Studies on the Blends of CO_2 Copolymer. IV. Natural Rubber/Poly(propylene carbonate) Systems

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ABSTRACT: The blends of a carbon dioxide copolymer, poly(propylene carbonate)(PPC) with natural rubber (NR), were prepared and their mechanical properties and morphology were studied. The optimum formulation blend was obtained by orthogonal experiments. The tensile strength of the blend containing 30 phr PPC was 18.9 MPa, with an elongation at break of 755%. The factors such as PPC and dicumyl peroxide content, PPC molecular weight, sulfur content, curing time, and curing temperature responsible for controlling the mechanical properties were discussed. Transverse electron micrographs showed a two-phase structure for this blend. Gel content data revealed that PPC was crosslinked. The phase stability of PPC in the blend improved because of the interpenetrating new work structure. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2140–2144, 2002

Key words: poly(propylene carbonate); blends; crosslinking; elastomers; carbon dioxide copolymer

INTRODUCTION

The emission of CO_2 from industries and municipal wastes is causing serious environmental problems. Conversion of CO_2 into useful polymers may solve this problem to some extent. Moreover, the synthesis of CO_2 polymers is economical. In the CO_2 copolymer family, poly(propylene carbonate) (PPC) is a popular member.[1] PPCs are used as adhesives, solid electrolytes, polyols, photoresists, barrier materials, flexibilizers, and plasticizers. In our research group, we are attempting to blend PPC with rubbers to obtain elastomers with soft molecular segments, low glass transition temperature, and amorphous nature. The PPC/nitrile butadiene rubber (NBR),[2] and PPC/styrene butadiene rubber (SBR)[3] developed by us possess better mechanical properties. In the present work, we developed PPC/natural rubber (NR) blends and studied their mechanical properties. The optimum formulation for these blend elastomers was achieved by orthogonal experiments. The factors controlling their mechanical properties are discussed.

EXPERIMENTAL

Materials

Poly(propylene carbonate) (PPC) with a viscosity average molecular weight of 26,800 was synthesized in our institute. Natural rubber was supplied by Guangzhou the Sixth Rubber Factory, diphenyl guanidine (Accelerator D), 2-mercaptobenzothiazole (Accelerator M), stearic acid, zinc oxide, 2-mercaptobenzimidazole (Antioxidant MB), sulfur, maleic anhydride (MA), and dicumyl peroxide (DCP), were the other commercial materials used as additives.

Processing of the PPC/NR systems

Different of compositions of NR, PPC, and other additives were uniformly mixed in an XKR-160A type two-roll mixer at room temperature and then compressed with a QLB-D type of flat vulcanizing heater at 130°C at a certain temperature under a certain pressure.

Measurements

The tensile strength and elongation at break of the elastomers were determined employing a DXLL-2500 type Electron Tensile Testing Machine as per the Chinese National Standard GB/T 528-92 method. The Shore A Hardness was measured as per the GB/T 531-92 method. Thermogravimetric analysis (TGA) was carried out on a Dupont 2000 thermo-balance at a heating rate of 10°C/min up to 600°C. Transverse electron micrographs (TEMs) were recorded with a JEM-100XII instrument. The samples were microtomed and stained in OsO_4 vapor before use. The gel contents were measured by extracting with toluene for 24 h.

TABLE I
Dimensions and Factors of the Orthogonal test

				Factor							
				D			E		F	G	H
	A	B	C	Accelerators			Other Assistant		Time	Temperature	Pressure
Dimension	DCP	MA	S	M	D	ZnO	Stearic Acid	Antioxidant	(min)	(°C)	(MPa)
1	0	0.5	1.8	0.4	0.35	3.5	1.4	0.7	11.5	140	10
2	1	2	2.1	0.5	0.43	4.3	1.7	0.85	16.5	150	15
3	2	0	2.5	0.6	0.5	5	2	1	21.5	160	—

RESULTS AND DISCUSSION

Formulation design with orthogonal experiments

PPC is a polar polymer that is incompatible with nonpolar NR. Adding PPC directly into NR will re-duce the mechanical properties. Hence, it is necessary to design and adjust the formulation to obtain better strength. The basic formulation we generally adopt is as follows: NR, 70 phr; PPC, 30 phr; ZnO, 4 phr; stearic acid, 1.5 phr; antioxidant MB, 1 phr; accelerator M, 0.5

TABLE II
Mechanical Properties of Orthogonal Test

Samples	Factors								Shore A Hardness	Tensile Strength (MPa)	Elongation at Break (%)
	A	B	C	D	E	F	G	H			
1	1	1	3	2	2	1	2	1	21	11.7	872
2	2	1	1	1	1	2	1	1	20	10.8	936
3	3	1	2	3	3	3	3	1	24	8.6	665
4	1	2	2	1	2	3	1	1	20	8.2	958
5	2	2	3	3	1	1	3	1	22	10.0	800
6	3	2	1	2	3	2	2	1	23	9.8	741
7	1	3	1	3	1	3	2	1	22	12.6	770
8	2	3	2	2	3	1	1	1	27	19.6	784
9	3	3	3	1	2	2	3	1	27	9.2	636
10	1	1	1	1	3	1	3	2	20	8.8	927
11	2	1	2	3	2	2	2	2	26	15.1	746
12	3	1	3	2	1	3	1	2	28	14.6	720
13	1	2	3	3	3	2	1	2	20	7.5	950
14	2	2	1	2	2	3	3	2	20	7.2	834
15	3	2	2	1	1	1	2	2	20	7.0	985
16	1	3	2	2	1	2	3	2	22	13.0	805
17	2	3	3	1	3	3	2	2	29	14.6	710
18	3	3	1	3	2	1	1	2	26	18.9	755
Sum of hardness of dimension 1[a]	126	139	131	137	134	136	142	207			
Sum of hardness of dimension 2	144	126	139	141	141	138	141	211			
Sum of hardness of dimension 3	148	153	147	140	143	144	135	—			
Difference of hardness sums[b]	22	27	16	4	9	8	7	4			
Sum of tensile strength of dimension 1	61.8	69.6	68.1	58.6	68.0	76.0	79.6	100.5			
Sum of tensile strength of dimension 2	77.2	49.6	71.5	75.9	70.3	65.4	70.8	106.7			
Sum of tensile strength of dimension 3	68.1	87.9	67.5	72.7	68.9	65.8	56.8	—			
Difference of tensile strength sums	15.5	38.2	4.0	17.3	2.4	10.6	22.8	6.2			
Sum of elongation at break of dimension 1	5282	4866	4963	5152	5016	5123	5103	7162			
Sum of elongation at break of dimension 2	4810	5268	4943	4756	4801	4814	4824	7432			
Sum of elongation at break of dimension 3	4502	4460	4688	4686	4777	4657	4667	—			
Difference of elongation at break sums	780	808	275	466	239	466	436	270			

[a] Refers to the sum of hardness of the samples that the certain factors are in dimension 1 in the 18 samples.
[b] Refers to the difference of the maximum sum and minimum sum of a certain factor.

TABLE III
Formula Adjust and Mechanical Properties[a]

Property	Sample			
	A-1	A-2	A-3	A-4
Nature Rubber	70	70	70	70
PPC	30	30	30	30
ZnO	5	4.3	5	4.3
Stearic acid	2	1.7	2	1.7
Antioxidant MB	1	0.8	1	0.8
Accelerator M	0.6	0.5	0.5	0.6
Accelerator D	0.5	0.4	0.4	0.5
S	1.8	2.1	2.1	1.8
DCP	1	2	1	2
Tensile strength (MPa)	16.3	16.3	18.8	18.9
Elongation at break (%)	740	786	795	755
Shore A hardness	30	27	29	30

[a] Curing time, 11.5 min; curing temperature, 140°C.

TABLE IV
Influence of PPC on Mechanical Properties (PPC + NR = 100 phr)

Property	PPC (phr)						
	0	5	10	15	20	25	30
Tensile strength (MPa)	24.2	26.6	25.9	24.8	23.1	20.2	18.9
Elongation at break (%)	767	755	803	760	797	830	755
Hardness (Shore A)	35	37	34	34	31	28	30

phr; accelerator D, 0.4 phr; sulfur, 2.5 phr; and DCP, 2 phr. Seven factors in three dimensions and one factor in two dimensions were evaluated by the $L_{18}(3^7 \times 2^1)$ orthogonal test. The factors and the dimensions are shown in Table I and the results are presented in Table II.

Orthogonal experimental analysis shows that there are four important factors affecting the mechanical properties: MA, curing temperature, accelerators, and DCP. The optimum dimensions are A2B3C2D2E2F1G1. The combination of the optimum dimensions may not provide optimum properties. To get the optimum value, the formulation was adjusted. It is clear from the results in Table III that the best formulation is as follows: NR, 70 phr; PPC, 30 phr; ZnO, 4.3 phr; stearic acid, 1.7 phr; antioxidant MB, 0.8 phr; accelerator M, 0.6 phr; accelerator D, 0.5 phr; sulfur, 1.8 phr; and DCP, 2 phr.

Influence of different factors on mechanical properties

The influence of content of PPC on the mechanical properties is shown in Table IV. The tensile strength reaches the maximum and then decreases with increase of PPC. PPC increases the tensile strength when its content is in the range 5–15 phr. The influence of PPC content on Shore A is similar to tensile strength, and the elongation at break is almost invariant.

The results on the effects of sulfur, DCP, curing time, and curing temperature on mechanical properties are presented in Tables V, VI, VII, and VIII, respectively. From these results it is clearly evident that the best conditions are as follows: sulfur, 1.8 phr; DCP, 2 phr; curing time, 11.5 min; curing temperature, 140°C.

The effect of molecular weight of PPC on the mechanical properties is presented in Table IX. It is clearly evident that the molecular weight has little

TABLE V
Influence of Sulfur on Mechanical Properties (PPC/NR = 30/70)

Property	Sulfur (phr)				
	1.3	1.8	2.3	3.3	4.3
Tensile strength (MPa)	14.0	18.9	17.4	18.4	15.4
Elongation at break (%)	839	755	658	646	583
Hardness (Shore A)	25	30	36	36	38

TABLE VI
Influence of DCP on Mechanical Properties (PPC/NR = 30/70)

Property	DCP (phr)				
	0	1	2	3	4
Tensile strength (MPa)	12.9	17.9	18.9	15.8	15.3
Elongation at break (%)	709	692	755	574	607
Hardness (Shore A)	30	32	30	35	34

TABLE VII
Influence of Curing Time on Mechanical Properties
(PPC/NR=30/70)

Property	Curing Time (min)			
	5	11.5	15	20
Tensile strength (MPa)	4.3	18.9	17.1	16.0
Elongation at break (%)	914	755	715	660
Hardness (Shore A)	<20	30	36	35

TABLE VIII
Influence of Curing Temperature on Mechanical
Properties (PPC/NR = 30/70)

Property	Curing Temperature (°C)				
	130	135	140	150	160
Tensile strength (MPa)	11.8	16.9	18.9	17.6	15.4
Elongation at break (%)	923	814	755	708	639
Hardness (Shore A)	26	27	30	32	35

effect on the tensile strength and percent elongation at break of the blend. However, the hardness is increased with molecular weight.

Structure of elastomers

Phase structure

PPC is a polar polymer because it contains a large number of carboxyl and hydroxyl groups. The NR is a hydrocarbon polymer, and so the compatibility of the two is poor. The TEMs (Figure 1) reveal two phase structure for the PPC/NR blend. The double bonds were dyed by OsO_4. In the micrographs, the NR phase is black and PPC phase is white. The small deep black dots correspond to the inorganic activator. The area of white fields is increasing with PPC content.
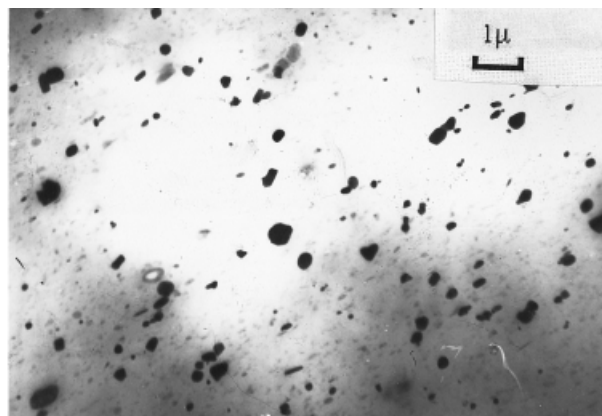
Gel content

Toluene is a good solvent for both PPC and uncured NR. The PPC/NR blends with different PPC contents were extracted with toluene. During the process of abstracting, the samples swell and the molecular chains that are not crosslinked get abstracted into the solvent. The results are presented in Table X.

In the PPC/NR system, sulfur is the main crosslinking agent. It can crosslink only the NR molecules in

TABLE IX
Influence of PPC on Mechanical Properties

| Property	Molecular Weight of PPC	
	M = 26,800	M = 75,000
Tensile strength (MPa)	18.9	18.4
Elongation at break (%)	755	734
Hardness (Shore A)	26	35

the blend. DCP was added for most of the samples as an auxiliary crosslinking agent. It can generate free radicals to facilitate crosslinking reactions. The free radicals generated from the decomposition of the DCP during heating process react with both NR and PPC.

a.
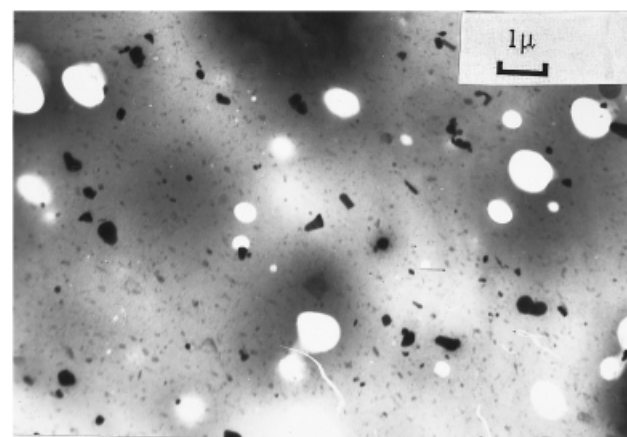
b.
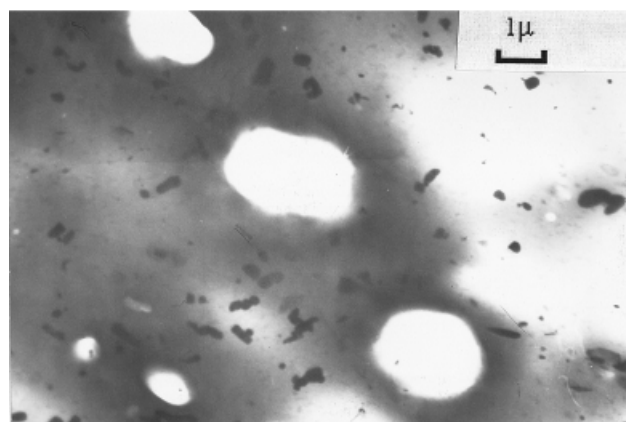
c.

Figure 1 TEM pictures of PPC/NR blends: (a) PPC/NR = 0/100; (b) PPC/NR = 10/90; (c) PPC/NR = 30/70.

TABLE X
Gel Contents of PPC/NR Samples

Property	Sample								
	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
NR (phr)	100	100	95	90	85	80	75	70	70
PPC (phr)	0	0	5	10	15	20	25	30	30
DCP (phr)	0	2	2	2	2	2	2	2	0
Caculated gel contents (%)	—	94.7	89.9	85.2	80.6	75.9	71.1	66.3	66.3
Real gel contents (%)	96.5	95.8	92.5	91.6	90	85.2	83.9	82.9	76.8
Tensile strength (MPa)	—	24.2	26.6	25.9	24.8	23.1	20.2	18.9	12.9
Elongation at break (%)	—	767	755	803	760	797	830	755	709

The samples A-1 and A-2 show that DCP has no effect on NR gel content under the certain formulations and processing conditions. However, for samples A-8 and A-9, which contain PPC, the gel content is higher with than that without DCP. This result indicates that PPC was partially crosslinked by DCP. The calculated gel contents in Table IX were calculated basing on two assumptions: PPC was not crosslinked, and all the NR molecular were crosslinked. It is obvious that the real gel content is higher than the calculated one, indicat-

ing that PPC molecules are partially crosslinked. The mechanical properties of samples A-8 and A-9 are quite different. The TEMs show that the PPC/NR system has a two-phase structure, so the crosslinking of PPC may be due to the formation of an interfacial interpenetrating network.

TGA of PPC/NR

The TGA and DTG curves of PPC/NR blends are depicted in Figure 2. The temperature corresponding to maximum decomposition rate ($T_{d\ max}$) of NR or NR phase is ~370°C. The $T_{d\ max}$ of pure PPC is 252°C, and for the 20% PPC sample, the $T_{d\ max}$ is increased to 316°C. This observation indicates that blending is promoting the stability of PPC, possibly because of the interpenetrating of PPC molecules.
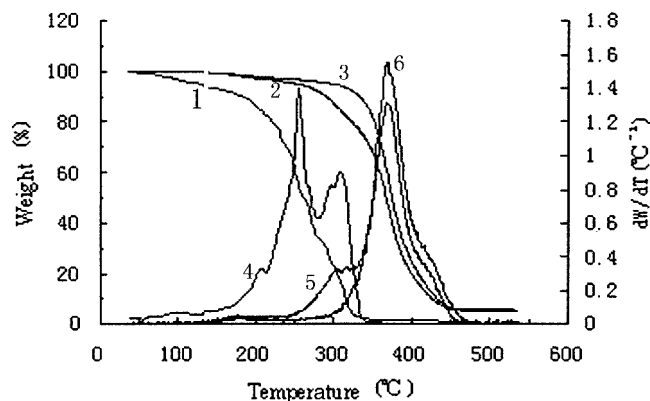
Figure 2 TD (1–3) and DTG (4–6) curves of PPC/NR. Key: (1) PPC/NR = 100/0; (2) PPC/NR = 20/80; (3) PPC/NR = 0/100; (4) PPC/NR = 100/0; (5) PPC/NR = 20/80; (6) PPC/NR = 0/100.

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