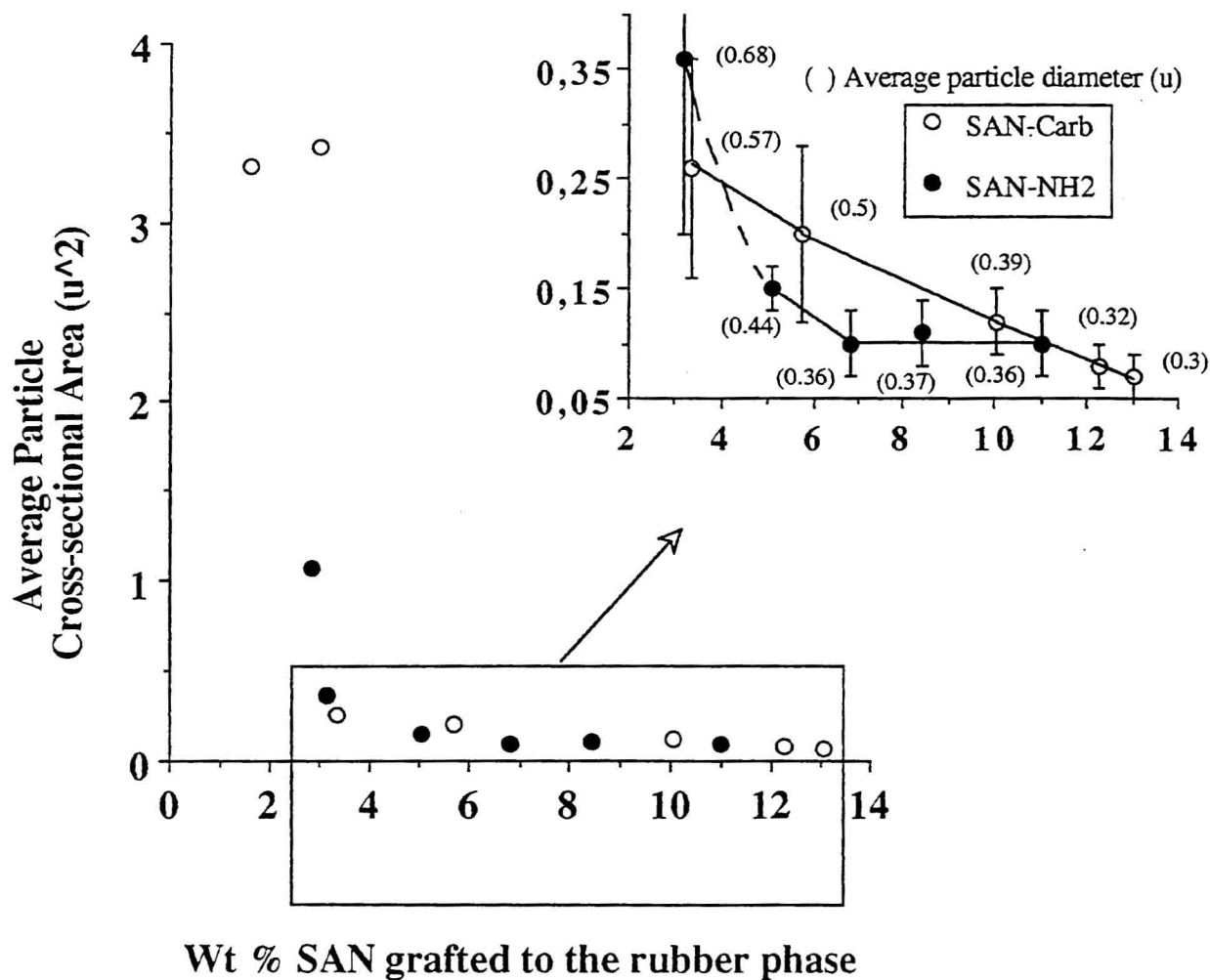
**Table 1: Charpy impact strength of (SAN-NH<sub>2</sub>/SAN)/(EP-g-MA/EPDM 1/1) 75/25 quaternary blends containing 20 wt % SAN-NH<sub>2</sub> (type C, 0.049 mol/wt % NH<sub>2</sub>) in the SAN matrix: effect of the amount of phthalic anhydride added in the blends.**

Anh. (wt %) *	$\sigma_y$ (MPa)	$\sigma_B$ (MPa)	$\epsilon_B$ (%)	Impact (kJ/m <sup>2</sup> )
0	35.5	31	11	22.5±0.7
0.5	38	31	16±4	25±5
1	38	31	14.5±0.2	27±2
1.5	39	31	23±2	30±1
2	41	32	30±1	38±2

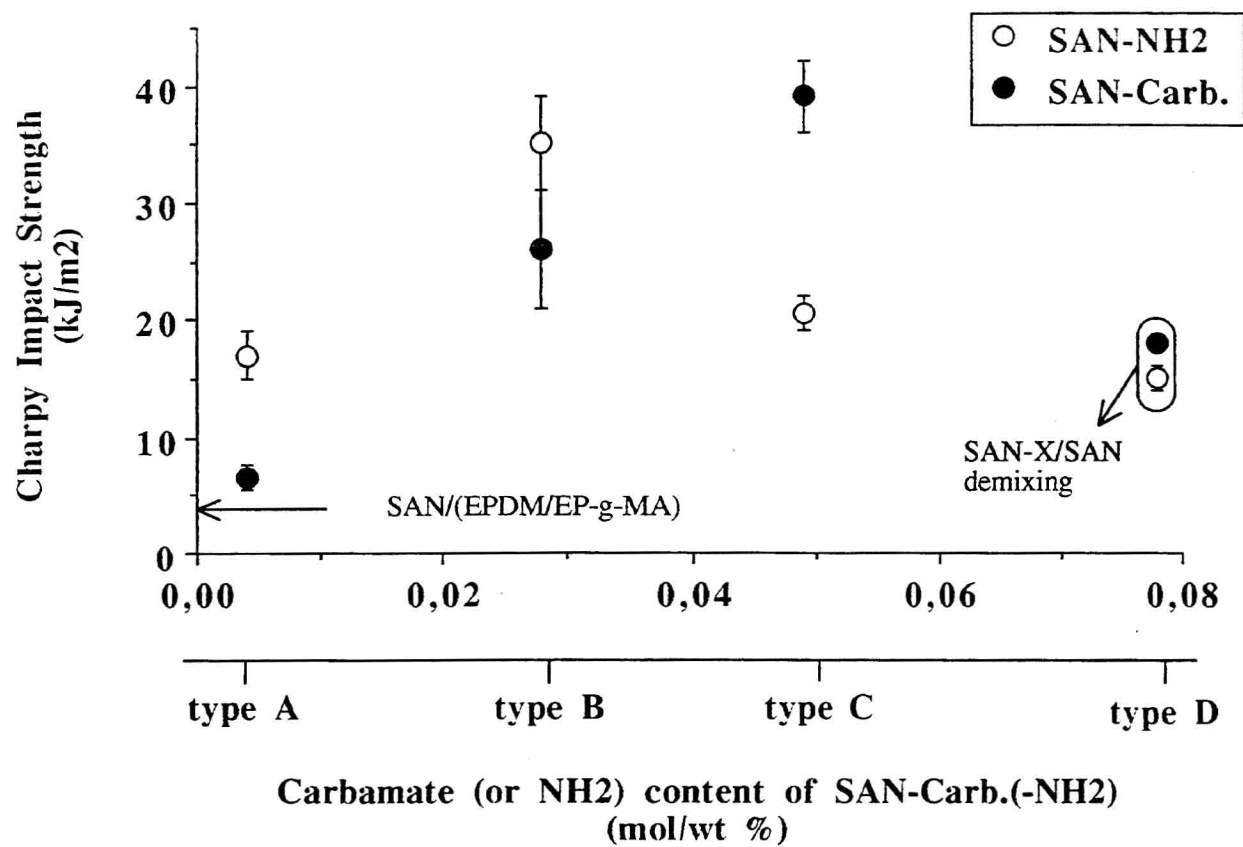
\* Phthalic anhydride wt % in the blend



**Figure 1.** Charpy impact strength as a function of the wt % unextractable (bound) SAN for blends containing SAN-NH<sub>2</sub> (-Carb) (0.028 mol/wt % NH<sub>2</sub> or carbamate).

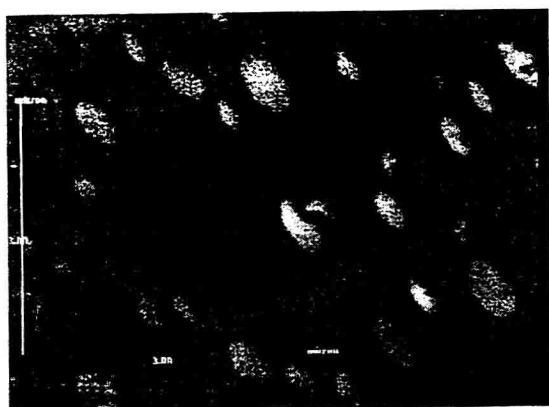


**Figure 2.** Average cross-sectional area ( $\mu^2$ ) (and average diameter in  $\mu$ ) of dispersed phase as a function of the wt % unextractable (bound) SAN for blends containing SAN-NH<sub>2</sub> (-Carb) (0.028 mol/wt % NH<sub>2</sub> or carbamate).



**Figure 3.** Charpy impact strength of (SAN-X/SAN 33.33/66.66)/(EP-g-MA/EPDM 1/1) 75/25 quaternary blends as a function of both the content and the type of SAN reactive groups.





4a



4b



4c



4d

**Figure 4.** TEM of (SAN-NH<sub>2</sub>/SAN)/(EP-g-MA/EPDM 1/1) 75/25 quaternary blends containing 33.33 wt % SAN-NH<sub>2</sub> (type B, 0.028 mol/wt % NH<sub>2</sub>) in the SAN matrix. The reactive SAN is added either to the rubber phase (micrographies c and d) - presence of a composite dispersed phase with a large amount of sub-inclusions- or to the neat SAN (micrographies a and b)- only a few sub-inclusions are observed within the rubber domains.