Studies on the Blends of Carbon Dioxide Copolymer. III. NBR/PPC Systems

Y. H. HUANG,* X. H. YANG, S. L. ZHAO, G. LIN, M. C. CHEN, B. LIAO, C. Q. WANG, G. M. CONG, and L. B. CHEN
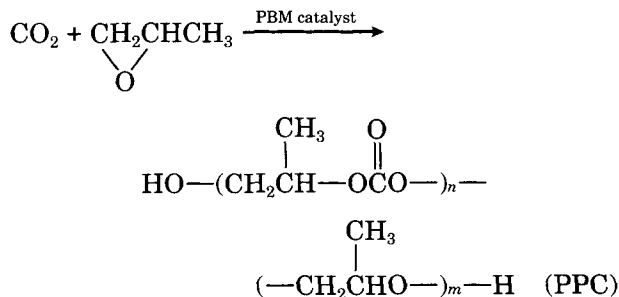
Guangzhou Institute of Chemistry, Academia Sinica, Guangzhou, 510650, P. R. China

SYNOPSIS

In this paper, the blends of the carbon dioxide copolymer, poly(propylene carbonate) (PPC), with nitrile rubber (NBR) were studied by DSC, DMA, TEM and TG. PPC can enhance the mechanical properties of NBR, while oil resistance and tensile set at break of NBR/PPC systems were as good as that of NBR. The coagent of triallylisocyanurate or maleic anhydride with carbon black can much improve the curing efficiency of dicumyl peroxide in NBR/PPC systems. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Carbon dioxide is as abundant as 10^{14} tons in the earth. Meanwhile, it is produced by industries at a rate of about 10^9 tons a year. This generates the serious problem upon the global environment: the ozonosphere of atmosphere is damaged, resulting in the "greenhouse effect." An attractive strategy to deal with this situation is to convert CO_2 into valuable substances. It has been known that CO_2 can be reduced from its stable highest oxidative state to obtain carbon monoxide, methane, alcohol, formic acid, acetic acid and their esters, formaldehyde, and so forth. However, syntheses of such small molecular materials are extremely energy consuming. A much better choice is to produce polymer materials from CO_2. So that, using CO_2 as a monomer to synthesis polymers has received great attention in recent decades.[1-5] The bright examples are the aliphatic polycarbonate, such as poly(propylene carbonate) (PPC) from CO_2 and epoxides by using a high efficient catalyst, polymer chelated bimetallic (PBM) catalyst,[6] which has been conducted successfully in our institute.

$$CO_2 + CH_2CHCH_3 \xrightarrow{\text{PBM catalyst}}$$

$$HO-(CH_2\overset{\displaystyle CH_3}{\underset{}{CH}}-O\overset{\displaystyle O}{\overset{\|}{C}}O-)_n-$$

$$(-CH_2\overset{\displaystyle CH_3}{\underset{}{CH}}O-)_m-H \quad (PPC)$$

In comparing with other catalyst reported in literature, PBM catalyst has not only high efficiency ($\sim 2.2 \times 10^4$g PPC/mol Zn) but also stable to air and can be handled and stored easily. Therefore, PPC could become a practical useful new functional polymer material because of its terminal hydroxyl groups and low costs, as well as helping the environment. About 40–50% of units in the copolymer chain are carbonate, implying that a large amount of CO_2 was fixed in the alternating structure copolymer.

However, under the single component PBM catalyst, the molecular weight of PPCs are in the range of $0.2-2 \times 10^4$. It is a viscous fluid in room temperature. Many efforts to apply PPC as plasticizer for rubber or thermoplastics,[7] surfactant,[8] and toughness agents[9] have been conducted in our laboratory

Table I Basic Formulation of NBR/PPC

Components	Formulation					
	B-0	B-1	B-2	B-3	B-4	B-5
NBR (wt %)	100	90	80	70	60	0
PPC (wt %)	0	10	20	30	40	100
DCP (phr)	1.5	1.5	1.5	1.5	1.5	1.5
MB (phr)	1.5	1.5	1.5	1.5	1.5	1.5
CHPPDA (phr)	1.0	1.0	1.0	1.0	1.0	1.0

in recent years. In this article, PPCs were used to reinforce the nitrile rubber (NBR). The aim is to extend the application field of PPC to promote its industrial production early.

EXPERIMENTAL

Materials

Poly(propylene carbonate) with molecular weight 2 × 10⁴ was synthesized in our Institute. Nitrile-butadiene rubber (NBR), with 26–40% of acrylonitrile contents, $ML_{1+4}(100°C)$: 80–89, made in France, was used as received.

Dicumyl peroxide (DCP), maleic anhydride (MA), and triallylisocyanurate (TAIC) were used for vulcanization of the NBR/PPC system. 2-mercaptobenzimidazole (MB) and N-cyclohexyl-N'-phenyl p-phenylenediamine (CHPPDA) were used as the accelerator and antioxidant, respectively. All of the above chemical compounds are commercial products, made in China.

Processing of the NBR/PPC Blends

A series of compositions of NBR, PPC, MB, and DCP are uniformly mixed by an XKR-160A type of two-roll mixer at room temperature and then compressed by a QLB-D type of flat vulcanizing heater at 130°C and a pressure of 20 MPa for 10 min.

Measurements

The glass transition temperatures (T_g) for all of the polymers were tested by Perkin Elmer DSC-2C at a heating rate of 20°C/min. Dynamic viscoelastic properties were measured with a DDV-2 type Rheometric between −150 and 250°C at a heating rate of 3°C/min and 3.5 Hz frequency. TEM micrographs were measured by using a JEM-100XII instrument, samples were microtomed, and stained in OsO_4 vapor. Thermogravimetric analysis (TG) was carried out on a DT-30B apparatus at a heating rate of 10°C/min in N_2. Mechanical properties were obtained according to ASTM D412-51T, D395-51T, and D676-52T. The stress/strain graphs were obtained by an INSTRON 1121-mode, and the strain rate was 500 mm/min. To test for aging resistance, we maintained the samples at 100°C for 72 h in an air oven or oil and then measured the mechanical properties of the resultant materials.

RESULTS AND DISCUSSION

Structure and Properties of the NBR/PPC Systems

Nitrile rubber has been widely used as oil resistant rubber because of its polar nitrile groups on polymer chain. But its molecular chains are hard to crystallize in the elongated state, because they lack reinforcing ability themselves. The physical properties of NBR can be enhanced by blending other polymers such

Table II Gel Content for Cured NBR/PPC Mixtures (Extracting Solvent: Acetone)

Sample		B-0	B-1	B-2	B-3	B-4
Gel contents (wt %)	Experimental	90.6	93.7	92.7	92.0	91.6
	Calculated[a]	97.1	87.4	77.7	68.0	58.3

[a] Assume that PPC is unable to cure and was extracted by acetone.
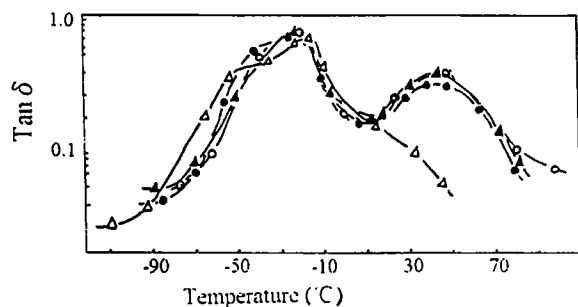
Figure 1 Dynamic loss properties of NBR/PPC elastomers: △, B-0; ○, B-1; ●, B-3; ▲, B-4.

as CPE, EPDM, and PVC.[10] Here, PPC was blended with NBR, and the resultant mixtures were vulcanized by dicumyl peroxide (DCP). The basic formulation of PPC/NBR is given in Table I.

In a peroxide curing system, free radicals are formed along the polymer backbone, and coupling reactions with radicals on adjacent polymer chains result in the formation of cross-link; thus, it can cure saturated and unsaturated polymers.

For evaluating the degree of cross-linking, the cured NBR/PPC elastomers were extracted by acetone, which is a good solvent for both PPC and NBR. From Table II we found both NBR and PPC molecular chains were cross-linked by DCP.
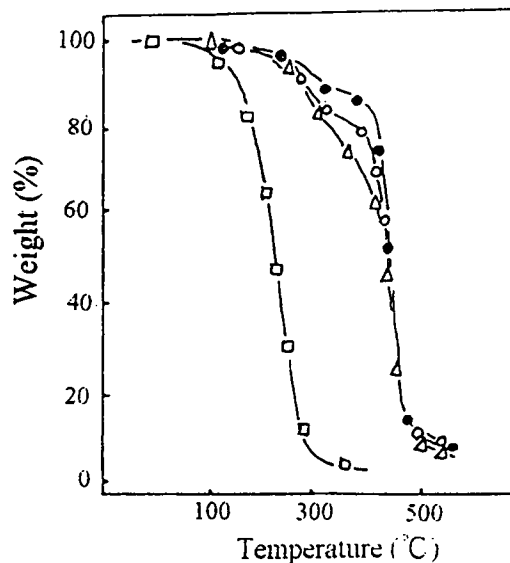

Figure 3 TG curves of NBR/PPC elastomers: ●, B-0; ○, B-1; △, B-3; □, B-5.

The DMA (Fig. 1) and TEM (Fig. 2) measurements show that NBR/PPC systems are two-phase structures. Two relaxation peaks, located at about −30 and 45°C, respond to the NBR phase and PPC phase in tanδ versus temperature curves. The TEM micrographs show the cell-type phase separation
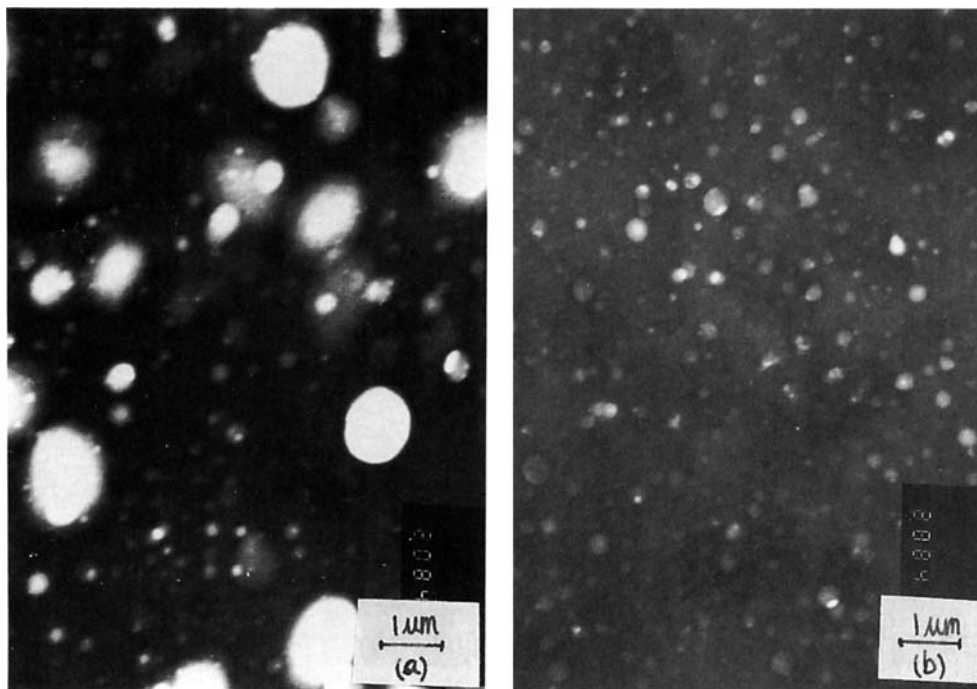

Figure 2 TEM micrograph of NBR/PPC elastomers (NBR/PPC = 70 : 30): (a) uncured, (b) cured.
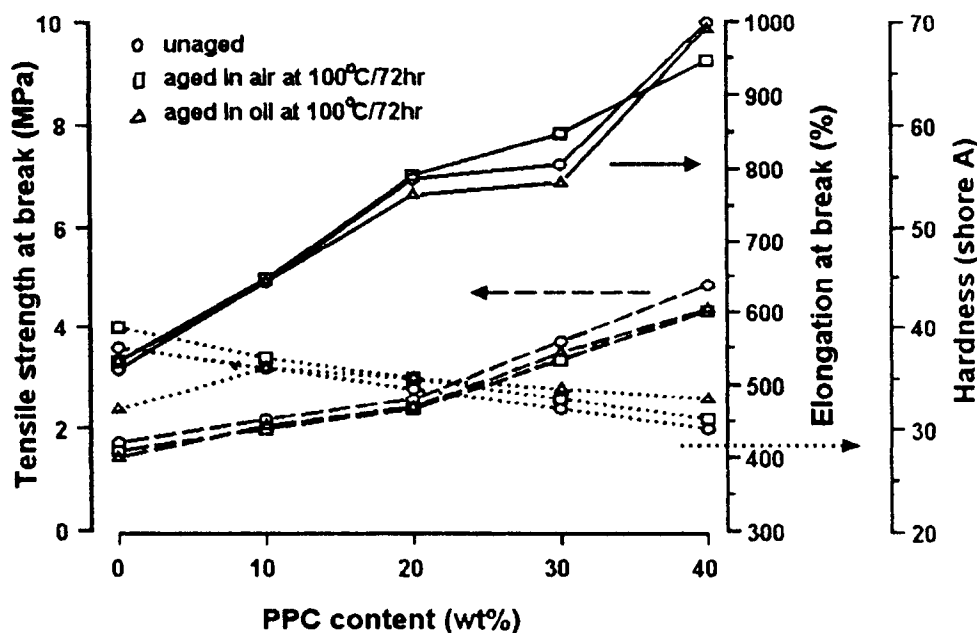
Table III   Mechanical Properties of the NBR/PPC Elastomers

Properties	B-0	B-1	B-2	B-3	B-4
Tensile strength at break (MPa)	1.72	2.17	2.58	3.69	4.82
Elongation at break (%)	520	641	789	806	998
Hardness (shore A)	38	36	34	32	30
Tensile set at break (%)	6	6	6	6	6
Aged in air: 100°C for 72 h					
Tensile strength at break (MPa)	1.56	1.98	2.38	3.33	4.30
Elongation at break (%)	531	647	792	848	946
Hardness (shore A)	40	37	35	33	31
Tensile set at break (%)	6	6	6	6	6
Aged in transformer oil: 100°C, 72 h					
Tensile strength at break (MPa)	1.42	2.04	2.41	3.47	4.34
Elongation at break (%)	531	642	765	781	989
Hardness (shore A)	32	36	35	34	33
Tensile set at break (%)	6	6	6	6	6
Density ($\times 10^3$ kg/m^3)	0.97	0.99	1.01	1.05	1.06

structure. PPC is shown as bright cell with 1000–10,000 A of phase size for the uncured mixture, and the cell wall of NBR is shown as a continual phase. After the mixture was cured, the cell phase tended to be small, and the cell-wall became dimmer, which may result from the interpenetration or graft of NBR and PPC chains. The phenomena coincided with those of many IPN materials which have cell-type morphologies[11] and indicated that the increments of cross-linking densities of NBR main networks controlled the PPC phase size, even if PPC is also cross-linked. This may imply that NBR/PPC elastomers are with IPN structures.

Thermal stabilities of the NBR/PPC elastomers

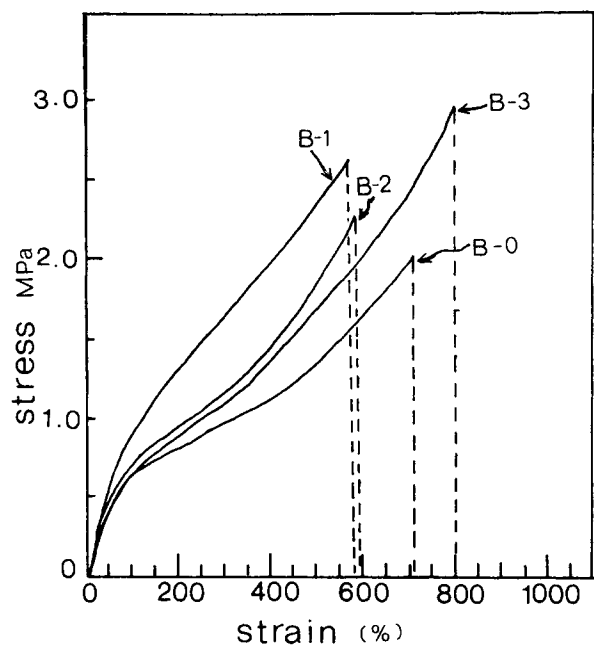**Figure 4**   The mechanical properties of NBR/PPC elastomers.

Figure 5   The stress/strain curves for NBR/PPC cured blends with basic formulation in Table I.
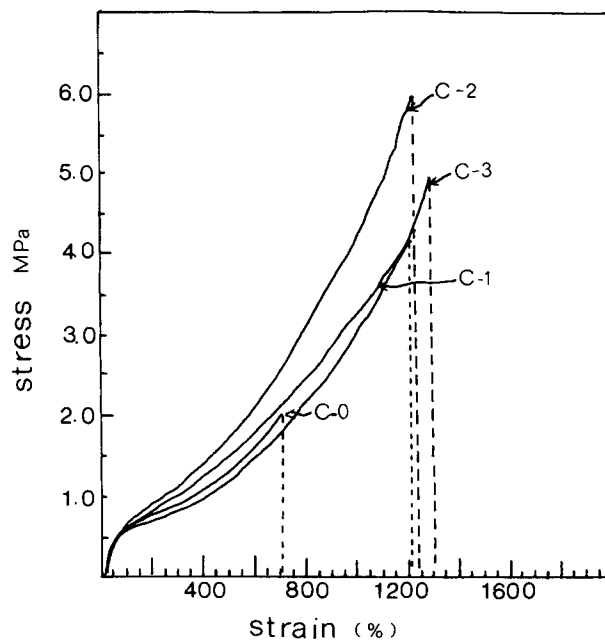
Figure 6   The stress/strain curves for NBR/PPC cured blends with basic formulation and coagent MA

Table IV   The Formulation and Mechanical Properties of the NBR/PPC Elastomer Cured by a Coagent/Peroxide System

Component	C-0	C-1	C-2	C-3	C-4	C-5
NBR (wt %)	100	100	100	70	70	70
PPC (wt %)	—	—	—	30	30	30
DCP (wt %)	1.5	1.5	1.5	1.5	1.5	1.5
MB (phr)	1.5	1.5	1.5	1.5	1.5	1.5
CHPPDA (phr)	1.0	1.0	1.0	1.0	1.0	1.0
MA (phr)	—	—	10	—	10	—
TAIC (phr)	—	3	—	—	—	3
Tensile strength (MPa)	1.72	1.84	1.71	3.69	4.02	5.34
Elongation at break (%)	520	540	525	840	623	1162
Hardness (shore A)	38	38	37	33	36	32
Tensile set (%)	6	6	6	4	4	4
Aged in air: 100°C for 72 h						
Tensile strength (MPa)	1.56	1.67	1.56	3.33	6.84	3.78
Elongation at break (%)	531	550	540	848	637	959
Hardness (shore A)	40	40	40	33	39	30
Tensile set (%)	6	6	6	6	4	4
Aged in transformer oil: 100°C for 72 h						
Tensile strength (MPa)	1.42	1.58	1.43	3.47	4.30	5.39
Elongation at break (%)	531	535	530	781	628	1131
Hardness (shore A)	32	33	32	34	38	37
Tensile set (%)	6	6	6	6	6	6

Table V The Swelling Volume Fraction-Time Relationship of the NBR/PPC Elastomers in Solvents

		Time (min)							
		0	60	120	240	360	480	1080	1200
B-0	Benzene	0	176	325	362	370	376	381	381
	Acetone	0	196	202	212	223	223	223	223
	90# gasoline	0	15	40	45	46	46	47	45
B-1	Benzene	0	288	341	370	375	377	386	385
	Acetone	0	197	204	208	225	225	225	225
	90# gasoline	0	8	35	41	42	43	46	46
B-2	Benzene	0	302	361	381	383	383	383	383
	Acetone	0	198	205	226	226	226	226	226
	90# gasoline	0	12	25	34	36	38	38	38
B-3	Benzene	0	340	356	366	371	377	384	384
	Acetone	0	208	216	218	219	219	219	219
	90# gasoline	0	20	34	35	37	37	37	37

are shown in Figure 3. The degradation temperature (T_d) of pure PPC is as low as 120°C. But in NBR/PPC elastomer, T_d of PPC phase is in the range of 220–320°C; T_d of the NBR/PPC elastomers is 280°C. The main decomposition of crosslinking chains are 370–500°C. It is considered that NBR/PPC elastomers have good heat stability.

significantly with increasing of PPC content. Their tensile sets at break are the same as that of the pure NBR elastomer. The stress/strain graphs showed that NBR is not only reinforced but also enhanced in ductility by adding PPC. These illustrate that NBR/PPC elastomers have excellent elasticity, ductility, heat stability, and oil resistance properties.

Mechanical Properties of the NBR/PPC Elastomers

The NBR elastomer lacks reinforcing ability and usually shows poor tensile strength and elongation at break. Adding PPC can improve the mechanical properties of NBR greatly. The resulting data are shown in Table III and Figures 4 and 5.

It is obvious that the tensile strength and elongation at break of NBR/PPC elastomers increase

Effects of Coagents on the Properties of the NBR/PPC Elastomers

For increasing the cure efficiency of peroxide in NBR/PPC systems, the coagents, triallylisocyanurate (TAIC) or maleic anhydride (MA), were added to the peroxide curing system. The formulation and resulting mechanical properties are shown in Table IV and Figure 6. The results illustrated that the addition of co-agent for the peroxide system can fur-

Table VI Formulation for the Carbon Black Filled NBR/PPC Blends

Sample Component	E-0	E-1	E-2	E-3	E-4	E-5
NBR	100	90	80	70	60	70
PPC	0	10	20	30	40	30
DCP	1.5	1.5	1.5	1.5	1.5	1.5
MB	1.5	1.5	1.5	1.5	1.5	1.5
CHPPDA	1.0	1.0	1.0	1.0	1.0	1.0
Carbon black	40	40	40	40	40	40
MA	—	—	—	—	—	10
DOP	10	10	10	10	10	10

ther improve the curing efficiency in the NBR/PPC system.

Solvent and Oil Resistance of the NBR/PPC Systems

Vulcanized samples were immersed in an excess of solvents for different periods of time. The swelling volume fractions (V_s) of elastomers were calculated by using the relation:

$$V_s = \frac{(W_1 - W_0) \times \rho_p}{W_0 \times \rho_s} \times 100$$

where, W_o is the weight of the original sample, W_1 is the weight of the swollen sample, ρ_p is the density of the elastomer (see Table III), and ρ_s is the solvent density ($\times 10^3$ kg/m³: 0.879 for benzene, 0.784 for acetone, and 0.730 for 90# gasoline).

The results were shown in Table V. From Table V, we found that the NBR/PPC elastomers have the same equilibrium swelling behavior as NBR in benzene and acetone. Its $V_{s_{max}}$ doesn't change as PPC increases in the elastomer. But the $V_{s_{max}}$ of the NBR/PPC elastomers in 90# gasoline became smaller as the PPC was added so that the hydrocarbon solvent resistance of NBR could be improved by adding PPC.

Mechanical Properties of the Carbon Black Reinforcing NBR/PPC Elastomers

Basic formulation for carbon black filled NBR/PPC blends are listed in Table VI. The mechanical properties of carbon black reinforcing NBR/PPC systems are shown in Figures 7 and 8. The results show
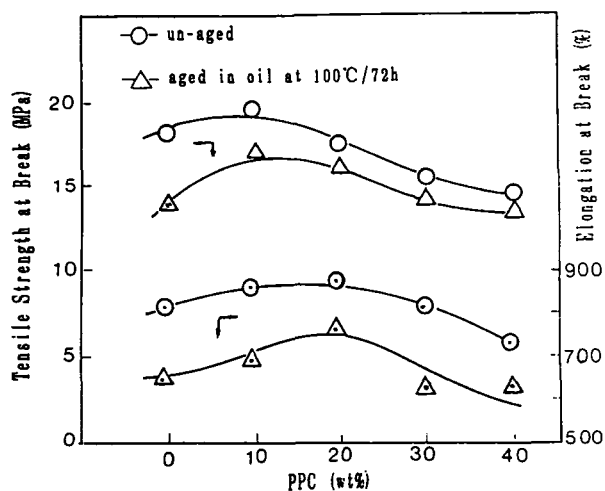

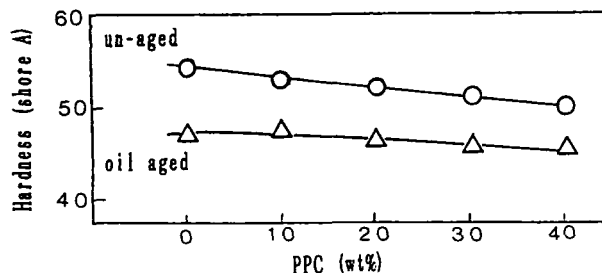**Figure 7** The mechanical properties of NBR/PPC systems filled with carbon black.

Figure 8 Dependence of hardness on PPC content for NBR/PPC systems filled with carbon black.

that the optimum NBR/PPC composition is 100/10–30, in which the excellent mechanical properties were obtained.

CONCLUSIONS

1. As a CO₂ epoxide copolymer, PPC can be used as a new functional polymer to enhance the mechanical properties of NBR.
2. The tensile strength and elongation at break of NBR/PPC system were dramatically increased by increasing the PPC content within 40%, while their oil resistance property and tensile set at break were as good as that of NBR.
3. When the NBR/PPC system was reinforced by carbon black, optimum properties of the NBR/PPC elastomers appear at the 20% PPC composition. The coagent of TAIC or maleic anhydride can much improve the curing efficiency of peroxide and result in excellent mechanical properties in the NBR/PPC systems.
4. The heat stability of the NBR/PPC elastomers was much improved, from 120°C for pure PPC to 280°C in the elastomer.

REFERENCES

1. S. Inoue, H. Koinuma, and T. Tsuruta, *Makromol. Chem.*, **130**, 210 (1969).
2. M. Kobayashi, Y. L. Tang, T. Tsuruta, and S. Inoue, *Makromol. Chem.*, **169**, 69 (1973).

3. A. Rokicki and W. Kuran, *J. Macromol. Sci., Chem.,* **C21,** 135 (1981).
4. T. Aida, M. Ishikawa, and S. Inoue, *Macromolecules,* 19, **8** (1986).
5. N. Kihara and T. Endo, *Macromolecules,* **27,** 6239 (1994).
6. L. B. Chen, *Makromol. Chem., Macromol. Symp.,* **59,** 75 (1992).
7. L. Chen, Y. H. Huang, and G. M. Cong, *Chinese Polym. Sci. J.,* **10,** 20 (1992).
8. X. Y. Hong and Y. H. Huang, *Chinese Polym. Mater. Sci. Eng.,* **3,** 101 (1992).
9. J. Z. Wang, Y. H. Huang, and G. M. Cong, *Chinese J. Appl. Chem.,* **11,** 54 (1994).
10. J. B. Johnson, *Rubber Age,* **107,** 29 (1975).
11. L. H. Sperling, *IPN and Related Materials,* Plenum New York, 1981, Chap. 6.