

4) 1995

63

THE TECHNOLOGICAL COMPATIBILIZATION OF NATURAL RUBBER/POLYSTYRENE BLENDS BY THE ADDITION OF NATURAL RUBBER-*graft*-POLYSTYRENE

R. ASALETHA AND SABU THOMAS*

SCHOOL OF CHEMICAL SCIENCES, MAHATMA GANDHI UNIVERSITY, PRIYADARSHINI HILLS P.O.,
KOTTAYAM-686 560, KERALA, INDIA

AND

M. G. KUMARAN

RUBBER RESEARCH INSTITUTE OF INDIA, KOTTAYAM, KERALA-686 009, INDIA

ABSTRACT

Compatibility of natural rubber (NR)/polystyrene (PS) blend is poor and can be enhanced by the addition of a graft copolymer of natural rubber and polystyrene (NR-*graft*-PS). The effects of homopolymer molecular weight, copolymer molecular weight, copolymer concentration, processing conditions and mode of addition on the morphology of the dispersed phase have been investigated by means of optical microscopy. The addition of a small percentage of the compatibilizer decreases the domain size of the dispersed phase. The effect levels off at higher concentrations. The leveling off could be an indication of interfacial saturation. The experimental results were compared with the theoretical predictions of Noolandi and Hong. The addition of the graft copolymer improves the mechanical properties of the blend and attempts were made to correlate the mechanical properties with the morphology of the system. Attempts were also made to understand the conformation of the graft copolymer at the interface.

INTRODUCTION

Thermoplastic elastomers (TPEs) are a relatively new class of materials which combine the excellent processing characteristics of the thermoplastics and the elastic characteristics of the rubbers. They can be obtained by blending the constituent materials. Various parameters like the selection of the rubber and thermoplastic, blend ratio, processing conditions, etc., affect the properties of the TPEs.

Nowadays blending of different polymers which will combine the properties of the constituent materials is a commonly accepted method. Even though blending is an easy method for the preparation of TPEs, most of the TPE blends are immiscible. Very often the resulting materials exhibit poor mechanical properties due to the poor adhesion between the phases. Over the years different techniques have been developed to alleviate this problem. These include (1) the addition of a third homopolymer or graft or block copolymer which is miscible with the two phases, and (2) the introduction of covalent bonds between the homopolymer phases. The first approach can be considered as nonreactive compatibilization and the second as reactive compatibilization. This paper, in fact, deals with the nonreactive compatibilization technique instituted by the addition of graft copolymer.

There are several studies in literature in which the addition of copolymer increases the technological compatibility of immiscible polymer pairs. Incorporation of a copolymer usually improves the interaction between the constituent homopolymers and thereby slows down the phase separation process.¹⁻⁴ It was reported by Paul^{5,6} that the copolymer addition will provide finer dispersion, improve interfacial adhesion, stability against gross segregation and will reduce the interfacial tension.

In a pioneering work, Riess and coworkers reported on the compatibilizing action of copolymers in polystyrene/poly(methylmethacrylate) and polystyrene/polyisoprene

* Author to whom all correspondence should be addressed.

blends.^{7,8} They have reported that block copolymers are more effective than graft copolymers in the above systems. They further concluded that the solubilization occurs only when the molecular weight of the homopolymers are less than or comparable to the molecular weight of the corresponding segment in the block copolymer.

Compatibilizing action of poly(styrene-*block*-isoprene) in polystyrene/polyisoprene blend has been reported by Inoue and coworkers.^{9,10} Morphology of the system was analyzed and it was found that a fine morphology is obtained by the addition of a few percentage of the block copolymer. Teyssie and coworkers¹¹⁻¹³ have examined the compatibilizing action of copolymers in a large number of systems. They suggested that molecular weight and structure of the copolymer are the controlling parameters which will effect the efficiency of the compatibilizer. They have compared the efficiency of tapered and pure block copolymer in polystyrene/polyethylene system and was found that tapered block copolymer is more effective than the pure block copolymer.

Patterson, Hu and Grindstaff¹⁴ have studied the poly(dimethylsiloxane)/poly(oxyethylene-*block*-oxypropyl ene) blends, compatibilized by the addition of poly(dimethyl siloxane-*block*-oxyethylene). The lowering of the interfacial tension upon the addition of the copolymer was reported by several researchers. For example, Gailard and coworkers¹⁵ have reported on the reduction in interfacial tension in polystyrene/polybutadiene/styrene ternary blend by the addition of poly(styrene-*block*-butadiene) copolymer. Studies of Willis and Favis dealt with polystyrene-maleic anhydride/bromobutyl rubber blends which was compatibilized by the addition of dimethylaminoethanol. More recently,¹⁷⁻¹⁹ forward recoil spectroscopy, small angle x-ray scattering, neutron reflectivity methods were successfully used to analyze the interface of various polymer blends in the presence and absence of copolymers.

Coran and Patel²⁰⁻²² reported a series of thermoplastic elastomer compositions. These include blends of nylon and various synthetic rubbers like ethylene-vinyl acetate, ethylene-propylene-diene monomer rubber, chlorinated polyethylene, polyurethane rubber, etc.²³ Coran and Patel²⁴ further reported on thermoplastic elastomers from blends of polystyrene and various rubbers such as IIR, ethylene-propylene-diene monomer, natural rubber, styrene-butadiene rubber, butyl rubber, acrylate rubber, chloroprene rubber, nitrile rubber, and poly(*trans*-pentamer) rubber. The mechanical properties of the blends were correlated with parameters like critical surface tension for wetting, crystallinity, tensile strength of the hard phase and critical entanglement spacing.

Technological compatibilization of dissimilar rubber-plastic blends were also discussed in detail by Coran and Patel.²⁵ For example, in the case of the polyolefin/nitrile rubber system, compatibilization using phenolic modified, maleic modified, triethylenetetramine modified, and chlorine treated powdered polyolefin was discussed. The *in-situ* formed modified polyolefin-rubber copolymer acts as the compatibilizer in the above cases. Dynamic vulcanization as a technique for compatibilization was adopted by Gessler²⁶ and Fischer.²⁷

Finally Leibler,^{28,29} Noolandi and Hong³⁰⁻³² developed thermodynamic theories concerning the effect of copolymers in heterogeneous polymer blends. According to Leibler, the reduction in interfacial tension is due to the adsorption of copolymers at the interface. An asymmetric copolymer will be less active as a compatibilizer compared to a symmetric one. The aim of Noolandi and Hong's theory was to obtain an expression for interfacial tension reduction. The reduction in interfacial tension for a range of copolymer and homopolymer molecular weights was calculated. The results were then compared with the experimental results of Riess and coworkers.

In this paper we report on thermoplastic elastomers from blends of natural rubber (NR) and polystyrene (PS) which are highly incompatible. Until now, no serious attention has been given to the compatibilizing action of copolymers in these blends. The effects of the graft copolymer of NR and PS (NR-*graft*-PS) on the mechanical and morphological properties of NR/PS blends have been analyzed. The influence of copolymer concentration, molecular weight of homo and copolymers, mode of addition and nature of casting solvents on the morphology and properties of the blends has been quantitatively investigated. Attempts

were made to deduce the graft copolymer conformation at the interface. Finally, the experimental results were compared with the current theories of Noolandi and Hong.

EXPERIMENTAL

Polystyrene was supplied by Poly Chem Ltd., Bombay, India. Natural rubber (ISNR-5) was supplied by Rubber Research Institute of India, Kottayam. The characteristics of the materials used are given in Table I.

The graft copolymer of NR and PS (NR-*graft*-PS) was prepared by polymerizing styrene in rubber latex using ^{60}Co γ radiation as the initiator.³³ Styrene monomer was made into an emulsion which was then mixed with NR latex of known dry rubber content (DRC) at room temperature and exposed to ^{60}Co γ radiation for 16 h. The dose rate was 0.1166 Mrd/min. The free homopolymers natural rubber and polystyrene were removed from the crude sample by extraction with petroleum ether and methyl ethyl ketone, respectively.

BLEND PREPARATION AND CHARACTERIZATION

Natural rubber (NR) and polystyrene (PS) were blended together in a common solvent: chloroform (A 5% solution was made for casting). Different compositions of the blends: 40/60, 50/50 and 60/40, were made with and without the addition of the graft copolymer. To study the effect of casting solvent, blends were also made from carbon tetrachloride. Natural rubber, polystyrene and the graft copolymer were mixed in chloroform. The mixture was kept overnight and then stirred for eight hours with a magnetic stirrer. Films were cast on a glass plate and dried in a vacuum oven at 80°C for 48 h, and then at 120°C for a further 4 h. The morphologies of the samples were studied by optical microscopy and the mechanical properties were determined according to ASTM standard procedures using a Zwick Universal Testing Machine.

The influence of the mode of addition of the graft copolymer was studied in three ways. In the first case the minor phase (PS) and the graft copolymer were premixed, kept overnight and stirred for 7 h; then NR was added to the mixed solution, kept overnight again and stirred for a further 7 h. In the second case, the same was repeated by premixing the major phase (NR) and graft copolymer. In the third case, the graft copolymer was added to the NR/PS blend directly. The morphologies of all the systems were examined as mentioned earlier. The effect of homopolymer and graft copolymer molecular weight on compatibilization was studied by using natural rubber, polystyrene and NR-*graft*-PS of different molecular (Table I).

TABLE I
CHARACTERISTICS OF THE MATERIALS USED

Material	Density (g/cm ³)	Solubility parameter (cal/cm ³) ^{1/2}	Molecular weight (M_n)
NR ₀	0.90	7.75	7.79×10^5
NR ₅	0.90	7.75	3.7×10^5
NR ₁₀	0.90	7.75	2.49×10^5
NR ₁₅	0.90	7.75	1.62×10^5
PS ₁	1.04	8.56	3.51×10^5
PS ₂	1.04	8.56	2.073×10^5
G ₁ (NR- <i>graft</i> -PS)	—	—	3.95×10^5
G ₂ (NR- <i>graft</i> -PS)	—	—	1.009×10^5
CHCl ₃	—	9.30	—
CCl ₄	—	8.60	—

RESULTS

GRAFT COPOLYMER CHARACTERIZATION

Graft copolymer (NR-*graft*-PS) was characterized by FTIR spectroscopy, ^1H NMR spectroscopy and gravimetric methods. The grafting efficiency and percentage of PS grafted were 49% and 20%, respectively. This has been estimated by gravimetric analysis as reported earlier.³⁴

The FTIR spectrum shows peaks at 3026 and 2855 cm^{-1} which correspond to aromatic C—H stretching in PS. Peaks at 1601 cm^{-1} and 1541 cm^{-1} correspond to C=C stretching of the aromatic ring of PS. The peaks at 1452 and 1375 cm^{-1} correspond to the aliphatic C—H stretching in NR.

The ^1H NMR spectrum obtained at 90 MHz shows chemical shifts at 1–2, 4.6–4.8, and 6.6 ppm corresponding to alkyl protons of NR, vinyl protons and aromatic protons of polystyrene, respectively.

EFFECT OF GRAFT COPOLYMER CONCENTRATION ON MORPHOLOGY

NR/PS blends are completely immiscible. Large polystyrene domains are dispersed in the continuous NR matrix. The compatibility of the above system can be improved by the addition of a compatibilizer *i.e.*, a graft copolymer of NR and PS (NR-*graft*-PS). It was seen that the size of the dispersed polystyrene domains decreases with the increasing percentage of the graft copolymer. Figure 1 shows the optical microphotographs of 50/50 NR/PS blends with and without the addition of the copolymer. In this blend the NR is the continuous phase and PS is the dispersed phase. The number average domain size measurements were done by noting the diameter of about 100 domains at random in each blend system. The average domain size decreases with increasing concentration of the compatibilizer and finally levels

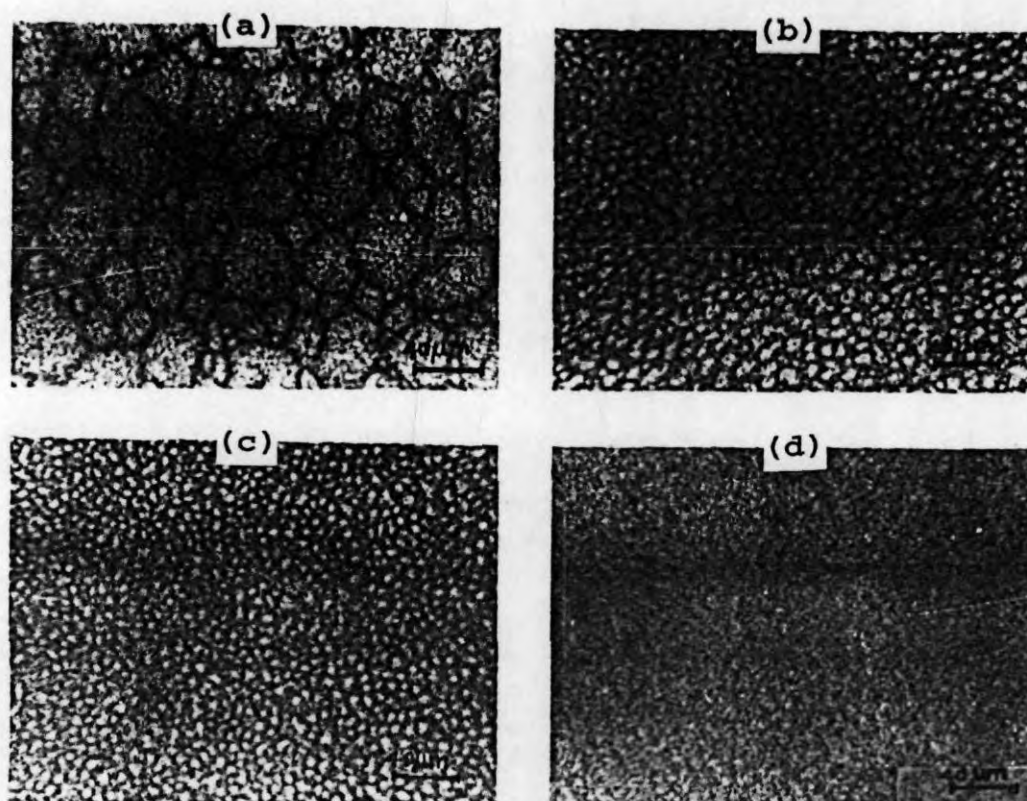


FIG. 1. — Optical photographs of 50/50 NR/PS blends with variable amounts of graft copolymer; (a) 0%; (b) 1.5%; (c) 3%; (d) 6%.

off at higher concentrations (Figure 2). This leveling point can be considered as the so-called apparent critical micelle concentration (CMC) *i.e.*, concentration of the copolymer at which micelles are formed. This sort of micelle formation is highly undesirable. From Figure 2, the CMC values were, in fact, estimated from the intersection of the straight line drawn in the low concentration and the leveling off line at high concentration. It is important to indicate that generally CMC is estimated from the plot of interfacial tension versus copolymer concentration. Since the interfacial tension is directly proportional to the domain size, the estimation of CMC from the plot of domain size versus concentration is justified.³⁵

Let us now look at 50/50 blend in detail. Here the leveling point (CMC) was found to be at 0.8% compatibilizer loading. The domain size of the blend without graft copolymer is 26.88 μm . Addition of 1.5% graft reduces the domain size to 3.493 μm ; *i.e.*, a reduction of 82.7% occurs. Addition of another 1.5% causes a reduction of 38% in the domain size. Finally the domain size levels off at higher concentrations. In the case of 60/40 and 40/60 NR/PS blends the percentages of graft copolymer required to saturate the interface (*i.e.*, CMC) are 1.5% and 0.6%, respectively.

The domain size distribution for 50/50 NR/PS blend with and without the addition of the compatibilizer is given in Figure 3. Table II gives the standard deviation values of the blend (50/50) with and without the addition of the copolymer. These values decrease with increasing loading of the copolymer. The uncompatibilized blend contains large numbers of bigger particles. The polydispersity is higher for the blend without compatibilizer and is much reduced at higher concentration of the compatibilizer, which is evident from the width of the distribution curve. Similar studies have been reported by Willis and Favis³⁶ and by Djakovic *et al.*³⁷

Figure 4 shows the effect of compatibilizer on the interparticle distance of dispersed domains in the 50/50 NR/PS blend system. The interparticle distance decreases with increasing concentration of the compatibilizer and finally levels off at higher compatibilizer loading.

EFFECT OF HOMOPOLYMER AND GRAFT COPOLYMER MOLECULAR WEIGHTS ON MORPHOLOGY

The compatibilizing effect of the graft copolymer in NR/PS blends depends very much on the molecular weight of the homopolymer. Generally, the amount of the graft copolymer

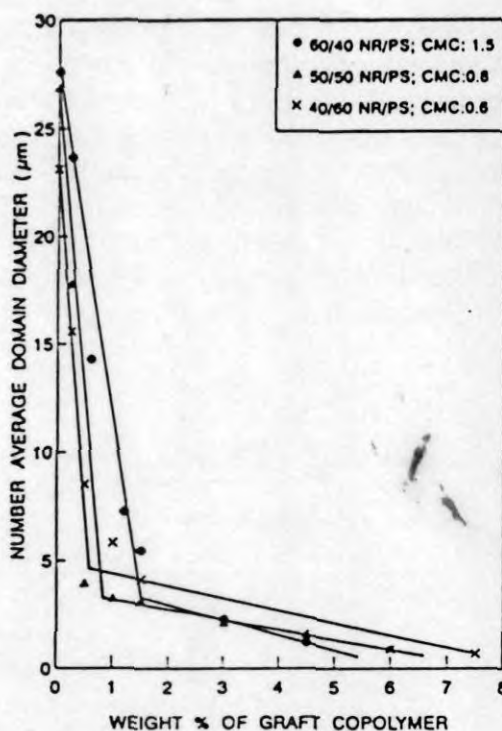


FIG. 2. — Effect of copolymer concentration on the average domain size of the dispersed phase for different NR/PS blends.

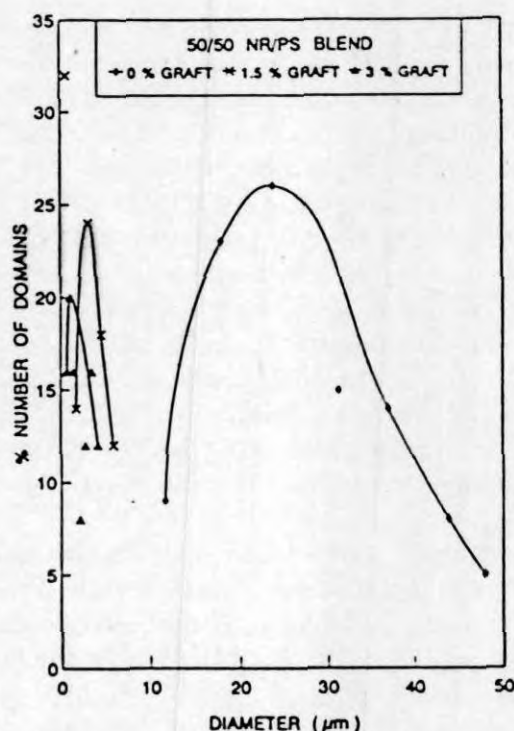


Fig. 3. — Effect of copolymer concentration on the average domain size distribution of 50/50 NR/PS blends.

required for compatibilization is proportional to the molecular weight of the homopolymer. Natural rubbers and polystyrenes of the following molecular weights were used to study the effect of homopolymer molecular weight on the compatibilizing action of the graft copolymer — natural rubber: $NR_0 = 7.79 \times 10^5$; $NR_5 = 3.7 \times 10^5$; $NR_{10} = 2.49 \times 10^5$; $NR_{15} = 1.62 \times 10^5$; and polystyrene: $PS_1 = 3.51 \times 10^5$; $PS_2 = 2.073 \times 10^5$.

The amount of graft copolymer required to saturate unit volume of the interface (CMC) was found to decrease with decrease in molecular weight (Figures 5 and 6) of the homopolymers. The average domain size decreases with an increase in graft loading. The influence of polystyrene molecular weight on CMC values and domain size is given Table III.

Molecular weight of the copolymer (NR-graft-PS) influences the interfacial saturation point. We have used graft copolymers of molecular weight $G_1 = 3.95 \times 10^5$ and $G_2 = 1.009 \times 10^5$. The amount of graft copolymer needed for interface saturation decreases with increase in molecular weight of the compatibilizer. The critical micelle concentration was found to be 1.5% in the case of 60/40 NR/PS blends compatibilized with sample G_1 . The same blend system with sample G_2 gives a higher CMC value; i.e., a 3% compatibilizer loading was required to saturate unit volume of the interface.

TABLE II
STANDARD DEVIATION VALUES OF 50/50 NR/PS BLEND

% Graft copolymer	Average domain size	
	(μm)	Standard deviation
0.5	3.5	25.45
1	3.2	23.40
1.5	3.4	24.95
3	2.1	7.40
4.5	1.6	11.70
6	0.9	2.15

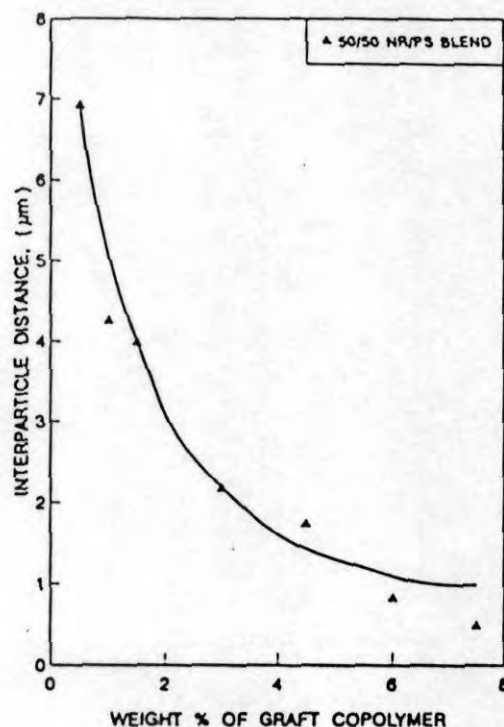


FIG. 4. — Effect of copolymer concentration on the interparticle distance of the dispersed phase of 50/50 NR/PS blend.

EFFECT OF MODE OF ADDITION OF GRAFT COPOLYMER ON MORPHOLOGY

Morphology of the blend depends very much on the mode of preparation of the blends. Variation in the conditions of blend preparation can change the morphology. Cimmino *et al.*³⁸ have observed a drastic change in the domain size of nylon/rubber blends when prepared in two steps compared to one-step mixing.

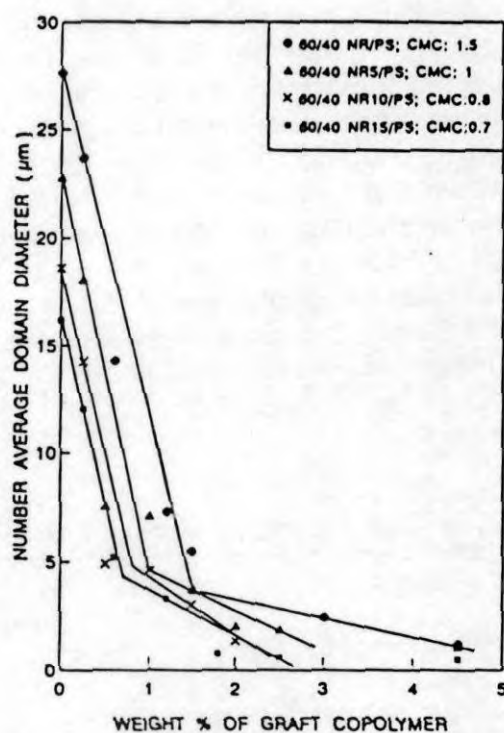


FIG. 5. — Influence of NR molecular weight on morphology of different NR/PS blends.

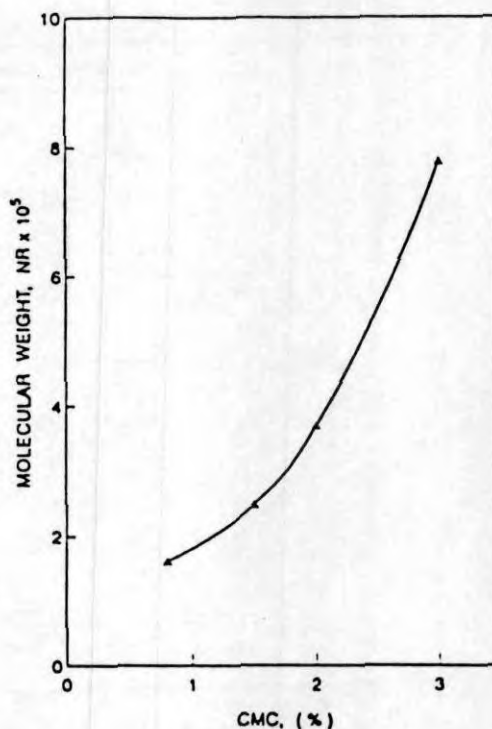


FIG. 6. — Effect of NR molecular weight on the apparent critical micelle concentration, CMC.

The two-step mixing can be done in two ways. Blending the solution of the dispersed phase (PS) with the compatibilizer first and then blending with the matrix polymer (NR). In the second case the matrix polymer is blended with the compatibilizer first and then blending with the dispersed polymer. Solutions were blended and then evaporated to get thin films. Preblending the compatibilizer with the dispersed phase (PS) is found to improve the interaction between the copolymer and the dispersed phase.

The particle size and CMC of NR₀/PS blends were measured in the two-step mixing and were compared the values with those of one-step mixing. In the case of 60/40 NR/PS blends (one-step) the CMC was attained at 1.5% of the graft copolymer. When the copolymer phase was preblended with the dispersed phase, the CMC was attained at 1.3% of the graft copolymer loading and there is much reduction in the domain size of the dispersed phase. In one-step mixing, the particle size of the domains at 1.5% graft copolymer loading was found to be 5.08 μm whereas in two-step mixing the corresponding value is 3.70 μm ; at 2.5% graft loading, the values are 2.45 μm and 1.84 μm , respectively. When the matrix polymer was preblended with the copolymer, the CMC was the same as in the case of one-step mixing (1.5%) (see Table IV).

The above findings reveal that the mode of addition of the compatibilizer has an important role in the morphology of the blends. Compared to one-step mixing, in two-step mixing *i.e.*, by preblending the compatibilizer with the dispersed phase, the amount of the compatibilizer

TABLE III
EFFECT OF MOLECULAR WEIGHT OF PS ON CMC VALUES

Sample	Mol wt. (M_n)	CMC (%)	Domain radius (r) at CMC (μm)
PS ₁	3.51×10^5	1.5	1.80
PS ₂	2.07×10^5	1.2	1.28

TABLE IV
DISPERSED PHASE RADIUS (r) AT CMC AND ' Σ ' VALUES OF THE SYSTEM

Polymer blends	Solvent	CMC (m) (%)	Radius r at CMC (μm)	' Σ ' (nm^2)
40/60 (NR ₀ /PS ₁ /G ₁)	CHCl ₃	0.6	1.30	100.9
50/50 (NR ₀ /PS ₁ /G ₂)	CHCl ₃	0.8	1.71	71.9
60/40 (NR ₀ /PS ₁ /G ₁) ^a	CHCl ₃	1.5	2.54	30.98
60/40 (NR ₀ /PS ₁ /G ₁) ^b	CHCl ₃	1.3	1.85	49.10
60/40 (NR ₀ /PS ₁ /G ₁) ^c	CHCl ₃	1.5	2.45	32.12
60/40 (NR ₀ /PS ₁ /G ₁)	CCl ₄	1.1	1.30	82.55
60/40 (NR ₀ /PS ₁ /G ₂)	CHCl ₃	3.0	0.65	15.46
60/40 (NR ₆ /PS ₁ /G ₁)	CHCl ₃	1.0	2.36	50.02
60/40 (NR ₁₀ /PS ₁ /G ₁)	CHCl ₃	0.8	2.45	60.08
60/40 (NR ₁₅ /PS ₁ /G ₁)	CHCl ₃	0.7	2.60	64.97

^a One-step mixing.

^b Two-step mixing NR to PS + G.

^c Two-step mixing PS to NR + G.

diffused into the interface can be increased and the distance travelled by the compatibilizer to reach the blend interface can be minimized. This leads to better interfacial interaction of the compatibilizer and results in a finer morphology. A speculative model has been given to illustrate this behavior (Figure 7).

EFFECT OF CASTING SOLVENTS ON MORPHOLOGY

Casting solvent plays an important role in the morphology of blends. The same blend system can give different morphologies in different casting solvents.

We have selected two solvents for comparison: chloroform and carbon tetrachloride. There is much difference in the resulting domain size for the two solvent systems. Films cast from carbon tetrachloride show a finer morphology than chloroform cast films (Figure 8). The difference in the behavior may be due to the difference in the level of interaction between the copolymers and solvents. This has been well addressed by the pioneering studies of Cobard and Patterson.³⁹

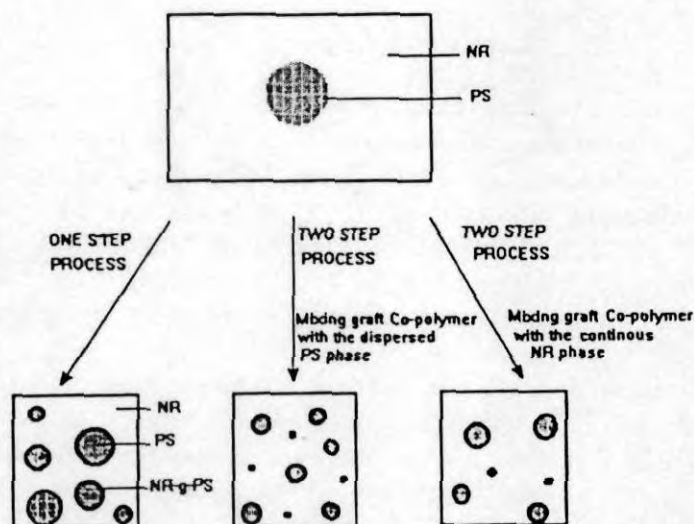


Fig. 7.—Speculative model illustrating the compatibilization efficiency under different modes of copolymer addition.

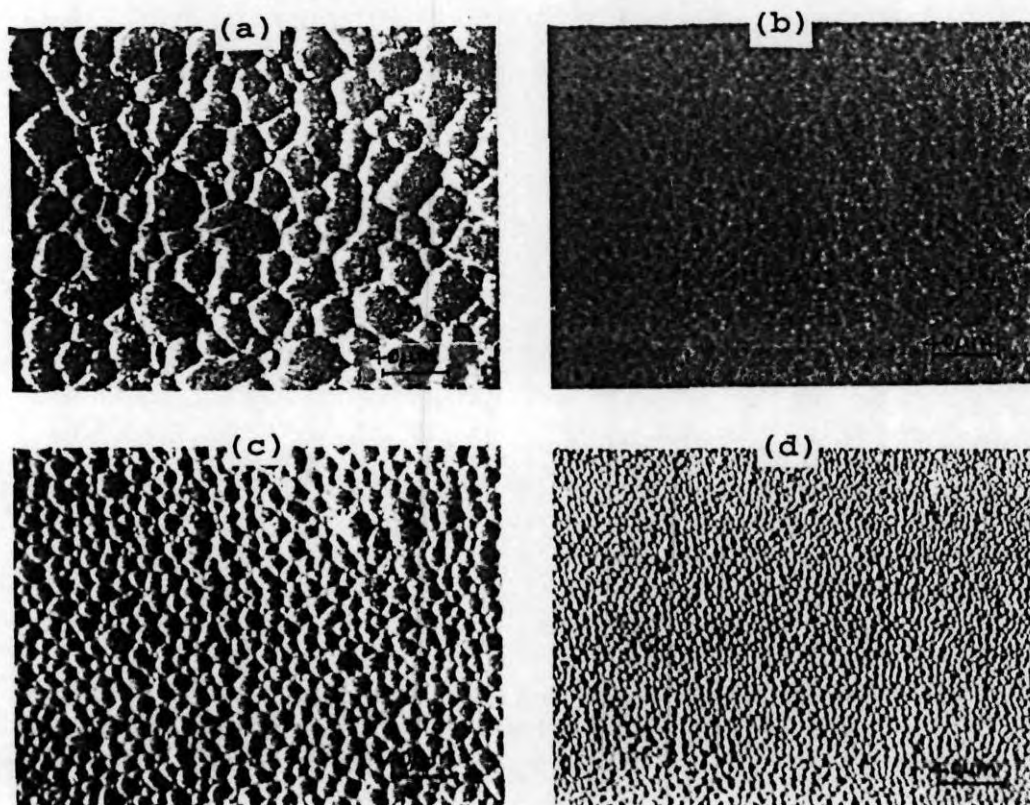


FIG. 8. — Optical photographs of 60/40 NR/PS films casted from CCl_4 and CHCl_3 containing variable amounts of graft copolymer; (a), 0% graft from CHCl_3 ; (b), 1.2% graft from CHCl_3 ; (c), 0% graft from CCl_4 ; (d), 1.2% graft from CCl_4 .

In both cases the addition of graft copolymer reduces the domain size.⁴⁰ The concentration of the graft copolymer required to saturate unit volume of the interface is less for carbon tetrachloride cast film (CMC — 1.1%) than for chloroform cast film (CMC — 1.5%). The sizes of the domains of the uncompatibilized blends of chloroform cast and carbon tetrachloride cast films are $27.6 \mu\text{m}$ and $17.6 \mu\text{m}$, respectively. This behavior is due to the fact that the solubility parameter of CCl_4 ($\delta = 8.6$) is closer to those of the polymers (PS, $\delta = 8.56$; NR, $\delta = 7.75$) than is the solubility parameter of CHCl_3 ($\delta = 9.3$).

MECHANICAL PROPERTIES

Blend morphology has a significant effect on the mechanical properties of the blends. Many research studies have been reported on the morphology-mechanical property relationships of polymer blends. Paul, Locke and Vinson⁴¹ have studied the mechanical properties of PE/PVC blends containing chlorinated PE as compatibilizer. Mechanical properties of nylon/PP was studied by Ide and Hasegawa.⁴² Lock and Paul⁴³ studied the improvement in mechanical properties of PS/PE blends by the addition of graft copolymer. In all the above cases, the graft copolymer improved interfacial adhesion and hence the mechanical properties of the blends.

The influence of addition of graft copolymer on tensile strength and modulus was studied. Figure 9 shows the variation in tensile strength and modulus with percentage of the compatibilizer loading. Table V shows that the tensile strength and modulus increase with the addition of the copolymer and finally level off at higher concentrations. The impact strength increases up to 3% compatibilizer loading and then it decreases at higher concentration (Table V). These changes are in accordance with the morphology of the blends. Addition of the copolymer results in an improvement in tensile strength, modulus and impact strength due to the enhanced interfacial bonding between PS and NR through the graft copolymer.

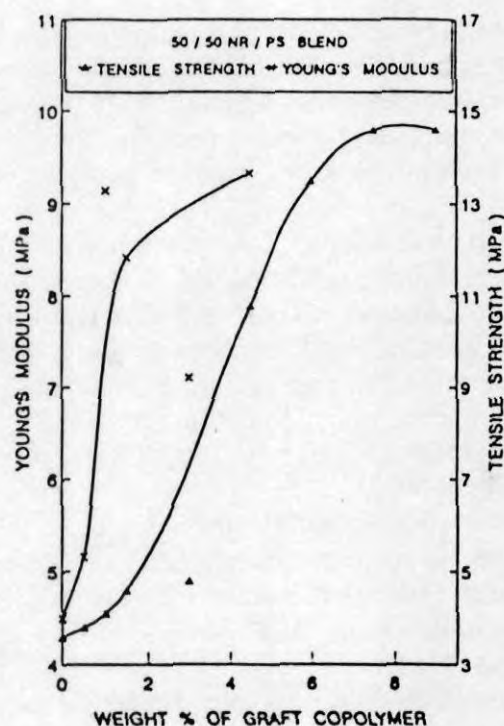


FIG. 9. — Effect of copolymer concentration on the tensile strength and modulus of 50/50 NR/PS blend.

DISCUSSION

In the case of heterogeneous polymer blends, several research studies have concentrated on the compatibilizing action of the block and graft copolymers. The high interfacial tension existing between the phases which is responsible for macrophase separation can be reduced by the addition of the compatibilizer. There are different parameters which govern the interfacial saturation. These include molecular weight of the homopolymers, molecular weight of the copolymer, polymer(s) structural details, mode of addition of compatibilizer, processing conditions, affinity of the copolymer for the dispersed phase, orientation of the copolymer at the interface, etc.

The experimental and theoretical studies on the compatibilization of immiscible blends report on the so-called interfacial saturation by the addition of copolymers. For example in the case of polyethylene/natural rubber blends,⁴⁴ 5% of the compatibilizer (polyethylene-

TABLE V
MECHANICAL PROPERTIES OF 50/50 NR/PS BLENDS

Wt. % graft polymer	Stress at % elongation (MPa)			Tensile strength (MPa)	Elongation at break (%)	Tensile impact strength (J/mm ²)
	15%	30%	50%			
0	1.24	1.78	2.37	3.60	454	0.30×10^5
1	—	—	—	—	—	1.43×10^5
1.5	1.54	1.82	2.45	3.86	194	1.64×10^5
3	1.96	2.05	2.75	4.50	190	2.10×10^5
4.5	1.99	2.28	3.07	10.10	252	1.63×10^5
6	2.56	2.78	3.24	13.24	247	1.39×10^5
7.5	3.20	3.47	3.88	13.15	241	1.37×10^5

block-polyisoprene) was found to be sufficient for interfacial saturation. The compatibilizing action of poly(styrene-*block*-1,2-butadiene) in heterogeneous polystyrene/1,2-polybutadiene blends was reported by Spiros, Gancarz and Koberstein.⁴⁵ Interfacial tension reduced parallel with copolymer addition up to the critical micelle concentration (CMC) and thereafter leveled off at higher concentration. Beyond the CMC, further addition of the copolymer leads to micelle formation.

Willis and Favis¹⁶ reported that about 5% of the ionomer is sufficient for polyolefin/polyamide blend system for interfacial saturation. Fayt, Jerome and Teyssie^{11,12} found equilibration of domain size by the addition of 0.5%–1% by weight of the compatibilizer. The recent studies of Thomas and Prud'homme⁴⁶ and Oommen and Thomas⁴⁷ also report on the interfacial saturation by the addition of copolymers in PS/PMMA and NR/PMMA systems, respectively. The theoretical predictions of Noolandi and Hong³⁰⁻³² indicated that micellar aggregation of the copolymer takes place at the interface of the blend beyond a critical concentration of the copolymer (CMC).

Almost all the experimental and theoretical studies related to the compatibilization of heterogeneous blends, including the present work, suggest that there is a critical concentration of the compatibilizer required to saturate the blend interface (CMC) beyond which addition of the compatibilizer leads to undesirable micelle formation which very often reduces the total performance of the blend system.

One can also explain the interfacial saturation point using Taylor's Equation.³⁶

$$W_c = \frac{\eta_m d n \dot{\gamma}}{2\gamma_{12}}; \quad (1)$$

where W_c is the critical Weber number; η_m is the viscosity of the matrix, $\dot{\gamma}$ is the shear rate; γ_{12} is the interfacial tension, and dn is the number average diameter of the dispersed phase. On the addition of the compatibilizer, the interfacial tension decreases and there is a consequent particle break down (deformation). However, at a particular compatibilizer loading there is a balance of interfacial tension and particle deformation. Thus, there is a critical value of W_c below which no particle deformation occurs and at this point, the compatibilizer occupies the maximum interfacial area. Therefore, there is a maximum quantity of the compatibilizer required to saturate the blend interface and beyond this level further addition of compatibilizer will not reduce the particle size. The studies of Favis and Willis⁴⁸ and White⁴⁹ also report similar observations.

The compatibilizer added to a heterogeneous blend locates at the interface and reduces the interfacial energy. Based on thermodynamics, Noolandi and Hong³⁰⁻³² developed an expression for interfacial tension reduction. Accordingly, the interfacial tension reduction $\Delta\gamma$ in a heterogeneous binary blend A/B — upon the addition of a copolymer, A-*block*-B — is given by

$$\Delta\gamma = d\phi_c \left[\left(\frac{1}{2} \chi + \frac{1}{Z_c} \right) - \frac{1}{Z_c} \exp \left(Z_c \frac{\chi}{2} \right) \right]; \quad (2)$$

where d is the width at half height of the copolymer profile reduced by Kuhn statistical segment length; χ is the Flory Huggins interaction parameter between the A and B segment of the AB copolymer; and Z_c is the degree of polymerization of the copolymer. According to this theory, the interfacial tension reduction $\Delta\gamma$ is proportional to the copolymer volume fraction ϕ_c until the system reaches the CMC. However, beyond the CMC $\Delta\gamma$ levels off with ϕ_c . Although this expression was developed for block copolymers, our recent investigations indicated that this theory can be applied to graft copolymers as well.⁴⁷ Since interfacial tension reduction is directly proportional to particle size reduction Δd , it can be shown that

$$\Delta d = K d \phi_c \left[\left(\frac{1}{2} \chi + \frac{1}{Z_c} \right) - \frac{1}{Z_c} \exp \left(Z_c \frac{\chi}{2} \right) \right]; \quad (3)$$

where K is the proportionality constant. The plot of experimental values of Δd vs. ϕ_c is given in Figure 10. It can be seen that at low concentration of the compatibilizer Δd decreases

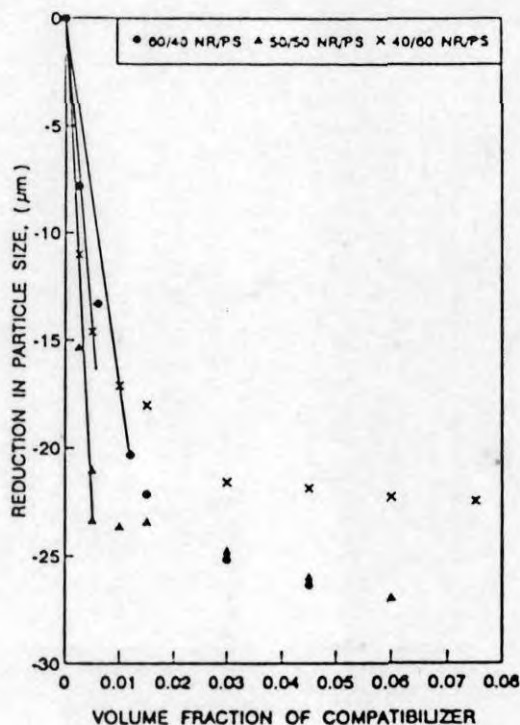


Fig. 10. — Effect of graft copolymer volume fraction on particle size reduction.

linearly with copolymer loading and at high concentration Δd levels off as indicated by Noolandi and Hong.

Valuable information can be obtained by calculating the area, Σ , occupied by the copolymer molecule at the blend interface. Let us consider a binary blend that contains a volume fraction ϕ_A of polymer A as spherical domains of radius r in a matrix B. The total interfacial area per unit volume of the original blend is equal to $3\phi_A/\gamma$. If each copolymer molecule occupies an area, Σ , at the interface, the mass M of the copolymer required to saturate unit volume of the blend is given by the following equation⁵:

$$\Sigma = \frac{3\phi_A M}{mrN}; \quad (4)$$

where M is the molecular weight of the copolymer and N is Avogadro's number. In the present study, since CMC is the interfacial saturation point, it would be reasonable to consider CMC to have the value m .

The radius r of the dispersed domain at CMC, the CMC values (m values), and Σ are given in Table IV. The CMC values are estimated from Figure 2 by the intersection of the straight line drawn at the low concentration and the leveling-off line at high concentration.

It can be noticed that the area occupied by the compatibilizer molecule at the interface (Σ) increases as the molecular weight of the homopolymer decreases (Figure 11). The ' Σ ' values also depend on the mode of addition of the compatibilizer to the blend system. In the two step process where the copolymer is preblended with the dispersed phase, the Σ value is 49.10 nm^2 . This indicates that the interaction of the copolymer and homopolymer is higher in the two-step process, compared to the one-step process where $\Sigma = 30.98 \text{ nm}^2$. Greater interaction would increase interfacial area and reduce interfacial tension.

The nature of the casting solvent can also influence the ' Σ ' values. In the case of CCl_4 Σ is higher (82.55 nm^2) compared to chloroform (30.98 nm^2). In a good solvent like CCl_4 , interaction between the copolymer and homopolymer is greater than in chloroform and hence the interfacial area occupied by the copolymer is larger. Similarly the copolymer molecular weight is also a controlling parameter. When the copolymer molecular weight is reduced,

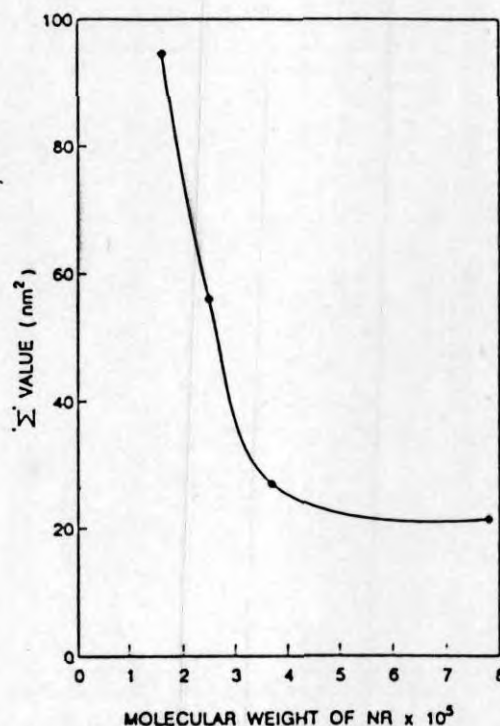


FIG. 11. — Effect of homopolymer molecular weight on the calculated area occupied by the copolymer molecule at the blend interface, Σ .

the interaction between the copolymer and homopolymer is reduced. Hence the area occupied by the copolymer at the interface is ($\Sigma = 15.46 \text{ nm}^2$) lower than the area of a copolymer with a higher molecular weight ($\Sigma = 30.98 \text{ nm}^2$).

One can also comment on the conformation of the copolymer based on the Σ values. Figure 12 depicts three different physical models representing the conformation of the copolymer at the blend interface. Model (a) indicates a conformation in which the graft copolymer extends into the corresponding homopolymer phases. In this case the occupied area at the interface is the cross-sectional area of the extended copolymer molecule. This is approximately equal to 0.6 nm^2 . In the (b) model [Figure 12(b)], the copolymer lies flat at the interface and here the occupied area is the lateral surface area of the entire copolymer

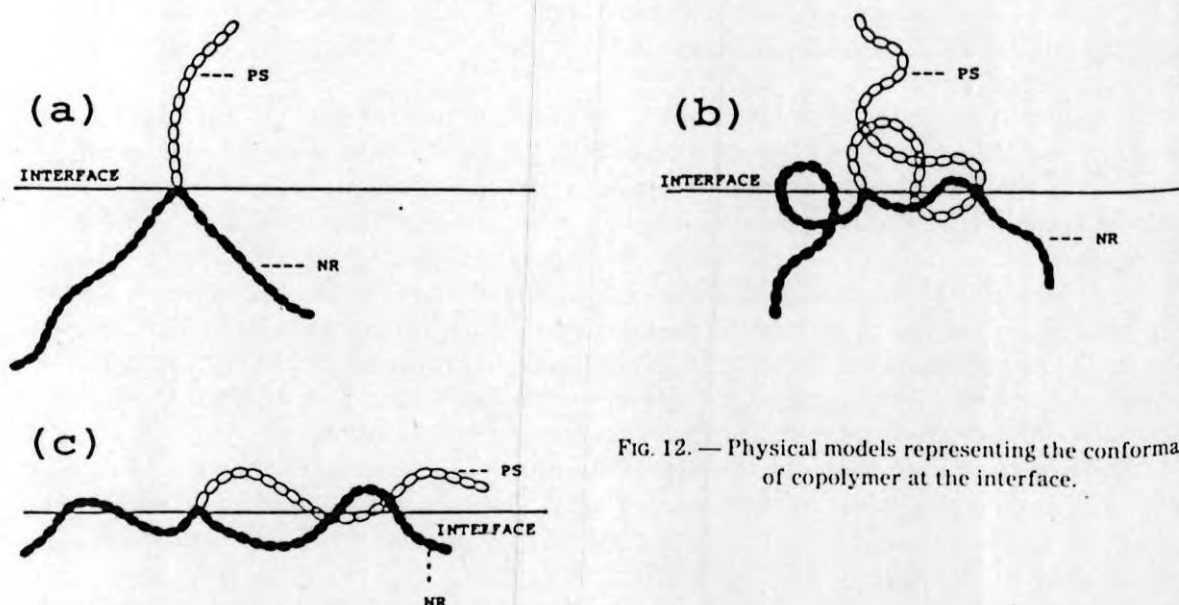


FIG. 12. — Physical models representing the conformation of copolymer at the interface.

molecule. By considering each segment of the graft copolymer as a spherical random coil, we have calculated the lateral surface area of the copolymer by using the experimental values of the root-mean-square radius of gyration of the PS block reported in literature.⁴⁶ The lateral surface area was approximately equal to 106 nm².

A comparison of the experimental and calculated values of interfacial area will give the actual conformation of the copolymer at the blend interface. The experimental values of Σ as obtained from Equation (4), lie between 15.46 and 100.9 nm² (see Table IV). This is intermediate to those of models (a) and (b) (0.6 and 106 nm²) reported in the literature. This suggests that the actual conformation of the copolymer at the blend interface is neither fully extended nor completely flat. The actual position can be represented by model (c) in Figure 12, in which a portion of the copolymer remains at the interface and the rest penetrates into the corresponding homopolymer phases. This model is in agreement with the model suggested by Oommen and Thomas.⁴⁷ However, by controlling the physical parameters such as molecular weight of the homopolymer and copolymer, mode of preparation of the blends, casting solvents, etc., one can dictate the area occupied by the copolymer at the interface. For example, as the molecular weight of the copolymer increases or the molecular weight of the homopolymer decreases, the area occupied by the copolymer at the interface increases (see Table IV). For example, copolymer G₁ occupies an area of 30.98 nm², which is much higher than G₂ which occupies an area of 15.46 nm².

It is also important to consider the fact that as the molecular weight of the copolymer increases, macromolecular interactions, such as chain entanglement, hinder the complete penetration of each segment into the corresponding homopolymer phases. This suggests that the copolymer cannot penetrate completely into the homopolymer phases and therefore, it is expected that part of the copolymer may stay at the interface. This could lead to an increase in interfacial thickness which would be maximum in the case of copolymers having the highest molecular weight. According to Wu,³⁵ interfacial tension (γ_{12}) and interfacial thickness (L) are related by the following equation:

$$\gamma_{12} = 7.6/L0.86. \quad (5)$$

This indicates that the superior compatibilizing action of the high molecular weight graft copolymer is associated with the larger increase in interfacial thickness and consequent reduction in interfacial tension. Russel *et al.*¹⁸ also have reported that addition of copolymer increases the interfacial thickness of PS/PMMA blends. In this study the interfacial thickness was measured by neutron reflectivity. The thickness of the interface increased 50% by the addition of the copolymer. Recent experimental results of Anastasiadis, Gancarz and Koberstein⁵⁰ also support the conformation represented in Figure 12(c). They have reported on the compatibilizing action of poly(styrene-*block*-1,2-butadiene) in PS/1,2-poly(butadiene) and found that about 24% of the contour length of the copolymer chain is located at the blend interface and the rest penetrates into the corresponding homopolymer phases.

CONCLUSION

The compatibilizing activity of NR-graft-PS in heterogeneous NR/PS blends has been studied in detail. Both the morphology and mechanical properties of NR/PS blends have been investigated. Concentration and molecular weight of the copolymer, composition of the blend, mode of addition of compatibilizer, homopolymer molecular weight, and processing condition were the controlling parameters on blend morphology. Copolymer addition reduces the domain size of the dispersed phase and finally levels off at higher concentrations, an indication of interfacial saturation. The experimental results were in agreement with predictions of Noolandi and Hong.

The area occupied by the compatibilizer molecule at the interface (Σ) has been estimated. As the molecular weight of the homopolymer decreases, interfacial area occupied by the copolymer (Σ) increases, and hence more reduction in the domain size occurs. The ' Σ ' values were also influenced by the blend composition, mode of addition and the nature of the casting

solvents. By the selection of a suitable solvent, having a solubility parameter close to that of the homopolymers, the interaction of the compatibilizer with the interface can be enhanced.

The mechanical properties are in agreement with the morphological changes. It was found that the tensile strength and modulus increases upon the addition of the compatibilizer and finally levels off at higher concentration.

Attempts were made to establish the conformation of the compatibilizer at the blend interface. Different models were discussed. The actual conformation is neither fully extended nor flat. A portion of the copolymer penetrates into the corresponding homopolymer and the rest remains at the interface.

ACKNOWLEDGMENTS

The authors are thankful to Dr. Sankariammal, Cytogeneticist, Botany division, and to Mrs. Reethamma Joseph, RCPT Division, Rubber Research Institute of India for their valuable help in the morphological and mechanical analysis of the samples. One of the authors (RA) gratefully acknowledges the financial support from the Council of Scientific and Industrial Research, New Delhi.

REFERENCES

- ¹ G. E. Molau, in "Block Polymers," S. L. Aggarwal, Ed., Plenum Press, New York, 1970, p. 79.
- ² G. E. Molau and H. Keskkula, *Appl. Polym. Symp.* **n.7**, 35 (1968).
- ³ G. E. Molau, *J. Polym. Sci., Part A A3*, 1267 (1965).
- ⁴ G. E. Molau, *J. Polym. Sci., Part A A3*, 4235 (1965).
- ⁵ D. R. Paul, in "Polymer Blends," D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, ch. 12.
- ⁶ D. R. Paul and S. Newman, Eds., "Polymer Blends," Academic Press, New York, 1978, v. 1.
- ⁷ G. Riess, J. Kohler, C. Tournut, and A. Banderet, *Makromol. Chem.* **101**, 58 (1967).
- ⁸ J. Kohler, G. Riess, and A. Banderet, *Eur. Polym. J.* **4**, 173 (1968).
- ⁹ T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *Macromolecules* **3**, 87 (1970).
- ¹⁰ M. Moritani, T. Inoue, M. Motegi, and H. Kawai, *Macromolecules* **3**, 433 (1970).
- ¹¹ R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys. Ed.* **20**, 2209 (1982).
- ¹² R. Fayt, R. Jerome, and Ph. Teyssie, *Polym. Eng. Sci.* **27**, 328 (1987).
- ¹³ R. Fayt, P. Hadjilandreou, and Ph. Teyssie, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 337 (1985).
- ¹⁴ H. T. Patterson, K. H. Hu, and T. H. Grindstaff, *J. Polym. Sci., Part C, n. 34*, 31 (1971).
- ¹⁵ P. Gailard, Sauter M. Ossenbach, and G. Riess, *Makromol. Chem. Rapid Commun.* **1**, 771 (1980).
- ¹⁶ J. M. Willis and F. D. Favis, *Polym. Eng. Sci.* **30**, 1073 (1990).
- ¹⁷ K. R. Shull, E. J. Mramer, G. Hadzioanion, and W. Tang, *Macromolecules* **23**, 4780 (1990).
- ¹⁸ T. P. Russel, A. Menelle, W. A. Hamilton, G. S. Smith, S. K. Satija, and C. F. Majkrzak, *Macromolecules* **24**, 5721 (1991).
- ¹⁹ M. L. Fernandez, J. S. Higgins, J. Penfold, R. C. Ward, C. Shackelton, and D. Walsh, *Polymer* **29**, 1923 (1988).
- ²⁰ A. Y. Coran and R. Patel, *RUBBER CHEM. TECHNOL.* **56**, 1045 (1983).
- ²¹ A. Y. Coran and R. Patel, *RUBBER CHEM. TECHNOL.* **56**, 210 (1983).
- ²² A. Y. Coran and R. Patel, *RUBBER CHEM. TECHNOL.* **53**, 141 (1980).
- ²³ A. Y. Coran, R. Patel, and D. Williams-Headd, *RUBBER CHEM. TECHNOL.* **58**, 1014 (1985).
- ²⁴ A. K. Bhowmick and H. L. Stephens, "Handbook of Elastomers," Marcel Dekker, Inc., New York and Basel, 1988, ch. 8.
- ²⁵ A. Y. Coran and R. Patel, *RUBBER CHEM. TECHNOL.* **56**, 1045 (1983).
- ²⁶ N. R. Legge, G. Holden, and H. E. Schroeder, "Thermoplastic Elastomers," Hanser, Munich Vienna, New York, 1987, ch. 7.
- ²⁷ W. K. Fisher (to Uniroyal, Inc.), U.S. 3,758,643 (Sept. 11, 1973).
- ²⁸ L. Leibler, *Makromol. Chem., Macromol. Symp.* **16**, 17 (1985).
- ²⁹ L. Leibler, *Macromolecules* **15**, 1283 (1982).
- ³⁰ J. Noolandi, *Polym. Eng. Sci.* **24**, 70 (1984).
- ³¹ J. Noolandi and K. M. Hong, *Macromolecules* **15**, 482 (1982).
- ³² J. Noolandi and K. M. Hong, *Macromolecules* **17**, 1531 (1984).
- ³³ W. Cooper, P. R. Sewell, and G. Vaughan, *J. Polym. Sci.* **41**, 167 (1959).
- ³⁴ M. Goni, Gurru Chaga, J. Sam Roman, M. Valero, and G. M. Guzman, *Polymer* **34**, 512 (1993).
- ³⁵ S. Wu, *Polym. Eng. Sci.* **27**, 335 (1987).
- ³⁶ J. M. Willis and B. D. Favis, *Polym. Eng. Sci.* **28**, 1416 (1988).
- ³⁷ L. Djakovic, P. Dokie, I. S. Radivojevic, and V. Sovilij, *Colloid Polym. Sci.* **265**, 993 (1987).
- ³⁸ S. Cimmino, F. Coppola, L. D'orazio, R. Greco, G. Maglio, M. Malinconico, C. Man Carella, E. Martuscali, and G. Ragosta, *Polymer* **27**, 1874 (1986).

BLEND COMPATIBILIZATION

- ³⁹ A. Robard and D. A. Patterson, *Macromolecules* **10**, 1021, (1977).
- ⁴⁰ R. Asaletha, M. G. Kumaran, and S. Thomas, *Polym. Plast. Technol. Eng.* (in press).
- ⁴¹ D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.* **13**, 202 (1973).
- ⁴² F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.* **18**, 963 (1974).
- ⁴³ C. E. Locke and D. R. Paul, *J. Appl. Polym. Sci.* **17**, 2591 (1973).
- ⁴⁴ C. Qin, J. Yin, and B. Huang, *Polymer* **31**, 663 (1990).
- ⁴⁵ H. A. Spiros, Irena Gancarz, and J. T. Koberstein, *Macromolecules* **22**, 1449 (1989).
- ⁴⁶ S. Thomas and R. E. Prud'homme, *Polymer* **33**, 4260 (1992).
- ⁴⁷ Z. Oommen and S. Thomas, *Polym. Eng. Sci.* (in press).
- ⁴⁸ B. D. Favis and J. M. Willis, *J. Polym. Sci. Polym. Phys. Ed.* **28**, 2259 (1990).
- ⁴⁹ J. L. White, *Polym. Eng. Sci.* **13**, 46 (1973).
- ⁵⁰ S. A. Anastasiadis, I. Gancarz, and J. T. Koberstein, *Macromolecules* **22**, 1449 (1989).

[Received Nov. 15, 1994; revised May 26, 1995]