Polymer Bulletin 13, 35–42 (1985)

Polymer Bulletin

Improved Properties of Molecular Composite of Nitrile Rubber and Poly (p-Phenylene Terephthalamide) by Blending with Poly (Vinyl Chloride)

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SUMMARY

Nitrile rubber (NBR) was reinforced by poly(p-phenylene terephthalamide) (PPTA) with a coprecipitation method from a common solvent of them. PPTA was converted to N-sodium PPTA with sodium hydride in DMSO, forming homogeneous solution. DMF dissolves NBR. Both solutions were blended to form an isotropic solution. The precipitant was NBR reinforced by PPTA which was regenerated from N-sodium PPTA at coagulation as reported previously. The molecular composite thus obtained was mill-blended with poly(vinyl chloride) (PVC) in order to enhance solvent resistant property. The vulcanized composite of NBR/PVC reinforced by PPTA showed higher modulus, higher strength and more improved solvent resistance than the gum stock and the black stock of NBR/PVC. The properties of the molecular composite containing 5phr PPTA found approximately comparable to those of the black stock of NBR/PVC with 30-40phr ISAF carbon black.

INTRODUCTION

Molecular composite means the system in which the rigid molecules reinforce the matrix of flexible polymer molecules. This terminology was already employed in a book on Polymer Liquid Crystals (1). The basic idea was independently developed in Japan (2) and USA (3). Coprecipitation method is employed by using an isotropic solution of ternary system of rod, coil molecules and solvent, avoiding formation of crystals with low aspect ratio which tend to be formed from a liquid crystalline solution. The texture of molecular composite is wholly birefringent, but homogeneous in observation by a polarization optical microscope under crossed nicols (4,5). Electron microscopic observation frequently proved the existence of microfibrils of rigid molecules with ca. 30nm of diameter, which were uniformly dispersed in the matrix polymers. Molecular composite thus formed behaves as a new raw material in both properties and processability (1). It was found that a small fraction of rigid molecules in molecular composite provides conspicuous increase in modulus and strength together with improved heat resistance (4).

In our previous work (6,7), we reported molecular composite composed of poly(p-phenylene terephthalamide) (PPTA) and nitrile rubber (NBR). The reinforcing effects of PPTA in the composite were more conspicuous than those of carbon black when compared at the same volume fraction.

Blending of poly(vinyl chloride) (PVC) with NBR provides advantages in ozone resistance, tear and flex resistance, flame resistance and good processability in comparison with NBR, though poorer abrasion resistance, higher compression set and lower tensile strength were indicated.

In this paper, the reinforcing effects of PPTA on the highly compatible binary system of NBR and PVC were studied and compared with those of both original gum stock and regular black stock.

RESULTS AND DISCUSSION

Figure 1 shows the stress-strain curves of NBR/PVC gum stock and its molecular composites with 5phr PPTA. (Unit of phr is a part per 100 parts of matrix polymer.) With a small fraction of PPTA, tensile strength and modulus of the composites increased markedly. Tensile stress at 100% elongation, M_{100}, increased to 5.8MPa and 8.5MPa by employing PPTA of molecular weight, M*w*, 4900 and 25100, respectively, while M_{100} of the original gum stock was 2.1MPa. Tensile strength at break, T*b*, of NBR/PVC reinforced by PPTA with M*w* 4900 and 25100 increased to 23.4MPa and 24.5MPa, respectively, while T*b* of the gum stock was 15.9MPa. Table 1 lists the charateristic values of the gum stock, the black stock filled with 30phr and 40phr of carbon black ISAF and their molecular composites. With increasing amount of PPTA and M*w* of PPTA, tensile modulus and strength were increased. Comparing the

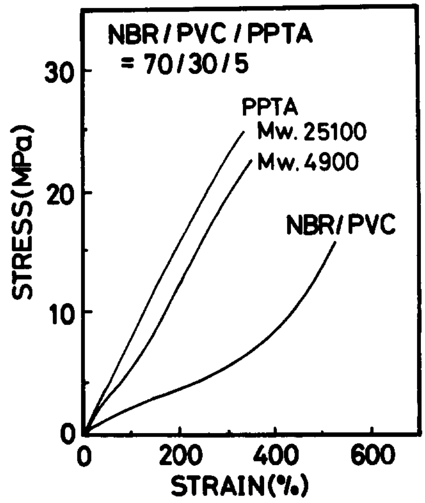


Fig.1 Stress-strain curves of NBR/PVC (70/30 by weight) gum stock and its molecular composites with 5phr of PPTA. M*w* of PPTA are 4900 and 25100, respectively.

Table 1 Tensile properties of gum stock, black stock and molecular composites of NBR/PVC reinforced by PPTA

Carbon Black (phr)	-	-	-	-	-	-	30	40	40
Mw of PPTA	-	4900	21900	25100	4900	25100	-	-	21900
PPTA (phr)	-	2.5	2.5	2.5	5.0	5.0	-	-	2.5
Tensile Stress at 100% Elongation, M_{100} (MPa)	2.1	3.9	4.5	4.8	5.8	8.5	6.4	8.4	13.0
Tensile Stress at 300% Elongation, M_{300}, (MPa)	5.6	12.7	14.6	15.3	19.7	22.6	20.6	24.7	-
Tensile Strength at Break, T_b (MPa)	15.9	18.2	17.6	20.7	23.4	24.5	24.6	27.7	29.6
Elongation at Break, E_b (%)	520	380	350	390	350	340	380	360	270

data of the black stock with those of the molecular composite without carbon black, M_{100} and T_b of the molecular composite reinforced by 5phr of PPTA (Mw 25100) showed the values close to those of the black stock with 30-40phr carbon black. In other words, the reinforcing effect of PPTA was estimated to be about 5-6 times effective in comparison with carbon black by taking into account both their stress-strain characteristics and densities. Molecular composite filled carbon black was also investigated. The values of M_{100} and T_b of the molecular composite increased to 1.55 and 1.07 times by adding only 2.5phr of PPTA, respectively.

Figures 2 (a) and (b) show the temperature dependence of M_{100} and T_b of the molecular composites and the original gum stock, respectively. Tensile modulus and strength decreased with a increase in temperature. The temperature dependence of M_{100} of the molecular composite (Mw 25100-5phr) was superior to that of the black stock filled with 40phr of ISAF carbon black. The latter sample showed M_{100} of 8.4MPa at 298K and 2.0MPa at 393K, respectively. The temperature dependence of T_b of the molecular composite was larger than that of the black stock, which had T_b of 27.7MPa at 298K and 8.8MPa at 393K, respectively.

Figure 3 shows the dynamic storage modulus, E', at 11Hz for the gum stock, the black stock and their molecular composites as a function of temperature. The E' curves showed a marked increase in the storage moduli of the molecular composites compared with those of the original binary blends of NBR/PVC over the whole temperature range in a rubbery region. The Figure shows that the transition temperature of the matrix of the molecular composite did not shift to higher temperature side as similar as the behavior of the black stock.

Figure 4 shows the solvent resistant effect of the molecular composites. Dichloromethane, tetrahydrofuran, acetone, toluene/ethanol (80/20 by volume) and toluene were employed, the swelling power of which was decreased with this order. The swollen volume of the vulcanizate was increased with better solvent. The degree of the restriction of reinforcement is increased with increasing interaction between matrix and reinforcement (8). The effect of PPTA (Mw 25100-5phr) was comparable to that of the black stock filled 40phr of ISAF carbon black. This tendency was similar to that of the reinforcing effect in tensile properties.

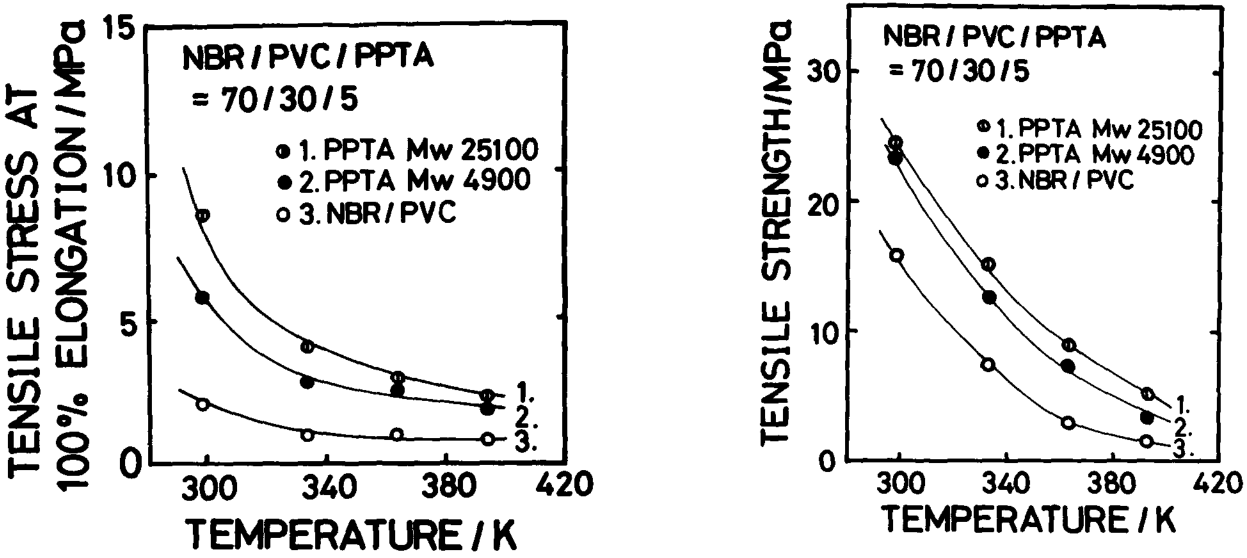
The molecular composite has a possibility to be an excellent candidate for solvent resisting rubber material for automobile use. In addition, the usage of the molecular composite leads to lighten rubber materials because of low density of PPTA ($d=1.44g/cm^3$) compared with that of carbon black ($d=1.70-1.95g/cm^3$).

Formation of PPTA microfibrillar network in the matrix as observed in PPTA/NBR system (6,7) is also favorable for mechanical and solvent resistant properties of the molecular composite composed of PPTA and NBR/PVC.

EXPERIMENTAL

Materials

NBR employed in this study was JSR NBR N220S® (Japan Synthetic Rubber Co., Ltd.) which contains 40wt% of bound acrylo-



(a)

(b)

Fig. 2 Temperature dependence of (a) M_{100} and (b) T_b for gum stock and its molecular composites with 5phr of PPTA. Mw of PPTA are 4900 and 25100, respectively.

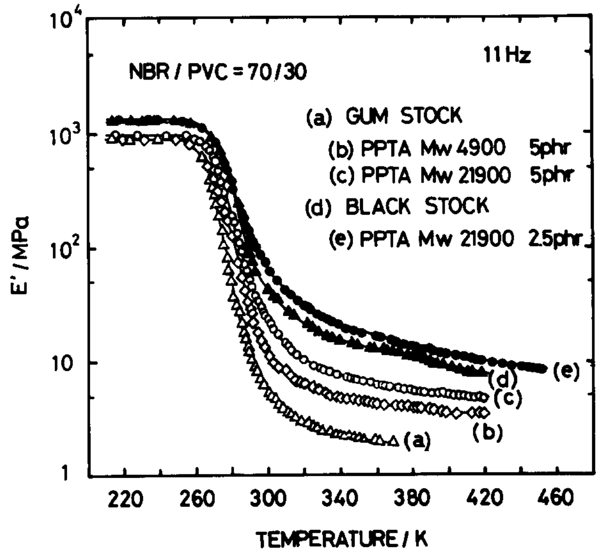


Fig. 3 Temperature dependence of E' for gum stock, black stock and their molecular composites.

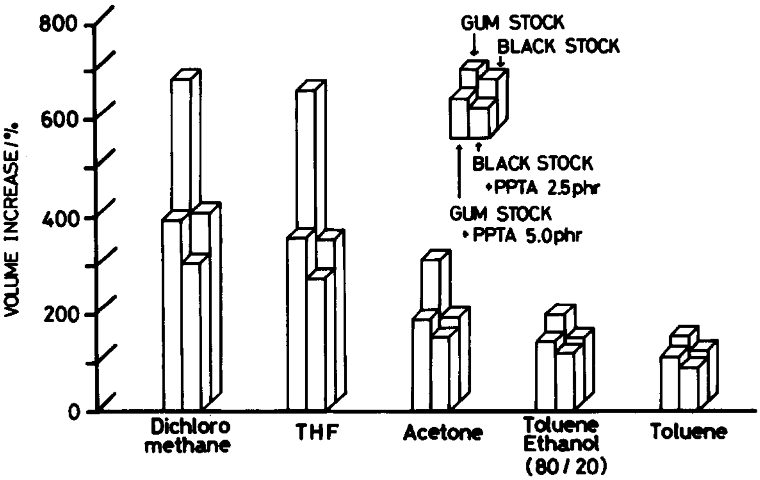


Fig. 4 Restriction effect on swelling in various solvents for gum stock, black stock and their molecular composites. 5phr of PPTA was employed in the case of gum stock and 2.5phr in the case of black stock. Mw of PPTA is 25100.

Table 2 Compounding Formulation

	A	B	C	D	E	F
NBR	70	70	70	70	70	70
PVC	30	30	30	30	30	30
Zinc Oxide	3.0	3.0	3.0	3.0	3.0	3.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
Stearic Acid	1.0	1.0	1.0	1.0	1.0	1.0
Antioxidant 1)	1.0	1.0	1.0	1.0	1.0	1.0
Vulcanization Accelerator 2)	0.7	0.7	0.7	0.7	0.7	0.7
Plasticizer 3)	8.0	8.0	8.0	8.0	8.0	8.0
Stabilizer 4)	2.0	2.0	2.0	2.0	2.0	2.0
Carbon Black 5)	-	-	-	30	40	40
PPTA	-	2.5	5.0	-	-	2.5

1) IPPD, N-phenyl-N'-iso-propyl-p-phenylenediamine

2) TBBS, N-tert-butyl-2-benzothiazole Sulfenamide

3) Dioctyl Phthalate

4) Organic Tin Compound

5) ISAF

nitrile. PVC used was Vinychlone 3000M® (Mitsui Toatsu Chemical Industry Co., Ltd.) PPTA was synthsized from terephthaloyl chloride and p-phenylenediamine by low temperature polycondensation (9). The molecular weight of PPTA was evaluated by the intrinsic viscosity (10). DMF and DMSO were purified by fractional distilation at reduced pressure over calcium hydride. Sodium hydride as a metalation agent was commercially obtained.

Preparation of molecular composite

N-sodium PPTA was synthesized from PPTA and sodium hydride in DMSO (11). The solution of metalated PPTA was blended with DMF solution of NBR by the method in the previous paper (6).

PVC was mixed with molecular composite of PPTA/NBR by Brabender mixer® at 423K for 10min. The mixing ratio of the sample was kept constant at NBR/PVC=70/30 (by weight). The mixed composite was compounded on a two-roll open mill according to the formulation listed in Table 2. Compounded composite was cured at 428K by compression moulding for 60min. Curing was monitored by Curelastometer® (Japan Synthetic Rubber Co., Ltd.), and its curing curve indicated the optimum cure condition.

Physical properties

Tensile properties of cured samples were measured on a ring shape specimen at 200%/min strain rate.

Dynamic storage modulus, E', was measured by Rheovibron DDV-IIB® (Toyo Baldwin Instruments Co., Ltd.) under nitrogen atmosphere at 11Hz. The measurements was conducted along the milling direction of the samples.

Swelling test was made by immersing cured specimens (20mm x 20mm x 1mm) according to JIS K6301. Solvent resistance was evaluated from the volume increase at equilibrium swelling.

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Accepted November 14, 1984