

molecular length is roughly unaffected by the R_n nature. The products 3-9 exhibit smectic A and/or nematic mesophases. The transition temperatures versus the number n of R_n carbon atoms are reported in Figure 5.

In homologous series of calamitic liquid crystals containing an n -alkyl chain as a terminal group, the clearing point and the transition temperatures normally display the odd-even effect and decrease with increasing the chain length.¹⁸ For both the S_A and the N phases these effects are apparent for compounds 4-9 too (Figure 5). However, it seems remarkable that the clearing points, in spite of the large difference in the R_n length, belong in a quite narrow range (i.e., 6 °C). This behavior might be the result of the above described molecular geometry.

The role played by the complexed 4,4'- n -alkoxyazoxybenzene ligand could deserve a further comment. Actually, none of the previously reported $[(R_nL)Pd(Azoxy-1)]$ species,¹⁴ wherein R_nL ($R_n = CH_3, C_2H_5,$ and C_4H_9), is the deprotonated form of some of the R_nLH Schiff bases shown in Scheme II and [Azoxy-1] is the cyclometalated p -azoxyanisole, display thermotropic properties. Therefore, comparing the two homologous series $[(R_nL)Pd(Azoxy-6)]$ and $[(R_nL)Pd(Azoxy-1)]$, it is apparent that the building of mesogenic materials demands azoxybenzenes bearing the appropriate number of carbon atoms in the n -alkoxy chains.

The structure of the mesophases displayed by 3-9 has been investigated by X-ray techniques. In particular, for R_n ranging from zero to C_4H_9 (compounds 3-7) two quite different periodicities (about 45 and 28 Å) characterize the low-angle diffraction pattern in the solid and smectic phases, respectively. In contrast, for $R_n = C_6H_{13}$ (8) or C_8H_{17} (9) the periodicities of 25 Å in the solid phase and

29 Å in the smectic one are seen. With reference to the molecular shape, in complexes 3-9 a metal atom binds two calamitic thermotropic ligands as in the bis(salicylidene)amine copper mesogen IV. The X-ray analyses concerning the copper complexes gave apparent molecular lengths shorter than the theoretical values, and consequently an interdigitated molecular arrangement was proposed.^{1,11} In the present case a molecular packing alike might be suggested for 8 and 9 only.

Finally, as far as the molecular structures are concerned, it should be pointed out that the mononuclear cyclopalladated liquid-crystalline materials reported up to now are acetylacetonate derivatives of ortho-palladated imines^{6a} or azoxybenzenes.¹⁹ Both these species have asymmetric rodlike shapes; therefore, 3-9 are the first examples of lateral-lateral fused organometallic palladium mesogens.

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(19) Ghedini, M.; Pucci, D.; Armentano, S.; Bartolino, R.; Versace, C. C.; Cipparrone, G.; Scaramuzza, N. Italian Patent VE 92A000003, Jan 16, 1992.

In Situ Polycondensation for Synthesis of Composites of Elastomeric Matrices and Wholly Aromatic Polyamides

Emmanuel Debeaupre, Masayoshi Watanabe, Kohei Sanui, and Naoya Ogata*

Department of Chemistry, Faculty of Science and Technology, Sophia University,
7-1 Kioi-Cho, Chiyoda-Ku, Tokyo 102, Japan

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Composites of rubbers containing poly(p -phenylene terephthalamide) (PPTA) were prepared by solution polycondensation and interfacial polycondensation methods from terephthaloyl chloride (TPC) and p -phenylene diamine (PPD) in the presence of some elastomers, e.g., styrene-butadiene-styrene (SBS) triblock copolymers and acrylonitrile-butadiene (NBR) random copolymers. The morphology of these composite polymers was characterized by electron microscopy, and their mechanical properties were investigated. The morphology of the blends and the reinforcing effect of the PPTA were dependent on the matrix, the polycondensation method, and the PPTA content in the blend.

Introduction

The concept of molecular composites was first proposed by Takayanagi et al. in Japan¹ and Helminak et al. in the United States.² Many papers have since been published in that field.

However, only a few papers about molecular composites containing wholly aromatic polyamides, e.g., poly(p -phenylene terephthalamide) (PPTA) as reinforcing polymer, have been published. These were almost exclusively

done by Takayanagi's group in Japan. Blends are achieved by different methods. One consists of solution blending of the rigid-rod polymer and the coil-like flexible polymer. However, the insolubility of PPTA in common solvents renders this method futile. Therefore, only some composites with aliphatic polyamides have been prepared by this method in sulfuric acid, which is one of the few good solvents of PPTA.³ Another method consists of chemical transformation of the surface of microfibrils of PPTA by

(1) Takayanagi, M. Japan Patent Application, 1977, 131436.

(2) Helminak, T. E. U.S. Patent, 1978, 902525.

(3) Takayanagi, M.; Ogata, T.; Morikawa, M.; Kai, T. *J. Macromol. Sci.-Phys. Ed.* 1980, B17, 591-615.

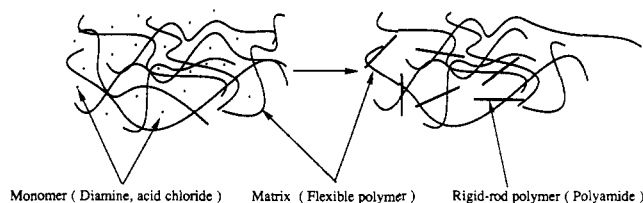


Figure 1. In situ polycondensation concept.

treatment with alkali metals in dimethyl sulfoxide (DMSO) to convert the surface amide groups into metal salts. This enhances solubility by reducing intermolecular hydrogen bonding of the polyamide. Some composites of poly(vinyl chloride) (PVC), acrylonitrile-butadiene-styrene (ABS), and nitrile-butadiene rubber (NBR) matrices with PPTA have been successfully synthesized by this method.^{4,5}

Polymer blends are also commonly prepared by melt coprocessing of the two polymers, but it cannot be applied when PPTA is to be used as reinforcing polymer since it decomposes at a temperature below its melting point.

Our purpose was to synthesize some blends of polyaramides and elastomeric polymers such as styrene-butadiene-styrene or nitrile-butadiene rubbers without using microfibrils. The obvious problem was the thermodynamic incompatibility of these two polymers, which created a very high obstacle for mixing.

We therefore tried to blend these two kinds of polymers by the so-called "in situ polycondensation" method. This involves polycondensation of the rigid-rod polymer, i.e., PPTA, in a solution of the matrix polymer and an appropriate solvent in order to obtain a fine dispersion of the PPTA in the matrix polymer. In this paper, we report results concerning in situ polycondensation carried out in SBS and NBR solutions.

This concept, illustrated in Figure 1, has already been used for the synthesis of microcomposites of aromatic liquid-crystalline polyesters (LCP) in a polyarylate⁶ and SBS,⁷ matrices, respectively. A fine dispersion of the reinforcing LCP and a good reinforcing effect were obtained.

Experimental Section

All solvents were distilled before use and stored over molecular sieves under nitrogen atmosphere. The monomers were purified as follows: terephthaloyl chloride (TPC) was recrystallized from dry hexane and stored in a desiccator under nitrogen. *p*-Phenylenediamine (PPD) was sublimed under nitrogen and vacuum to obtain white crystals with a sharp melting zone and stored in the dark under nitrogen.

Two types of rubbery matrix polymers were used for the experiments, namely, SBS and NBR. Further, two kinds of SBS polymers were used: S26 and S44, containing 26 and 44 mol % of styrene, respectively. These are commercially available products (TR2000 and TR2400) from the Japan Synthetic Rubber Co., Ltd (JSR). NBR was an acrylonitrile-butadiene random copolymer containing 33 mol % of acrylonitrile units. This was provided by the Goodyear Co.

In Situ Polycondensation Reactions. In situ polycondensation reactions were carried out either by interfacial or solution methods, both of which used the same monomers. In both cases, a high-speed homogenizer equipped with a helix made physical dispersion easier.

The interfacial polycondensations were carried out using cyclohexanone and water, as adapted from Morgan's method.⁸ A

typical procedure was as follows: 1.0151 g of TPC (0.005 mol) was dissolved in varying concentrations of a 50-mL cyclohexanone solution of the matrix. Meanwhile, 1.06 g (0.01 mol) of anhydrous sodium carbonate (used as an acceptor of the HCl formed during the condensation reaction) and 0.5407 g (0.005 mol) of PPD were dissolved in 40 mL of distilled water under nitrogen in the absence of light. The aqueous solution was then poured immediately into the cyclohexanone solution, which was stirred at 2000 rpm. Then the Erlenmeyer flask was rinsed with an additional 10 mL of distilled water. The speed was then raised to about 10 000 rpm, and the system was left to react at room temperature for 30 min. Addition of PPD solution immediately produced a yellow-colored, low-viscosity emulsion which remained stable even without agitation.

The solution polycondensations were carried out by using *N*-methyl-2-pyrrolidone (NMP) for the NBR matrix and a 75/25 solvent mixture of NMP and cyclohexanone for the SBS matrices.

A typical solution polycondensation was carried out as follows: to the solution of matrix polymer (of varying concentrations) in 50 mL of solvent, 0.5407 g (0.005 mol) of PPD, 0.4239 g of LiCl, and 1.0119 g of N(Et)₃ (0.01 mol) were added and dissolved under nitrogen. While stirring in the blender, 1.0151 g (0.005 mol) of TPC was added at once. Immediately, a very exothermic reaction occurred and the color of the solution became light brown while the viscosity quickly increased. Agitation was kept at about 4000 rpm for 1 h. At the end of the reaction, the solution was transparent and remained light brown.

In both cases, at the end of the reaction, the mixture of polymers was recovered by precipitation in a large amount of water (1.5 L) and a single product was obtained without any phase separation. The product obtained by the interfacial method was light yellow, whereas that obtained by the solution method was light brown. Each behaved like a single raw material. The blend was then washed thoroughly with water in the blender and then with methanol in order to remove the salts formed during the reaction, as well as the other salts used in the polycondensation. Each was then dried under vacuum for 24 h.

To study the morphology (phase separation) and the mechanical properties of the blends, these precipitates were suspended in toluene (1.0 g/10 mL) and cast on poly(tetrafluoroethylene) plates. It is important to mention that the PPTA itself is insoluble in toluene, and it was impossible to obtain some homogeneous films by blending of a solution of the matrix polymer in toluene with a "pseudosolution" of PPTA. However, in the case of composites, the precipitates could be finely dispersed in toluene. Thus, solution casting gave some homogeneous but opaque films, probably owing to a swelling of the PPTA finely dispersed in the matrix polymer.

Characterization of the Films. The dynamic mechanical properties and mechanical properties of the films obtained by solution casting were investigated.

DMS was performed using a Seiko I DMS 100 at 50 Hz, under a nitrogen atmosphere with a heating rate of 2 °C/min for NBR and its composites, mechanical measurements on a Shimadzu AGS-1kNA tensile machine at a crosshead speed of 10 mm/min for SBS and their composites and 20 mm/min for NBR and its composites.

The morphology of the SBS matrix polymers was observed by transmission electron microscopy (TEM Hitachi HS-9) after staining with osmium tetroxide.

The morphology of the fracture surfaces of matrices and their composites in liquid nitrogen (dispersion state of the PPTA in the matrix polymers) was observed by scanning electron microscopy (SEM Hitachi S-430).

Results and Discussion

Figure 2 shows FT-IR spectra of S26, NBR, and some of their composites. Here, we observe the characteristic absorption bands of both matrices and PPTA synthesized in situ. A blue shift (4 cm⁻¹ at most) of the characteristic amide I band (1649 cm⁻¹ for PPTA alone) was observed. This might come from specific interactions between the matrices and PPTA.

Table I shows experimental data concerning matrix concentration, yield in PPTA and viscosity of PPTA left

(4) Takayanagi, M.; Goto, K. *J. Appl. Polym. Sci.* 1984, 29, 2547-2559.

(5) Takayanagi, M.; Goto, K. *Molecular characterization of composite interfaces*; Plenum: New York, 1985.

(6) Ogata, N.; Sanui, K.; Itaya, H. *Polym. J.* 1990, 22, 85.

(7) Kamitani, K.; Watanabe, M.; Sanui, K.; Ogata, N. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(8) Morgan, P. W. *Condensation Polymers: By Interfacial and Solution Methods*; Interscience: New York, 1965.

Table I. Experimental Data for Interfacial and Solution in Situ Polycondensations

composition (feed wt %)	[matrix] (wt % in solvent)	[monomer] (M)	yield (%)	η_{sp}/c^a (dL/g)	PPTA content ^b (wt %)
Interfacial Polycondensation					
S26/PPTA					
0/100		0.1	100	0.48	
70/30	6.7	0.1	90	0.39	27
80/20	9.8	0.1	79	0.32	17
90/10	11.4	0.1	66	0.37	9
NBR/PPTA					
70/30	5.6	0.1	98		30
80/20	9.5	0.1	95		19
90/10	12.9	0.1	81		8
Solution Polycondensation					
S26/PPTA					
0/100		0.10	97	3.97	
70/30	5.6	0.05	98	2.40	27
80/20	6.3	0.07	91	1.60	18
90/10	10.7	0.05	86	1.43	8
NBR/PPTA					
70/30	3.7	0.10	98		29
80/20	9.5	0.10	83		17
90/10	10.3	0.05	47		5

^aReduced viscosity measured, after extraction, in H₂SO₄ at 30 °C at a concentration of 0.5 g/dL. ^bMeasured by elemental analysis.

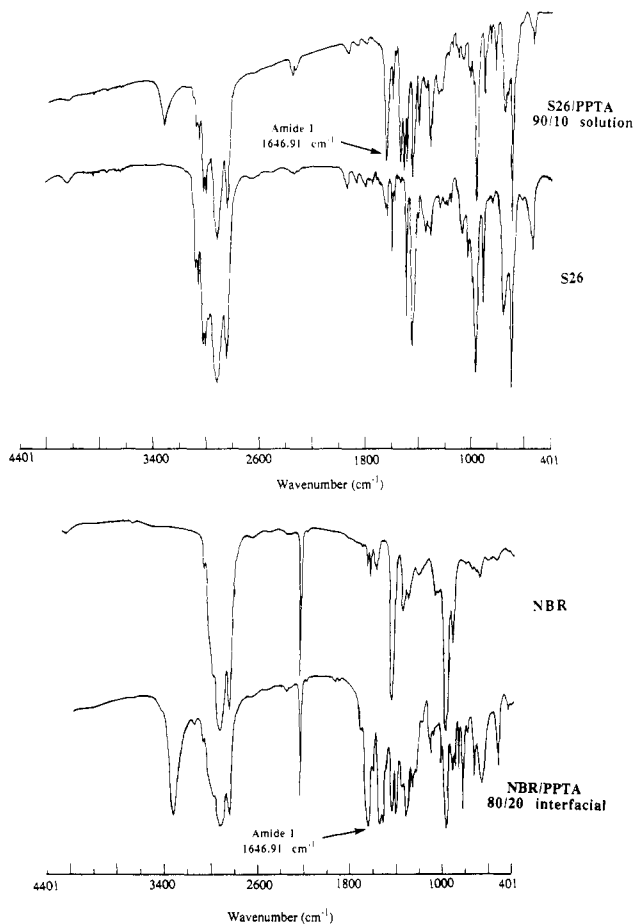


Figure 2. FT-IR spectra of the composite of S26 containing 10 wt % of PPTA synthesized by solution polycondensation and of the NBR composite containing 20 wt % of PPTA synthesized by interfacial polycondensation.

from extraction of matrix. The yield in PPTA was obtained from the recovered amount of composite and confirmed by elemental analysis. In the case of S26 composites, 48 h of reflux extractions of a chloroform solution were carried out with a Soxhlet extractor.

The two methods produce a big difference in range of viscosities and, therefore, molecular weights of PPTA. An explanation might be that during interfacial polycondensation,

Table II. Mechanical Properties of the Matrix Polymers and Composites

	<i>E</i> (MPa)	$\sigma_{200\%}$ (MPa)	σ_b (MPa)	ϵ_b (%)
PPTA/S26				
0/100	33.0	2.2	18.4	1150
10/90	90.0 (90.2) ¹	6.3 (5.2)	14.5 (19.5)	700 (963)
90/80	170.0 (131.0)	13.7 (7.5)	16.0 (19.8)	330 (762)
30/70	60.0 (195.2)	(8.2)	2.1 (18.6)	17 (774)
σ_Y (MPa)				
PPTA/S44				
0/100	266.2	7.4	29.8	1070
20/80	348.0	14.5	18.3	540
30/70	370.0	14.4	12.2	125
PPTA/NBR				
0/100	0.9		0.16	1800
20/80	81.0 (8.7)		3.4 (0.7)	112 (510)
30/70	(69.0)		(2.3)	(300)

^aValues in parentheses are for interfacial method. *E*, Young's modulus; $\sigma_{200\%}$, tensile strength at 200% of elongation; σ_Y , tensile strength at yield; σ_b , tensile strength at break; ϵ_b , elongation at break.

sation, the growth of the polyamide is limited by formation of the emulsion, resulting in polycondensation at the spherical surface. This produces an insoluble polymer which is kept at the interface. In contrast, in solution polycondensation, the growing polyamide remains dissolved even when molecular weight continues to increase.

Note that molecular weight is almost independent of matrix concentration for interfacially synthesized composites, whereas the opposite is true for blends. The limiting factors seem therefore to be different in these two cases. The interfacial polycondensation depends on the surface size of the spheres, at the interface of which the polymer is growing which seem not to depend on the matrix concentration in cyclohexanone, while the solution polycondensation depends on the diffusion of the growing polyamide and monomers in the matrix solution so that it is affected by the concentration of polymer or by the existence of less free volumes of the matrix polymer in which the polymer could grow when the concentration of matrix polymer is raised.

Table II summarizes data from Figures 3, 4 and 7. Figure 3 shows the behavior of Young's modulus, tensile strength at break and ultimate elongation of films of S26 and its composites. An increase in Young's modulus was

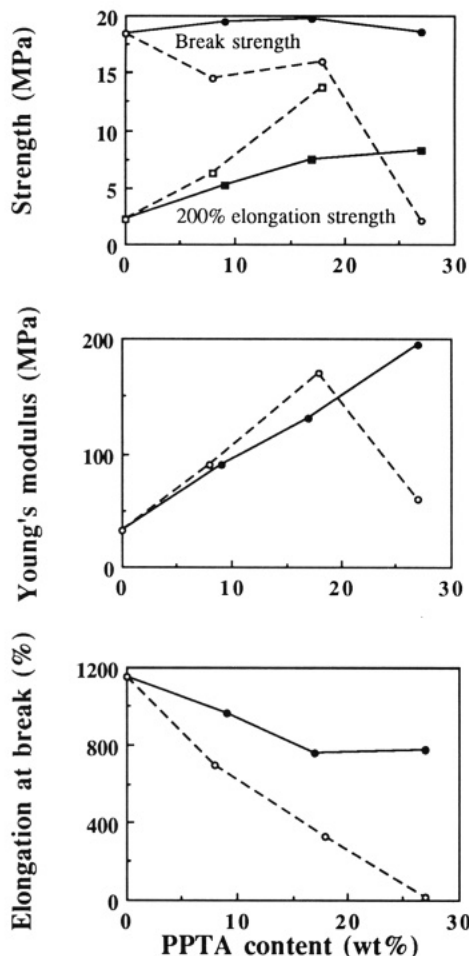


Figure 3. Mechanical properties of the composites of S26 synthesized by solution (---) and interfacial (—) polycondensation methods.

observed with increasing PPTA content and is probably caused by the dispersal of rigid-rod molecules in the matrix. Tensile strength of interfacially synthesized composites remained about the same regardless of the amount of PPTA, whereas a noticeable decrease is seen for solution blends. Both types of composites registered a decrease in elongation values, but it is more pronounced for solution blends. Figure 4 presents data for S44 and its composites formed by the interfacial method. Young's modulus shows a pattern similar to that of the S26 analogs. Also, parallel trends for S26 blends and S44 composites exist. However, for S44 composites, a linear decrease in strength at break contrasts with those of S26.

Figure 7 pertains to NBR and its composites cast from toluene solution. It must be noted that NBR has no cross-links and this causes large flow when stress is applied. However, decreased flow attended an increase in PPTA content. The composites obtained by solution and interfacial method showed similar behavior of Young's modulus, with greater change exhibited by those of the solution blends. This is very similar to those of SBS composites and reflects the increasing rigidity imparted by PPTA molecules to the rubber. Trends in strength, in this case maximum strength or strength at yield, parallel that of Young's modulus for the composites obtained by solution and interfacial methods. This is in direct contrast to those composites of SBS. This could be due to polar interaction or hydrogen bonding between $-\text{CN}$ of the acrylonitrile and $-\text{NH}$ of the amide.

Elongation values decreased for both composite types, being slightly smaller for interfacially synthesized ones.

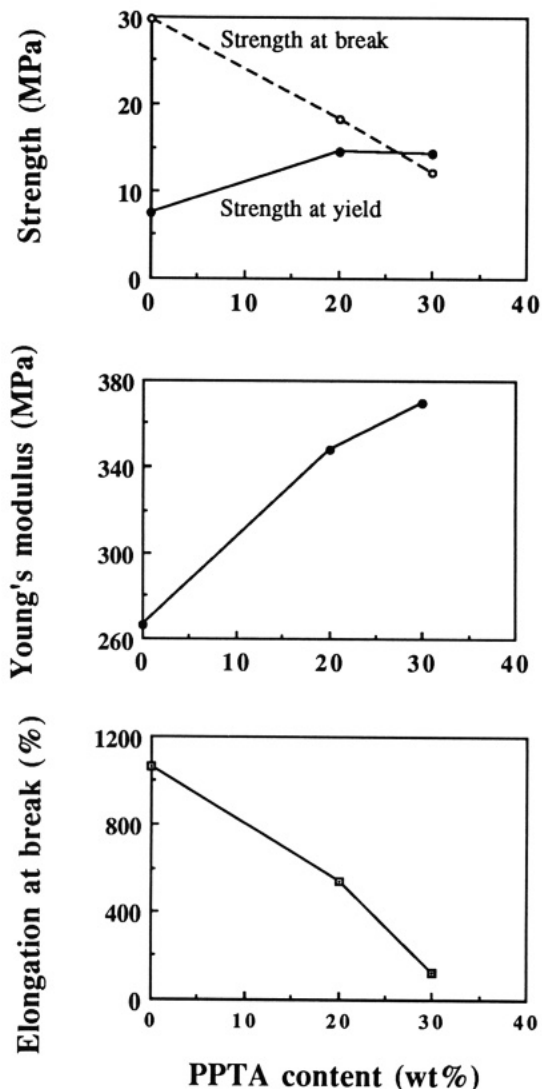


Figure 4. Mechanical properties of the composites of S44 synthesized by interfacial method.

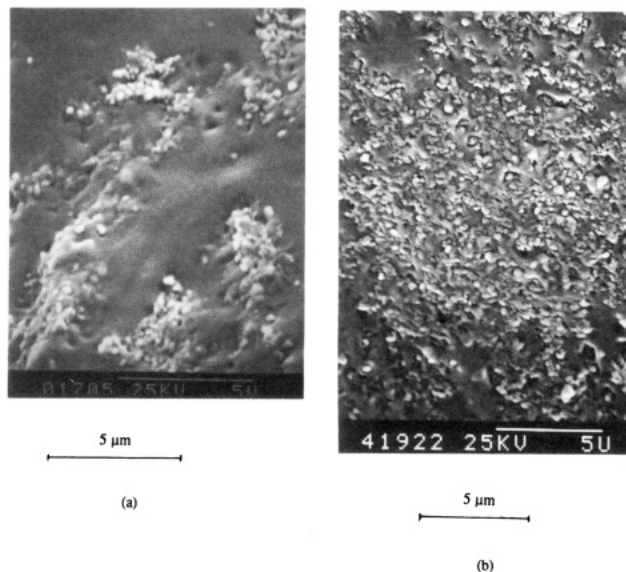


Figure 5. SEM micrographs of fracture surface of composites of S26 and PPTA (90/10) synthesized by solution (a) and interfacial (b) polycondensation methods.

Differences in reinforcing effect and rigidity exhibited by solution and interfacially prepared composites can be attributed to the disparity of molecular weights of the

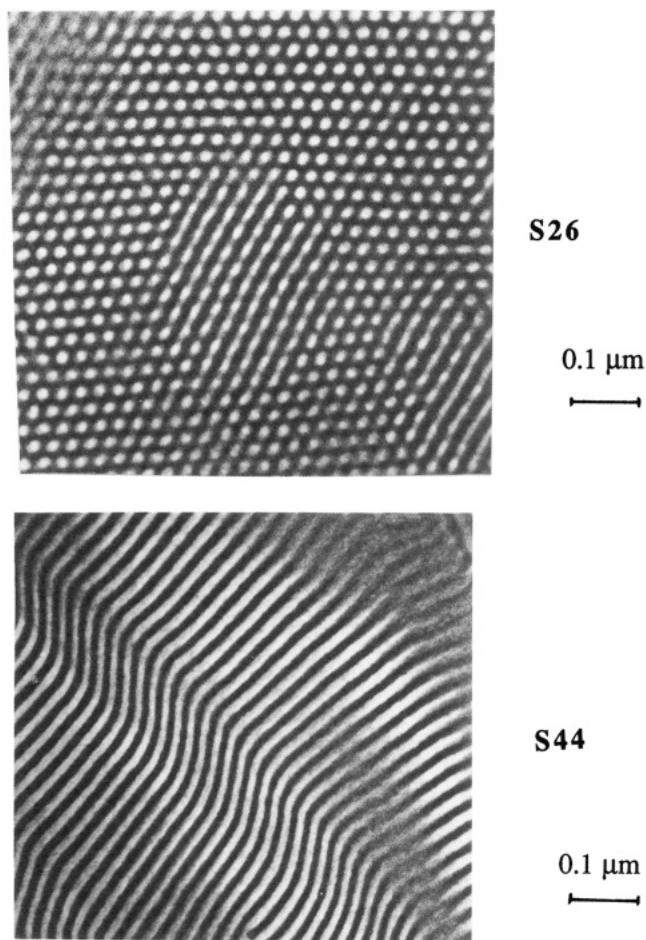


Figure 6. TEM pictures of ultrathin sections of S26 and S44 matrices stained by osmium tetroxide.

reinforcing polymer, which tend to be higher for the blends.

Morphology. To explain differing mechanical behavior, the fracture surfaces of matrices and their composites were studied. Surfaces were generated by physically breaking apart a strip of matrix or its composite while immersed in a liquid nitrogen bath. S26 had a very regular flat surface, while those of its composites became increasingly rough and irregular corresponding to an increase in the amount of PPTA. The size of aggregates generated by both solution and interfacial polycondensation were compared, and this showed a direct relationship between the amount of PPTA and the size of aggregates. Figure 5 shows such areas for composites containing 10 wt % PPTA, that is, the amount of PPTA seen in Figure 5 is consistent with 10 wt % composition. However, in this case SEM is hampered by contrast imperfections, and this does not permit a view of interpenetration between the PPTA and matrix, e.g., not all white areas correspond to PPTA. Irregularly shaped aggregates of PPTA with an average diameter of 2 μm correspond to the light areas in Figure 5a. These areas increase with an increase in the amount of PPTA and eventually affect the continuity of the matrix. These together with the lack of interaction between the matrix and the reinforcing polymer may be responsible for the drop in elongation and tensile strength. Figure 5b, on the other hand, shows a greater dispersion, with average spherical diameter of ca. 0.5 μm for composites containing up to 30 wt % PPTA. This indicates a more continuous matrix phase, regardless of the amount of reinforcing polymer. The difference in aggregation states of dispersed phase may be caused by differing molecular weights. Interfacial polycondensation might be

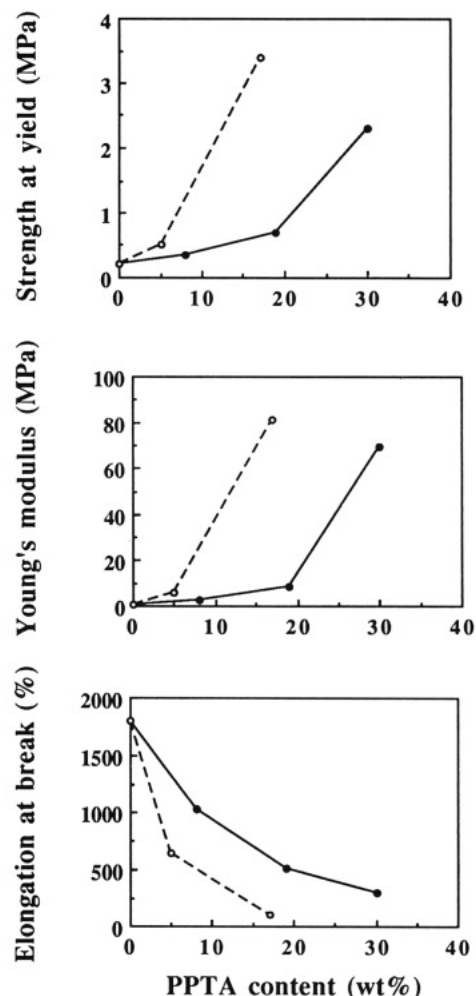


Figure 7. Mechanical properties of composites of NBR synthesized by solution (---) and interfacial (—) polycondensation methods.

affected by the emulsion state, which in turn may determine size and shape of the dispersed phase.

On the other hand, this does not explain the difference in elongation and strength observed for S26 and S44 composites obtained by the interfacial method. Transmission electron microscopy presents the well-known microphase separation of styrene and butadiene in SBS copolymers. S26 (26 mol % styrene) has a continuous butadiene phase dotted with islands of styrene, while S44 (44 mol % styrene) has alternating lamellae of polybutadiene and polystyrene (Figure 6). Therefore, the continuity of the polybutadiene phase can be maintained in the S26 composites even when PPTA aggregates become larger than either the polybutadiene or polystyrene phase. Also, rigidity may be due to slight interaction between PPTA and polystyrene. In contrast, in S44 composites, PPTA may break the continuity of the styrene phase (which gives its strength to the material) and lack of interaction with polystyrene causes decreased elongation and strength.

SEM pictures of NBR and blends containing 20 wt % PPTA are found in Figure 8. As with SBS, dispersion was more homogeneous in the interfacially synthesized analogs compared to those of the blends. However, NBR composites had finer dispersed phase probably due to better compatibility between NBR and PPTA. The surface of the solution blend was rough, with some voids. Surprisingly, the composites having the finest dispersion exhibited little reinforcing effect. Hence, reinforcement may be more

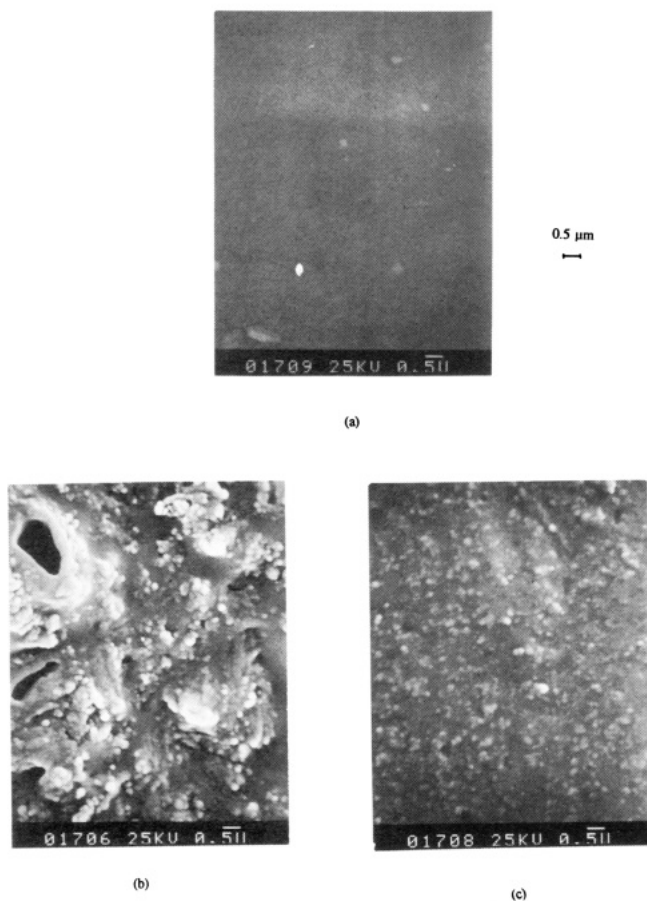


Figure 8. SEM pictures of fracture surface of NBR (a) and its composites containing 20 wt % of PPTA synthesized by solution (b) and interfacial polycondensation (c).

a function of molecular weight of dispersed polymer rather than interfacial area between matrix and dispersed phase.

The difference in trends in elongation between NBR and SBS composites may also be attributed to differing microstructures. NBR, having acrylonitrile groups randomly interspersed between butadiene moieties, has a homogeneous microstructure and shows only one transition temperature as seen from dynamic mechanical measurements.

The interaction effects (between PPTA amide linkage and acrylonitrile units of NBR) are randomly dispersed in the matrix, resulting in an important decrease of elongation when PPTA is incorporated.

On the other hand, S26 has a continuous butadiene phase and polystyrene microphases which both have small interactions with PPTA. In the case of interfacially synthesized composites, where the continuity of polybutadiene phase is kept, elongation thus remains to a high value.

Dynamic Mechanical Properties. Results from measurement of dynamic mechanical properties, i.e., loss tangent and storage shear modulus, are found in Figure

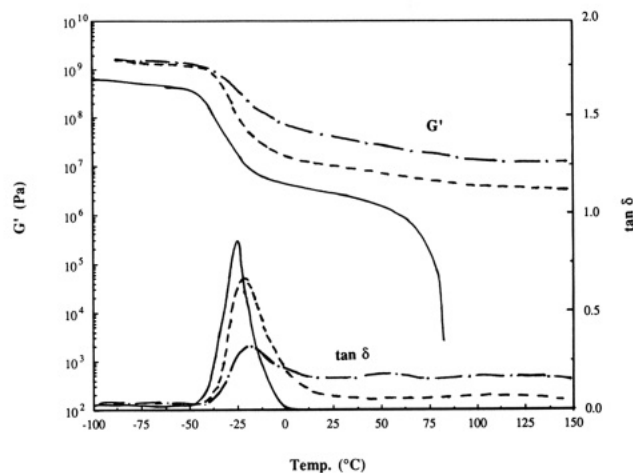


Figure 9. Viscoelastic spectra of NBR (—) and NBR composites containing 20 wt % of PPTA synthesized by solution (---) and by interfacial methods (-.-).

9. These are data for NBR and its composites (20 wt % PPTA) prepared by both methods. In both cases, storage modulus was larger than that of NBR alone over the temperature range indicated and remained higher for the solution-synthesized composites. Also, shear modulus remained at higher values, with the rubbery plateau extending up to 150 °C. These DMS curves indicate that PPTA acts as a cross-linker. The temperature corresponding to the peak of tan δ decreased with the addition of PPTA, especially for the blends. This implies that because PPTA is rigid, movement of NBR chains is restricted. However, this only causes a very slight change in the glass transition temperature probably because of low miscibility.

Conclusion

Polyaramides were successfully synthesized in elastomeric matrices by in situ interfacial and solution polycondensation methods under mild conditions. So-called microcomposites were obtained as a dispersion of the polyamide in the rubber, the reinforcing effect being strongly dependent on type of elastomer used. For both types of rubber, an increase in rigidity was observed but was more pronounced in NBR. The dispersion of PPTA (found as spherical particles) in the composites was dependent on the microstructure of the matrix and the method of preparation, i.e., interfacial or solution. By using in situ polycondensation, it was possible to obtain some blends of polyamide and elastomer which are thermodynamically incompatible.

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Registry No. PPTA (polymer), 25035-37-4; PPTA (SRU), 24938-64-5.