*Macromol. Symp.* ***149,*** *207–217 (2000)*

# REACTIVE COMPATIBILIZATION OF SAN/EPR BLENDS : EFFECT OF THE KINETICS OF THE COMPATIBILIZATION REACTION ON THE INTERFACIAL ADHESION

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Abstract: The very poor adhesion between films of styrene and acrylonitrile random copolymer (SAN) and maleic anhydride grafted polypropylene (PP-g-MA) can be dramatically improved by an intermediate thin layer of SAN bearing groups reactive toward maleic anhydride. The rate of the interfacial reaction, which is controlled by the reactive groups attached to SAN (amine vs. carbamate) and by the method used to build up the sandwich assembly, has a decisive effect on the capability of the SAN-g-PP graft copolymer formed at the interface to improve the fracture toughness in direct dependence on its molecular architecture.

## INTRODUCTION

Dispersion of rubber phases within a brittle polymer matrix is a way to impart impact resistance to this matrix to an extent that however depends on the interfacial adhesion (Refs. 1-2). Therefore, the capability of reactive compatibilization of immiscible polymers to control the interfacial adhesion is a key question for the production of toughened thermoplastics by traditional melt processing. Lee and Char addressed this question by placing a thin layer of styrene and maleic anhydride random copolymer (SMA) in between films of immiscible polystyrene (PS) and amorphous polyamide (PA) (Ref. 3). At high temperature, poly(styrene-g-polyamide) copolymer is expected to be formed at the interface as result of the intermolecular reaction between the amine end group of PA and the maleic anhydride units of SMA. The experimental data were accounted for by chain entanglements between the compatibilizer and the homopolymers. A previous paper from this laboratory has shown that kinetics of the interfacial reaction has significant effect on the phase morphology and the

CCC 1022-1360/00/$ 17.50+.50/0

ultimate mechanical properties of blends prepared by reactive mixing (Ref. 4). It is thus pertinent to investigate to which extent this kinetics (thus the progress of the interfacial reaction at constant time) can affect the interfacial fracture toughness. For this purpose, films of immiscible styrene and acrylonitrile random copolymer (SAN) and polypropylene grafted with 0.7 wt % maleic anhydride (PP-g-MA) have been assembled with an intermediate thin layer of SAN-X, thus SAN chains bearing X groups able to react with maleic anhydride although at different rates at the same temperature. Primary amine and carbamate have been used as X group, since carbamatye is thermally decomposed into amine (Ref. 5), which is then the rate determining step of the interfacial reaction. So, it is possible to change the kinetics of the interfacial reaction while keeping constant all the other molecular characteristics of SAN-X (molecular weight, length polydispersity, reactive groups content and distribution). The fracture toughness of the interface between SAN and PP-g-MA will be measured by the asymmetric dual cantilever beam technique (ADCB) (Ref. 6) (see experimental section), in relation to both the type and the amount of reactive SAN-X localized at the interface. Since the fracture toughness is known to depend on chain entanglements at the interface and on the areal density of the compatibilizer at the interface (Refs. 6-8), the film assembly will be built up in such a way that these parameters will be changed and their effect studied. From all these experimental data, information on the molecular conformation of the copolymer formed at the interface will be extracted and discussed.

## EXPERIMENTAL

### Materials

SAN used in this work was the RONFALIN 2770 from DSM containing 41.5 mol % acrylonitrile. The maleic anhydride grafted polypropylene (PP-g-MA) contained 0.29 mol % succinic/maleic anhydride groups. Terpolymerization of styrene (55 mol%), acrylonitrile (43 mol%) and a carbamate containing comonomer, {1-methyl-1-[3-(1-methylethenyl)-phenyl]ethyl}carbamic acid 1,1-dimethylethyl ester (2 mol%), was initiated by 2,2'-azobis(2-methylpropionitrile) (AIBN) in toluene at 60°C for 24 h. It was recovered by precipitation in methanol and characterized by NMR and FTIR. The carbamate pendant groups of functional SAN were derivatized into amines either in solution prior to interfacial adhesion experiments

(Ref. 9) or in situ during the melt processing (Ref. 5). The actual carbamate content was 2 mol %, and the molecular weight was $10^5$ with a polydispersity index of 1.5.

### SAN/SAN-X/PP-g-MA sandwich assembly.

In the case of SAN bearing primary amine, the sandwich assembly was built up according to three different routes.

(1) In a first approach, the reactive SAN dissolved in dioxane was spin cast onto the PP-g-MA layer (2 mm thick). The amount of compatibilizer was varied by changing the concentration of the solution from 0.5 to 6 wt %. The SAN sheet (1 mm thick) was then assembled with the reactive SAN coated PP-g-MA sheet. This sandwich was annealed at 200°C for 30 minutes under slight pressure to maintain the contact between the sheets. This first technique will be referred to as *(SAN+ SAN-X+ PP-g-MA).*

(2) In an alternative procedure, the PP-g-MA sheet coated by the reactive SAN layer was annealed for 30 minutes at 200°C prior to the sandwich assembly and final annealing (30 min at 200°C). This second route will be noted *(SAN-X + PP-g-MA)+ SAN.*

(3) In the third method, the reactive SAN dissolved in dioxane was spin cast onto the SAN sheet. This coated SAN strip was then annealed at 200°C for 30 min. The two polymer sheets, i.e. PP-g-MA and SAN coated by thin layer of SAN-X, were joined in the hot press and annealed under the usual conditions. This procedure will be denoted as *(SAN+ SAN-X)+ PP-g-MA.*

In the case of SAN-carb, only method 1 was worked out.

The initial thickness of the spin coated SAN layer was approximated from the thickness measured by optical interferometery for SAN films spin coated on glass wafers under the same spinning conditions as those used for the sandwich assemblies.

### Interfacial adhesion testing

After annealing, the sandwich assembly was cooled down under a small pressure and test samples of 0.9-1 cm width were cut out. The interfacial fracture toughness was measured with the dual cantilever geometry (Ref. 6). A razor blade was inserted between the two constitutive layers, and the length of the crack propagating ahead of the razor blade was measured with a traveling microscope after 24 hrs of equilibration at room temperature. The toughness of the interface ($G_c$) was calculated from equation 1 proposed by Ed. J. Kramer (Ref. 6).

$$G_c = \frac{3\Delta^2 E_1 h_1^3 E_2 h_2^3}{8a^4} \bullet \frac{E_1 h_1^3 C_2^2 + E_2 h_2^3 C_1^2}{\left(E_1 h_1^3 C_2^3 + E_2 h_2^3 C_1^3\right)^2} \qquad (1)$$

with $C_1 = 1+0.64h_1/a$ and $C_2 = 1+0.64h_2/a$. $E_i$ and $h_i$ are the elastic modulus and the thickness of each component i, $\Delta$ is the thickness of the razor blade, and a is the crack length.

## RESULTS AND DISCUSSION

According to Lee and Char (Ref. 3), the combined effect of chain diffusion and reaction at the interface influences the macroscopic fracture toughness. In this work, the reactive SAN chains originally placed between SAN and PP-g-MA can either react with PP-g-MA at the interface, or diffuse far away from the interface to the SAN phase at the annealing temperature. The interfacial adhesion will be controlled by the competition of these two opposite tendencies. Indeed, fast diffusion will decrease the concentration of the mutually reactive groups at the interface and thus the probability of grafting, while the molecular entanglement of reactive SAN chains with bulk SAN will be improved. Conversely, if the interfacial reaction occurs extensively at the interface thus at the expensed of the diffusion of SAN-X into SAN, more graft copolymer will be accumulated at the interface although less extensively entangled within the SAN matrix. So, the improvement of the interfacial adhesion by reactive SAN spin coated at the interface is expected to depend on a fine balance between the diffusion rate (that controls the chain entanglement of copolymer and bulk homopolymers) and the interfacial reaction rate (that controls the areal density of the copolymer at the interface). In this study, the relative importance of diffusion over reaction at the interface will be modified by changing the initial amount of reactive SAN, the SAN functional groups attached to SAN ($NH_2$ *versus* carbamate) and the method used to build up the sandwich assembly.

## Effect of the method used to build up the sandwich assembly

Figure 1 shows that the interfacial adhesion, $G_c$, depends on the thickness of the spin coated film of SAN-$NH_2$ in a way that however depends on the method used to prepare the sandwich assembly. In the case of method 3, thus *(SAN+ SAN-$NH_2$)+ PP-g-MA*, there is a critical thickness of the SAN-$NH_2$ film (ca. 2 μm) beyond which a sharp improvement in the fracture toughness is observed. The preannealing of the (SAN+ SAN-$NH_2$) double layer allows the reactive SAN chains to diffuse into the SAN film, which is favorable to their extensive mutual entanglements and thus to the entanglement of the SAN grafts of the copolymer formed at the interface with SAN. At low amount of reactive SAN originally deposited at the interface, diffusion of SAN-$NH_2$ dominates the reaction at the interface, most of the reactive SAN chains diffusing far away from the interface. Not enough SAN-g-PP graft copolymer is formed at the interface, which accounts for low fracture toughness. Beyond some critical amount of SAN-$NH_2$, diffusion of the SAN-$NH_2$ chains in the SAN matrix is steadily more efficiently counterbalanced by more extensive interfacial reaction, at the advantage of the interfacial strength. When the method 1, thus *(SAN+ SAN-$NH_2$+ PP-g-MA),* is used to prepare the sandwich assembly, $G_c$ increases much more rapidly compared to method 3. In the absence of preannealing, diffusion of the SAN-$NH_2$ chains in the SAN layer and reaction of SAN-$NH_2$ with PP-g-MA occur simultaneously, which is in favor of the interfacial reaction compared to method 3. The areal density of the copolymer at the interface increases thus more rapidly, so that less reactive SAN is required compared to method 3 to impart high interfacial adhesion to the SAN/PP-g-MA assembly. Nevertheless, beyond some critical SAN-$NH_2$ content, the interfacial reaction largely dominates the diffusion of SAN-$NH_2$ into the SAN film, which is detrimental to the entanglements of the graft copolymer chains with SAN. So, decrease of $G_C$ at high SAN-$NH_2$ content (thickness > 300 nm) more likely reflects increasingly less favorable balance between the interfacial reaction of SAN-$NH_2$ and diffusion of these chains apart from the interface. It must also be noted that when the interfacial reaction is fast, the mobility of the chains at the interface is rapidly lost, which prevents chains from reorganizing and thus from contributing to the efficient strengthening of the interface. The very weak interfacial adhesion observed in the case of method 2, thus *(SAN-$NH_2$ + PP-g-MA)+ SAN,* is in line with the aforementioned discussion. Indeed, preannealing of the (SAN-$NH_2$+ PP-g-MA) reactive double layer allows to completely dissociate the two competing processes, the interfacial reaction occurring now before the SAN-$NH_2$ chains have the opportunity to diffuse into the SAN layer. It is clear that the SAN branches of the ''preformed'' SAN-g-EP copolymer face severe restrictions of interdiffusion within the SAN film when the final sandwich is assembled and annealed, accounting for the dramatically low fracture toughness. The probability for the SAN-$NH_2$ chains to diffuse into the SAN layer before being immobilized by the interfacial reaction with PP-g-MA increases from method 2, to method 1 and finally to method 3. The probability for the interfacial reaction to occur preferably increases according to the reverse order and with the content of reactive SAN. Therefore, it is not surprizing that method 1 is most efficient at an intermediate SAN-$NH_2$ content, as shown in fig. 1. These data support that reactive SAN chains have to be sufficiently entangled with neat SAN before reacting at the interface, otherwise the SAN/PP interface remains fragile.

## Effect of the functional groups attached to SAN

The reactive groups attached to SAN, i.e. primary amines or carbamates, have a strong effect on the fracture toughness as shown by figure 2 in the case of method 1, thus *(SAN+ SAN-X+ PP-g-MA).* When the initial thickness of the reactive SAN film at the interface is increased, the probability for the interfacial reaction to occur is also increased with respect to diffusion (Ref. 3).Two regions, a and b, can be distinguished in figure 2, according to the way the fracture toughness depends on the reactive groups. In region a, the fracture toughness increases with the amount of SAN-X available. Consistently with the higher reactivity of the primary amine compared to carbamate, $G_c$ increases more rapidly. In region b, the reverse tendency is observed. Indeed, $G_c$ goes on increasing with the amount of SAN-carb until leveling off at ca. 700 J/$m^2$. In sharp contrast, when the more reactive SAN-$NH_2$ is concerned, further increase in the SAN-$NH_2$ amount is deleterious to the fracture toughness, since $G_c$ decreases sharply from 300 to 100 J/$m^2$, when the thickness of the spin coated film is increased from 300 nm to 2 μm. Thus SAN-$NH_2$ is much less effective than SAN-carb in promoting high ultimate fracture toughness.

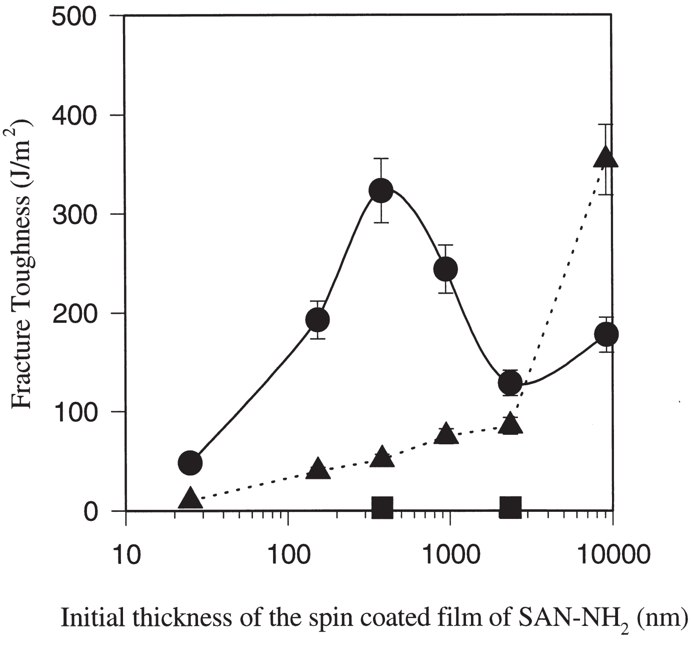

Fig. 1. Interfacial toughness of SAN/SAN-$NH_2$/PP-g-MA sandwich assembly as function of the thickness of the spin coated film of SAN-$NH_2$. Effect of the method used to build up the sandwich assembly : method 1 or *SAN+ SAN-$NH_2$+ PP-g-MA* (●) ; method 2 or *SAN+ (SAN-$NH_2$+ PP-g-MA)* (■) and method 3 or *(SAN+ SAN-$NH_2$) + PP-g-MA* (▲).

The way the interfacial reaction is conducted, i.e. the $NH_2$/MA pair *versus* the carbamate/MA pair, affects not only the extent of the interfacial reaction, but also the capability of the graft copolymer formed *in situ* to improve the fracture toughness in a strong dependence on its molecular architecture. Indeed, as reported elsewhere (Ref. 10), the maleic anhydride-primary amine reaction is rapid and more complete than the maleic anhydride-carbamate reaction. In the case of SAN-carb, the course of the interfacial reaction is controlled by the slow release of the amines which is the rate determining step. This very slow conversion of carbamates into amines (k= 0.0084 $min^{-1}$ at 200°C) strongly suggests that when one carbamate group has reacted at the interface, the chance for another carbamate of the same chain to be transformed into amine and to react at the interface is so small that another chain can compete efficiently for grafting at the same interface. In the case of SAN-$NH_2$, the interfacial reaction is much faster, so that when one amine has reacted, other amine groups of the same chain (there are 28 amines per chain on average) are prone to react with PP-g-MA immediately.

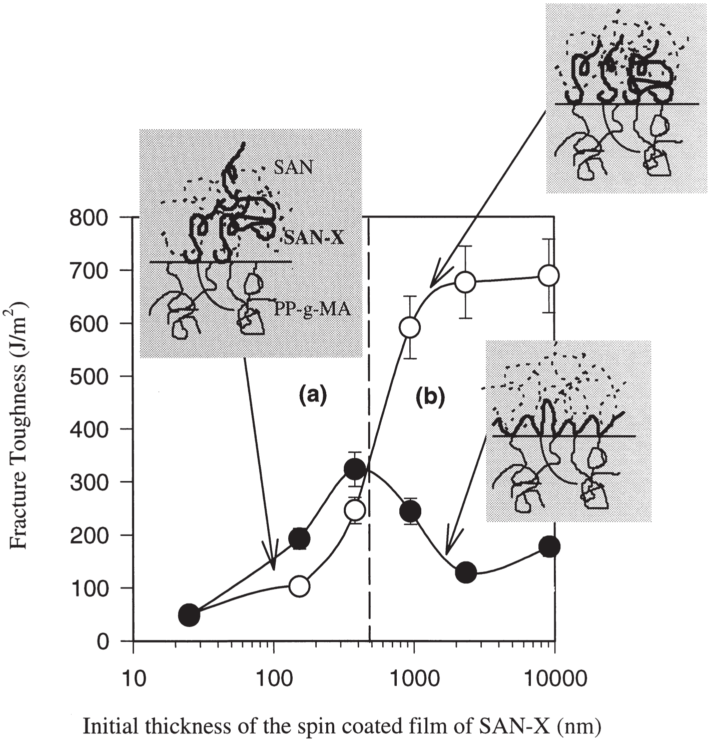

Fig. 2: Interfacial toughness for the SAN/SAN-X/PP-g-MA sandwich assembly prepared according to the method 1, thus *SAN*+ $SAN\text{-}NH_2$+ *PP-g-MA*. Effect as function of the thickness of the spin coated film of either SAN-$NH_2$ (●) or SAN-carb (○).

In consequence of the much higher probability for several amines of the same chain to react at the interface (Refs. 11-12), the grafted SAN-$NH_2$ chains are expected to be more extensively spread over the interface through multiple bonding, compared to the SAN-carb chains that are rather tethered to the interface through one or at least very few bonds. A tentative sketch of the architecture of the graft copolymer formed in the region (b) of figure 2 is shown in this figure. When grafted to PP-g-MA, the SAN-$NH_2$ chains have to form small loops which are not efficiently entangled with chains of the SAN film. In contrast, SAN-carb chains have the opportunity to penetrate the SAN layer and to contribute to the fracture toughness.

## CONCLUSIONS

Although the adhesion between premade films of SAN and PP-g-MA is expected to be improved by an intermediate layer of SAN reactive toward PP-g-MA (SAN-$NH_2$ or SAN-carb), the improvement of $G_c$ is strongly dependent on the capability of the SAN chains grafted at the interface to penetrate into and be entangled with the SAN layer. This mutual entanglement of the SAN-X and neat SAN chains before reaction appears to be prerequisite to provide polyblends with high interfacial adhesion. This requirement is actually met in real systems (thus melt blending), since both the reactive chains, i.e. SAN-X and EP-g-MA, are homogeneously dispersed in their host polymer phase before reaction (Ref. 13).

Moreover, the type of reactive group attached onto SAN affects not only the extent of the compatibilization reaction, but also the capability of the graft copolymer to improve the interfacial adhesion in direct dependence on its molecular architecture. SAN-carb imparts higher ultimate interfacial adhesion to the SAN/PP-g-MA assembly than SAN-$NH_2$, because the grafted SAN-carb chains are essentially tethered to the interface and prone to be entangled within the bulky SAN, as reported elsewhere (Ref. 13). In contrast, SAN-$NH_2$ chains are grafted through multiple bonding to PP, which is responsible for flat conformation less suited to physical anchoring to the bulk. This effect is as important as the content of reactive groups of SAN (of constant molecular weight) is high (Ref. 13).

## ACKNOWLEDGEMENT

C.P. and R.J. are grateful to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" for general support in the frame of the "PAI-4/11 : Chimie Supramoléculaire et Catalyse Supramoléculaire". They also thank N. Moussaif for stimulating and helpful discussions and C. Franssen and P.A. Blanche (Centre Spatial Liégeois) for assistance with interfacial adhesion measurements and measurements of film thickness by optical interferometry, respectively. The authors are much indebted to DSM for financial support and for a fellowship to one of them (C.P.).

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(13) C. Pagnoulle, R. Jérôme, "Reactive compatibilization of SAN/EPR blends : Effect of type and content of reactive groups randomly attached to SAN", in preparation. In order to investigate the effect of the compatibilization reaction in the case of melt processing, quaternary (SAN/SAN-X)/(EPDM/EP-g-MA) [(75-Y/Y)/(12.5/12.5)] mixtures have been melt blended with a laboratory two-roll mill at 200°C for 7 min, while changing the average number of reactive groups (X) per SAN chain, i.e. 0.004, 0.028 and 0.049 mol/wt % of either primary amine or carbamate. At constant $NH_2$/MA molar ratio (e.g. 3), it appears that the size of the dispersed EPDM phases (0.42 μm) is independent of the $NH_2$ content of the chains, whereas the impact strength of the blends decreases from 30 to 25 and 17 kJ/$m^2$, as the amine content is increased from 0.004 to 0.028 and 0.049 mol $NH_2$/wt %, respectively. In parallel, the cross-sectional surface area per SAN chain bound at the interface (A) is found to increase with the

amine content (0.004 mol $NH_2$/wt % : 9.05 $nm^2$, 0.028 mol $NH_2$/wt % : 22.6 $nm^2$ and 0.049 mol $NH_2$/wt % : 30.2 $nm^2$). In contrast, A is less sensitive to the carbamate content, a single value of ca. 9 $nm^2$ being calculated whatever the carbamate content of the SAN chains. These observations are indicative of the more flat conformation at the interface for the SAN-$NH_2$ chains grafted through multiple bonding in a strong dependence on the amine content. The slow conversion of carbamate into amine explains that the carbamate content has no marked effect on the conformation of the grafted SAN chains, which are basically tethered at the interface.