

Advances in Polymer Blends and Alloys Technology



VOLUME 4

Edited by Kier Finlayson

Advances in Polymer Blends and Alloys Technology

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EDITOR'S NOTE: Blends and alloys are now an active area of polymer research and development. This is the fourth volume in a series, which discusses the technology of a rapidly emerging area in polymer technology. These chapters are a collection of the views and efforts of the individual authors who are active in the field.

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Structure, Morphology and Physical Property of Dynamically Vulcanized Polyurethane/Nitrile Butadiene Rubber Blends

TAO TANG,* CHUN PU HU,* SHENG KANG YING*¹
and YING XI ZHANG**

ABSTRACT: The novel thermoplastic elastomers of dynamically vulcanized thermoplastic polyurethane (TPU) and nitrile butadiene rubber (NBR) blends were prepared for studying their structures, morphologies and physical properties. The experimental results showed that the dynamic vulcanization process mainly took place in the NBR phase and there was some compatibility between the TPU and NBR phases, whereas this kind of vulcanizate was essentially an incompatible system. The NBR phase could be transferred from continuous phase to dispersion phase during the vulcanization process progressively, and could enhance the hydrogen bonds between the hard segments in TPU appreciably. The superior physical properties of these vulcanizates (oil resistance performance at 393 K, resistance to ozone aging and mechanical properties) could be correlated well with their structures and morphologies. The mechanical properties for TPU/NBR vulcanizates studied in this chapter were much better than those for TPU/NBR simple blend systems, and the ultimate tensile strength of vulcanizates was even better than that of pure TPU, which exhibited a significant synergistic effect between the TPU and NBR phases.

KEY WORDS: polyurethane, nitrile butadiene rubber, dynamically vulcanized blend, morphology.

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INTRODUCTION

THE PREFERRED PROCESS for generating thermoplastic vulcanizates is dynamic vulcanization. Pioneered by Gessler [1] and Fisher [2], this kind of vulcanization has been extensively explored and studied [3–6] for preparing thermoplastic elastomers. Static vulcanization involves the heating of a rubber stock (fully compounded and mixed with a curing system) at a certain temperature for a specified time, during which time chemical cross-links are formed between the macromolecules of the elastomer. Dynamic vulcanization, on the other hand, embraces the curing of a rubber composition during its mixing or masticating, and one of the ingredients of this rubber composition is thermoplastic. This process results in very useful thermoplastic vulcanizates which operate as conventional thermoplastics.

In this chapter, novel blends containing various compositions of thermoplastic polyurethane (TPU) and nitrile butadiene rubber (NBR) prepared by using dynamic vulcanization were reported. The structures, morphologies and physical properties of such blends were observed and measured, respectively.

EXPERIMENTAL

Polytetrahydrofuran-based TPU was provided by the Tianjin Polyurethane Product Plant, and NBRs were supplied by Lanzhou Chemical Co. Other chemicals were standard laboratory chemicals obtained from various suppliers.

Vulcanized blends were prepared on a rubber mill whose temperature was set at 433 K. The TPU was charged onto the mill, then the NBR was charged. After mixing them, sulfur (vulcanizing agent) and other coagents (ZnO, stearic acid and bibenzothiazole disulfide) were added in and milling was continued for 12 min. After cooling the blend to 413 K, sheets with a thickness of around 3 mm were produced. The resulting blend sheets were pressed between the hot platens (403–443 K) for 8 min and then transferred to a cold press for making the specimens. Comparable blend specimens were prepared following the same procedure without adding any vulcanizing agents.

Infrared spectroscopy (IR) of the samples was made on a P983G IR spectrometer. Dynamic mechanical thermal analysis (DMTA) was carried out using a Rheovitron DDV-II at 35 Hz and 2 K/min. The morphology of these blend samples was observed by using an Hitachi transmission electron microscope (TEM).

The mechanical properties, such as ultimate tensile strength, stress at 100% strain, ultimate elongation, tension set, and split tear strength were measured according to GB 528-82 and GB 529-81, respectively. The oil resistance was determined according to GB 1690-82.

RESULTS AND DISCUSSION

Structure and Morphology

Dynamic vulcanizates always exhibit better mechanical properties than general polymer blends because one of the phases is cross-linked during the blending

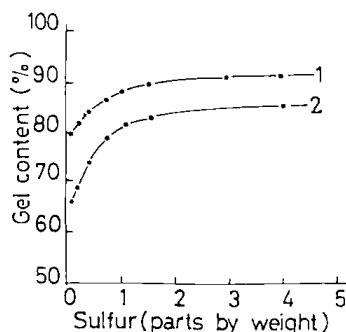


FIGURE 1. Gel contents as functions of applied amount of sulfur: 1—NBR and 2—TPU/NBR = 50/100 (by wt).

process. Thus, it is of interest to examine the cross-linking degree of such a phase and determine whether the other phase is vulcanized. Figure 1 shows that the insoluble part of the TPU/NBR system extracted by using tetrahydrofuran as solvent increases with increasing the amount of sulfur from 0 to 1.5 parts (by weight) rapidly. However, the gel content of TPU/NBR dynamic vulcanizate is lower than that of a pure NBR system, which may be attributed to the dilution effect of TPU existing in the blend so that the rate of the cross-linking reaction decreases. Figure 2 shows the IR spectra of the insoluble part of the dynamic vulcanizate. It can be seen that the characteristic peak of ether bonds ($-\text{C}-\text{O}-$) at 1100 cm^{-1} that existed in TPU decreases appreciably after extracting. It is clear that the insoluble part for this TPU/NBR system should consist mainly of cross-linked NBR, whereas some chemical linkages between these two rubbers are also formed during dynamic vulcanization.

The DMTA results of these TPU/NBR dynamic vulcanizates and comparable specimens of a simple blend of these two rubbers as well as their glass transition temperatures (T_g s) are shown in Figure 3 and listed in Table 1. Figure 3 shows

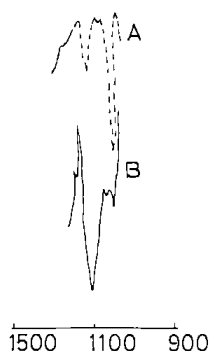


FIGURE 2. IR spectra of TPU/NBR vulcanizates before (B) and after (A) extraction of tetrahydrofuran. TPU/NBR = 50/100 parts (by wt).

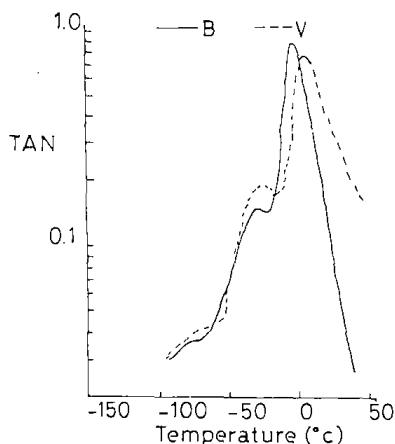


FIGURE 3. Dynamic mechanical spectra of TPU/NBR blends (B) and vulcanizates (V). TPU/NBR = 100/100 (by wt).

that there are two peaks for both systems indicating the phases existing in those blends are incompatible and the phase separation between these phases should be expected. As is shown in Figure 3, the peak for vulcanizate at low temperature, representing the soft segments of PU, exhibits approximately the same position as that of unvulcanizate, but the high temperature peak formed by the NBR phase shifts to a higher temperature than that of peak for comparable specimen. This behavior must result from the chemical cross-linking reaction mainly between the macromolecules in the NBR phase so that it gives rise to a higher T_g , and could be correlated well enough with the structure of this system discussed above. Table 1 shows that the T_g s of soft segments in PU decrease with increasing the content of NBR, whereas the T_g s of the NBR phase decrease with the lowering of NBR content. The T_g of soft segments in PU for this system is even lower

Table 1. Effect of TPU/NBR composition on glass transition temperatures of the blends.*

Composition of TPU/NBR (wt/wt)	T_g of NBR Phase (K)	T_g of Soft Segments in TPU (K)
0/100	278	—
50/100	273	243
100/100	273	243
100/30	270	246
100/0	—	246

* T_g s were 181 K (BR phase) and 243 K (soft segments in TPU) for comparable blend specimen of TPU/BR (wt ratio = 100/50) respectively.

than that of pure PU, while NBR amount increases to over 50% (by weight). Therefore, it could be attributed to the same compatibility between the soft segments in PU and the polybutadiene segments in NBR, which has a very low T_g (~ 183 K). In order to test this explanation, the T_g for TPU and polybutadiene rubber (BR) simple blend was measured and listed in Table 1. The experimental result indicates that for this simple blend the T_g of soft segments in PU also shifts to 243 K just the same as the values of T_g in those high NBR content blend vulcanizates. The lowering of T_g for low content of NBR systems seems to be related to the form of some chemical bonds between the NBR and soft segments in PU, as we mentioned before. In this case the NBR phase could give rise to lower T_g (see Table 1).

It is well known that TPU elastomers are composed of soft segments, hard segments, and a great deal of hydrogen bonds [7]. The latter case has been studied in detail by using IR; the free carboxyl group exhibits a characteristic absorption at 1730 cm^{-1} , whereas the hydrogen bonded carboxyl group gives rise to another one at 1700 cm^{-1} [8,9]. Figure 4 shows that the relative strength of the free carboxyl group peaks to hydrogen-bonded peaks decreases progressively with the increase of NBR amount in the dynamic vulcanizates. It is clear that the NBR phase enhances the formation of hydrogen bonds between the hard segments in PU. The reason for this behavior might be complicated. However, some compatibility between the soft segments in PU and the polybutadiene segments in NBR seems possible to suppress the formation of some hydrogen bonds between the soft and hard segments in PU and to increase the possibility of the formation of hydrogen bonds between the hard segments in PU.

In order to examine the morphology more directly, these blend systems were observed by using transmission electron microscopy (TEM), as shown in Figure 5. These TEM photos show that, for a simple blend of TPU/NBR, NBR exists as a continuous phase in which the TPU forms as domains, but the NBR phase progressively transfers to a dispersion phase during the dynamic vulcanization pro-

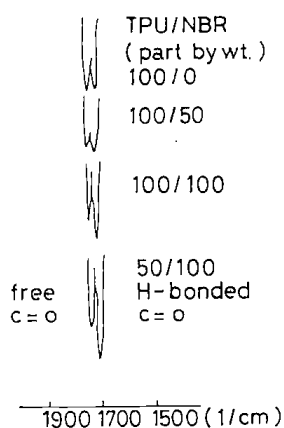


FIGURE 4. Effect of TPU/NBR proportion on relative content of free carboxyl groups and hydrogen-bonded carboxyl groups.

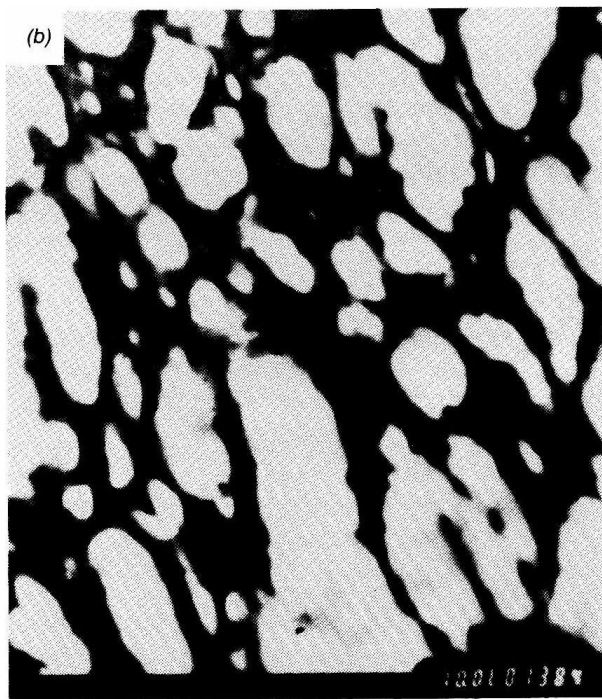
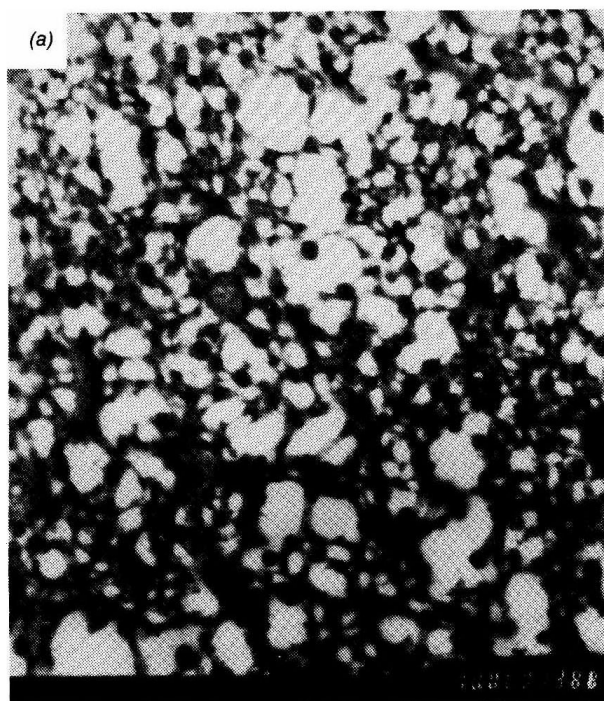


FIGURE 5. Transmission electron microscopy photos of TPU/NBR blends at different vulcanization times: (a) 0 min and (b) 1 min. TPU/NBR proportion = 50/100 parts (by wt).

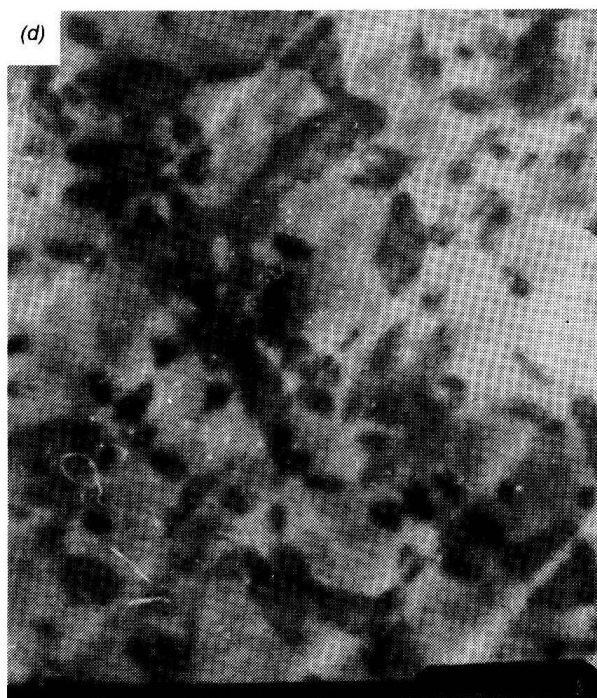
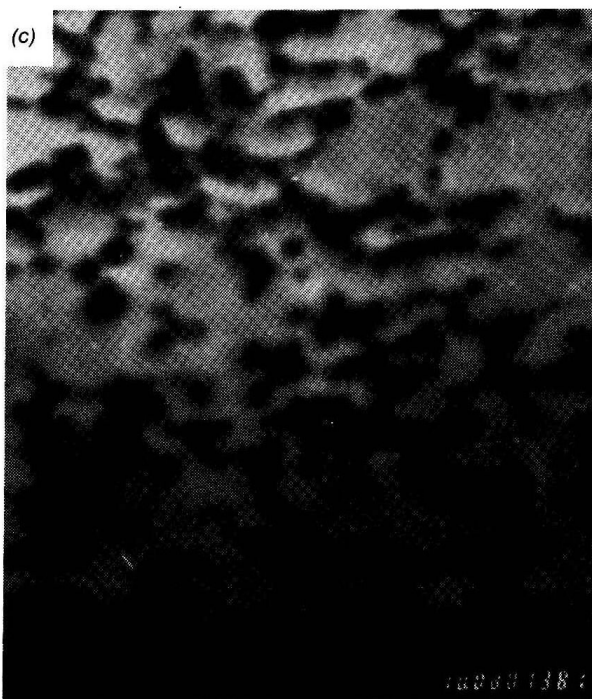


FIGURE 5 (continued). Transmission electron microscopy photos of TPU/NBR blends at different vulcanization times: (c) 10 min and (d) 25 min. TPU/NBR proportion = 50/100 parts (by wt).

Table 2. Physical properties of TPU/NBR blends.

Nitrile Content of NBR (%)	Ultimate Tensile Strength (MPa)		Stress at 100% Strain (MPa)		Ultimate Elongation (%)		Tension Set (%)		Split Tear Strength, 298 K (kN/m)		Hardness Shore A Scale		Brittle Point (K)		Volume Swell 393 K, 3#oil, 70 h (%)	
	V		V		V		V		V		V		V		V	
	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
0	4.1	0.7	1.7	—	470	150	27	10	19	5	48	34	212	—	—	—
18	9.5	2.6	2.2	1.6	630	370	43	30	42	23	62	58	218	60.9	60.9	60.9
26	11.4	4.2	2.4	2.1	660	520	43	70	47	31	62	58	217	29.3	29.3	29.3
40	14.7	7.6	2.7	2.6	630	740	40	107	51	44	66	44	218	19.8	19.8	19.8

V—dynamically vulcanized blend.

B—unvulcanized blend.

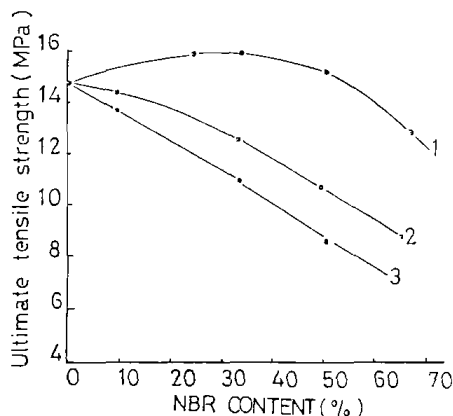


FIGURE 6. Effect of NBR content on ultimate tensile strength of vulcanized TPU/NBR blends: 1—NBR-18%, 2—NBR-26%, and 3—NBR-40%.

cess. This is direct evidence of the formation of chemical cross-linking bonds in the NBR phase. Following this phase inversion, TPU existing as matrix could be expected. However, the domains of hard segments in PU, which usually show in TEM photomicrographs for pure PU, are not found in Figure 5. Thus, it seems possible that for such complicated systems these domains may be too hard to be distinguished from our TEM photos. The same behavior has also been observed in PU/vinyl ester resin interpenetrating polymer networks [10].

Physical Property

Table 2 shows the physical property dependence of nitrile content in NBR for TPU/NBR vulcanizate and unvulcanizate, respectively. The results indicate that mechanical properties, except ultimate elongation and tension set, are enhanced with increasing the content of nitrile in NBR added for both blend systems; all of these properties for vulcanizate are much better than those for unvulcanizate, although the miscibility between the phases of vulcanizate seems not to be improved, which is very important for improving the mechanical properties of simple blend systems [11]. The system of NBR containing 40% nitrile (NBR-40) reveals the best mechanical properties, as well as the best oil resistance performance at 393 K, over all specimens studied in this paper, as also shown in Table 2. The increased concentration of nitrile in NBR with the enhancement of mechanical properties could be related to the reinforcement of NBR particles for TPU continuous phase in the blend, since the strength of such NBR particles should increase with the increase of more polar acetonitrile units in NBR.

Figure 6 shows the relationship between the ultimate tensile strength and the composition of NBR for these vulcanized blend systems. It is clear that there are positive deviation curves in this plot when the concentration of nitrile is over 18%. For NBR-40 systems, the ultimate tensile strength goes through a maximum with the increase of NBR content (around 30%), at which point the ultimate tensile strength is even higher than that of pure TPU. Such a synergistic effect be-