Selective Crosslinking in Polymer Blends. I. Novel Selective Crosslink Systems for Polypropylene/Unsaturated Elastomer Blends

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SYNOPSIS

Two novel systems were developed to selectively crosslink dispersed unsaturated elastomer particles in saturated polyolefin matrices under dynamic crosslinking conditions. One system comprises N,N'-m-phenylene-bis-maleimide (PM) as a crosslinker and 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline or polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline) as an activator. They are believed to form charge-transfer-complexes to produce PM radicals, which accelerate the crosslinking reaction of the elastomer. The other comprises PM as a crosslinker and 9,10-dihydrophenanthrene as an activator. These are believed to act as a hydrogen acceptor and a hydrogen donor, respectively, involving transference of a hydrogen radical between them to produce a PM radical. These crosslink systems convert the unsaturated elastomer particles in the polyolefin matrices to crosslinked particles selectively without causing degradation or crosslinking of the matrices, because the radicals produced from the systems are carbon radicals and abstract only hydrogen radicals at the allylic positions of the unsaturated elastomers and not a hydrogen radical at the secondary or tertiary carbons of the polyolefin. The reactions and their confirmed selectivity were conducted on PP/EPDM blend, PP/SBS blend, PP/SIS blend, PP/1,2-PB(1,2-polybutadiene) blend, and PP/PE/EPDM blend, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Purpose of the Research

W. K. Fisher of Uniroyal filed patent applications in 1971 on thermoplastics blends of partially crosslinked mono-olefin copolymer elastomers, such as ethylene–propylene copolymer (EPR) or ethylene–propylene–diene terpolymer (EPDM) with polyolefins, such as polypropylene (PP) or polyethylene (PE).[1-3] These are so-called thermoplastic olefinic elastomers (TPO). After that the number of reports on thermoplastic/crosslinked elastomer blends has been increasing.[4-9] In these blends crosslinking reactions generally proceed under intensive melt-blending conditions to give fine particles of crosslinked elastomers in matrices of thermoplastic and the process involved is known as "dynamic crosslinking."

Although the main purpose of these studies has been to develop novel thermoplastic elastomers, it also would be interesting to study the effect of dynamic crosslinking on the impact strength of the resultant blends, especially on that of PP/EPDM blends since the resultant blends will have a matrix of PP containing dispersed crosslinked particles of EPDM, a morphology which is similar to that of acrylonitrile–styrene butadiene copolymer (ABS) or that of high-impact polystyrene (HIPS).[10]

Studying the effect of crosslinking of dispersed particle by dynamic crosslinking on impact strength has proven difficult because systems used in present dynamic crosslinking of PP/EPDM blends are those developed for EPDM crosslinking in the rubber industry[11] and these not only crosslink the EPDM particles but also unfavorably affect the PP matrix and the resultant blends as a result.

The organic peroxide/coagent crosslink system, which is the most commonly used one, degrades the PP matrix and changes its mechanical and rheolog-

ical properties because highly active radicals pro-
duced from the organic peroxide abstract hydrogen
radicals not only from the allylic carbons of EPDM
but also from the tertiary carbons of PP.

The crosslinking reactions of the phenolic resin
crosslink systems proceeds at the unsaturated bonds
of EPDM without hydrogen radical abstraction (i.e.,
by addition of the phenolic resin to a carbon of the
double bond in EPDM). Thus, this system can be
considered to demonstrate a kind of selectivity with
no problems associated with degradation of PP ma-
trix. However, since considerable concentration of
phenolic resin, accelerator, and stabilizer are re-
quired for the crosslinking reaction to proceed ef-
fectively, the involved compounds negatively affect
the impact strengths of the resultant blends.

The crosslink reactions effected by sulfur/accel-
erator or sulfur donor/accelerator systems also
crosslink the EPDM with similar selectivity to the
phenolic resin system with no problem of degrada-
tion. However, the produced polysulfide crosslink-
age, i.e. — (Sn;n = 2–6)-type linkage, is unstable
at the required temperature for the melt-blending
process and the molding process of PP/EPDM
blends. Thus, this system is not suitable for material
of commercial use.

The purpose of the research described here and
the following article is to develop novel crosslinking
systems that are able to crosslink unsaturated elas-
tomer particles in a polyolefin matrix selectively,
especially EPDM particles in a PP matrix, without
causing the problems described above, and to in-
vestigate the effect of dynamic crosslinking on the
impact strength of PP/EPDM blends (and other
polyolefin/unsaturated elastomer blends) by utiliz-
ing these systems.

In Part 1 studies on the novel crosslinking sys-
tems are described and mechanisms to explain their
action are proposed. Their effect on the impact
strength of PP/EPDM blends and proposed mech-
anisms are described in Part 2.

Selection of Crosslink Agent

The primary objective of this research was to select
a suitable crosslink agent or multifunctional mono-
mer for the selective crosslink reaction.

N,N'-m-phenylene-bis-maleimide (PM) (Fig. 1a)
is known as a crosslinking agent only for highly un-
saturated rubbers, such as natural rubber (NR) sty-
rene–butadiene rubber (SBR), and butadiene rubber
(BR).[12-14] It is usually used with an accelerator or
a free radical generator such as an organic peroxide
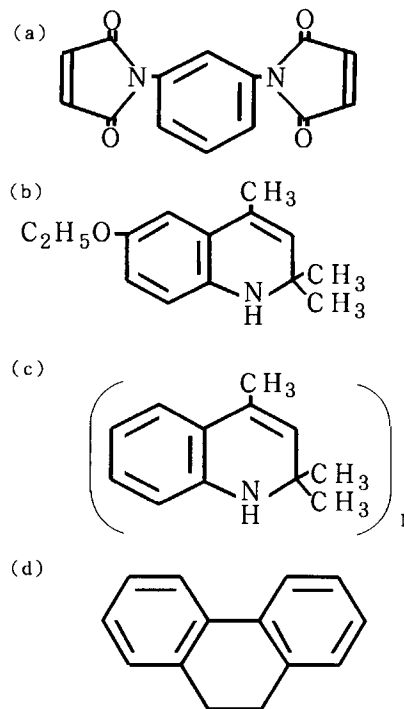or dibenzothiazyldisulfide (MBTS) or thiazole de-

Figure 1   Structures of PM and its accelerators. (a)
N,N'-m-phenylene-bis-maleimide (PM), (b) 6-ethoxy-
2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ), (c) po-
lymerized-(2,2,4-trimethyl-1,2-dihydroquinoline)
(PTMQ), (d) 9,10-dihydrophenanthrene (DPH).

rivative. It can also be used as a coagent in the per-
oxide crosslinking reaction of EPDM and EPR and
is recognized to have one of the highest reactivities
to free radical produced on carbon in EPDM or EPR
(carbon radical) among polyfunctional monomers
because of the high e-value of the double bond be-
tween two carbonyl groups.[15]

D. J. Elliot investigated the effect of the PM
crosslinking reaction in the absence of accelerators
on PP/NR blends under dynamic crosslinking con-
ditions and reported that the NR in the blends was
crosslinked.[16] The result indicates that under dy-
namic crosslinking conditions, free radicals are pro-
duced on carbon at the allylic positions of NR which
can add to PM to initiate the crosslink reaction.
Although several kinds of radicals are involved in
the crosslink reaction after the initiation, it is no-
table that all of them are free radicals on carbons
of alkyl groups (except hydrogen radicals). It is
known that alkylcarbon free radicals are less active
compared to that of oxy radicals, such as a radical
produced from peroxide, and unable to abstract hy-
drogen from secondary and tertiary carbons of po-
lyolefin. Therefore, under dynamic crosslinking of
PP/NR blends involving PM only, it could be con-

cluded that the PP matrix is not degraded during the crosslinking reaction of the NR particles except for the small amount unavoidably degraded by homolytic chain cleavage caused by the intensive mixing.

From this point of view, the crosslinking reaction of EPDM by PM in PP/EPDM blend seems to be a strong candidate. However, preliminary experiments revealed that addition of peroxide or sulfur donor compounds as an accelerator is needed in order to obtain highly crosslinked EPDM particles because of the low degree of nonsaturation of EPDM.

This led to a search for novel accelerators for the PM crosslink reaction in PP/EPDM blend (or saturated polyolefin/unsaturated elastomer blend), which promote the production of free radical on PM but do not produce any free radicals able to abstract hydrogen radical from PP (or other polyolefin).

EXPERIMENTAL

Materials

The saturated polyolefins used in this research are polypropylene homopolymer (h-PP), polypropylene block copolymer (b-PP), and very low-density polyethylene (VLDPE). The unsaturated elastomers are EPDM, styrene-butadiene-styrene block-copolymer (SBS), styrene-isoprene-styrene block-copolymer (SIS), and 1,2-polybutadiene (PB). All

of them are commercial products and their commercial names and properties are listed in Table I. All of the compounds investigated as crosslinking agents or accelerators are also commercial products and used without further purification. Their structures are shown in Figure 1.

Sample Preparation

Apart from a few exceptions, samples comprise 80 wt % of h-PP or b-PP and 20 wt % of the unsaturated elastomer. The extruder employed in the experiments was a 30-mm diameter twin screw extruder with an L/D of 31.5. The combination of screw segments was designed to give high-intensity mixing to the molten blends. The samples were extruded and pelletized twice. In the first extrusion, only the polyolefin and the elastomer were melt-blended. The purpose of the first extrusion was to disperse the elastomer particles in the polyolefin matrix thoroughly before the crosslinking reaction. In the second extrusion, a mixture of the resultant blends of the first extrusion and the candidate for the crosslink system were melt-blended (i.e. dynamically cross-linked).

The extrusion was conducted at a speed of 200 rpm and at a barrel temperature of 180–210°C. The residential time of the blends in the extruder was kept ca. 60 seconds by adjusting the extrusion rate. The same extrusion conditions were used throughout the research except for the blends containing PB. Because crosslinking reaction of PB occurs at 180°C in the absence of an accelerator, PB was blended

Table I   Properties of Raw Materials Investigated

Type of Material	Material Designation	Commercial Name	Supplier	Comments
PP	PP-1	J620G	Nippon Petrochemicals	MFR = 1.5, (230°C/2.16 kg load), Block-copolymer
	PP-2	J120G	Nippon Petrochemicals	MFR = 1.5, (230°C/2.16 kg load), Homopolymer
	PP-3	J650G	Nippon Petrochemicals	MFR = 8.0, (230°C/2.16 kg load), Block-copolymer
	PP-4	J871M	Nippon Petrochemicals	MFR = 23.0, (230°C/2.16 kg load), Block-copolymer
PE	PE-1	D9010	Nippon Petrochemicals	MFR = 1.0, (190°C/2.16 kg load), $d = 0.900$
	PE-2	D9550	Nippon Petrochemicals	MFR = 5.0, (190°C/2.16 kg load), $d = 0.905$
EPDM	EPDM-1	EP57P	Japan Synthetic Rubber	ML_{1+4} (100°C) = 88, Iodine value = 15
SBS	SBS-1	TR1150	Shell Chemical	Styrene/Butadiene ratio = 28/72, radial-type
	SBS-2	KX-65	Shell Chemical	Styrene/Butadiene ratio = 38/62, triblock-type
SIS	SIS-1	TR1107	Shell Chemical	Styrene/Isoprene ratio = 14/86, triblock-type
1,2-PB	PB-1	RB805	Japan Synthetic Rubber	$d = 0.899$, crystalinity = 14%
	PB-2	RB840	Japan Synthetic Rubber	$d = 0.913$, crystalinity = 34%

with VLDPE and extruded at a barrel temperature of 140–160°C.

The extruded samples were injection-molded into specimens for testing under conditions of barrel temperature of 210–230°C (140–160°C for VLDPE/PB blends), injection pressure of 1,000 kgf/cm², and mold temperature of 50°C. Vicat softening temperature (ASTM D1525) was determined on 2-mm thick injection-molded samples. In order to identify the character of the crosslinking reaction, hot-pressed $20 \times 50 \times 0.2$ mm sheets of the samples in wire net were immersed in refluxed xylene for 5 h. Two parameters are defined by eqs. (1) and (2). They are used to describe the character of the crosslinking reaction.

Xylene-insoluble fraction (%)

$$= \frac{\text{sheet weight after the immersion}}{\text{sheet weight before the immersion}} \times 100 \quad (1)$$

Degree of crosslinking (%)

$$= \frac{\text{xylene-insoluble fraction}}{\text{wt \% of the elastomer in the blend}} \times 100 \quad (2)$$

RESULTS AND DISCUSSIONS

PP/EPDM Blends

PM Crosslink Reaction in the Absence of Accelerators

Even in the absence of an accelerator, PM crosslinked EPDM particles in PP matrix under the given condition (Table II/B-01, C-01). It indicates that the EPDM in PP/EPDM blends produce free radicals by homolytic chain cleavage under dynamic crosslinking in a way similar to the NR in PP/NR blends discussed before.[16] The degree of crosslinking given by eq. (2) is about 50% and is less than that of the PP/NR blends,[16] because of the low degree of unsaturation of EPDM.

It is notable that in the PP/EPDM blend involving 0.3 wt % of PM, or 1.5 pwhr of PM to EPDM, the degree of crosslinking increases up to about 50% under dynamic crosslinking. The concentration of unsaturated bonds in EPDM is much less than that of NR and much greater concentrations of PM/accelerator systems usually are required to crosslink EPDM by Banbury mixer process. The behavior difference under dynamic crosslinking can be explained as follows: First, there is a favorable compatibility between PP matrix and EPDM particles which is

good enough to transmit the shear stress of the intensive mixing applied on the matrix to the particles effectively.[17] Second, the shear rate developed by the twin extruder is much higher than by Banbury mixer and is high enough to promote the homolytic cleavage of EPDM.

Novel Accelerators for the PM Crosslink Reaction

Dihydroquinoline Derivatives and Their Acceleration Mechanism. 6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline (ETMQ) (Fig. 1b) and polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline) (PTMQ) (Fig. 1c) are found to be accelerators for the PM crosslink reaction. By themselves they do not crosslink EPDM particles and do not lead to xylene insolubles under the dynamic crosslinking process. They, however, can crosslink them and increase the xylene-insoluble fraction when the PP/EPDM system involves PM. When the dihydroquinoline derivative is considered to be a vinyl monomer, it is interesting that it has a much higher e-value compared to that of PM. Suppose that the e-value of PM equals that of maleic anhydride (MAH) and the e-values of the dihydroquinoline that of styrene, the difference between them is 3.05,[18] which is large enough to form a charge-transfer complex. Actual difference of the value is probably greater than 3.05, since the dihydroquinoline derivative is a kind of 1-methyl-1-propyl-styrene derivative and both the methyl group and propyl group have electron-donating character. Thus, it is probable that the PM and the dihydroquinoline derivative forms a charge-transfer complex and that free radicals on carbon of PM (PM radical) are produced from it to accelerate the PM crosslinking reaction.

Although it is practically impossible to confirm the existence of the charge-transfer complex under dynamic crosslinking, the facts from the following experiments strongly suggest the formation of a charge-transfer complex between PM and the dihydroquinoline derivative under dynamic crosslinking and the production of PM radicals.

1. Although PM dissolved in ethanol and ETMQ dissolved in ethanol each have similar light yellow color, the mixture of them develops a deep orange color and indicates the maximum absorption bands of these compounds are shifted by an interaction. It is recognized that the formation of the ground-state charge-transfer complex is evidenced by the appearance of new absorption bands (i.e., a charge-transfer band).[19]

Table II Effects of the Developed PM Crosslinking Reaction of Various PP/Elastomer Blends

Sample Designation	Composition Polyolefin/ Unsaturated-elastomer (80 wt %)/(20 wt %)	Crosslink System (wphr)	MFR 230°C/2.16 kg Load (g/10 min)	Vicat-softening Temperature (°C)	Xylene-insoluble Fraction (wt %)
Reference	PP-2	PM/ETMQ (0.3/0.2)	—	—	< 1.0
A-00	PP-1/EPDM-1	None	1.4	134	< 1.0
A-01		PM/ETMQ (0.3/0.2)	2.2	140	20.8
A-02		DVB/ETMQ (0.4/0.2)	2.1	135	1.4
B-00	PP-2/EPDM-1	None	1.6	143	< 1.0
B-01		PM (0.3)	—	144	10.7
B-02		ETMQ (0.2)	—	144	1.4
B-03		PM/ETMQ (0.3/0.2)	2.4	148	18.0
B-04		PM/PTMQ (0.075/0.05)	—	147	12.0
B-05		PM/PTMQ (0.15/0.1)	—	146	16.0
B-06		PM/PTMQ (0.15/0.2)	—	147	15.6
B-07		PM/PTMQ (0.3/0.2)	—	149	17.0
B-08		PM/PTMQ (0.6/0.3)	—	147	19.0
C-00	PP-3/EPDM-1	None	4.5	135	2.5
C-01		PM (0.3)	—	—	11.5
C-02		ETMQ (0.2)	—	—	1.4
C-03		PM/ETMQ (0.15/0.1)	7.3	141	19.9
C-04		PM-ETMQ (0.3/0.2)	5.9	142	22.1
C-05		PM/DHP (0.3/0.2)	—	—	18.7
C-06		DVB/ETMQ (0.4/0.2)	5.5	138	3.5
D-00	PP-4/EPDM-1	None	11.0	135	1.8
D-01		PM/ETMQ (0.3/0.2)	5.0	140	20.8
E-01[a]	PP-2/PE-2/EPDM-1	PM/ETMQ (0.55/0.45)	—	—	28.6

[a] Sample E-01 comprises 40 wt % of PP-2, 30 wt % of PE-2, and 30 wt % of EPDM-1.

Abbreviations: PM = N,N'-m-phenylene-bis-maleimide; ETMQ = 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; PTMQ = polymerized-(2,3,4-trimethyl-1,2-dihydroquinoline); DVB = divinylbenzene.

2. A mixture of 1.50 mg (5.59 mmol) of PM and 0.50 mg of PTMQ (1.44 mmol) was sealed in an aluminum pan and analyzed by differential scanning calorimetry (DSC) at a scanning rate of 10°C/min from 40 to 220°C. Under the same conditions, the thermogram of PM alone exhibits a sharp endothermal peak of 103.5 mJ/mg at 202.7°C (Fig. 2 curve a) and that of PTMQ alone an endothermal peak of 11.8 mJ/mg at 87.0°C (Fig. 2 curve b). The above-mentioned mixture exhibited a trace at 87.4°C and described a slightly exothermal curve from 193.8°C. There was no peak assigned to PM at all (Fig. 2 curve c). The complete disappearance of the peak assigned to PM suggests that an interaction between PM and PTMQ occurred under the heating scan and changed all of the PM into its derivatives of higher melting point, probably polymerized PM.

It is difficult to suppose that the interaction is the Diels-Alder reaction between PM and PTMQ at the C-4 and C-10 positions of the latter. Because an excess of PM was involved in the mixture and the Diels-Alder reaction involving an aromatic compound seldom occurs where the aromatic resonance is lost in the resultant product.

3. A mixture of 85 wt % of PP-3 and 15 wt % of PM was extruded and pelletized. Its DSC thermogram at a scanning rate of 10°C/min from 40 to 220°C exhibits an endothermal peak of 16.4 mJ/mg at 202.2°C assigned to PM (Fig. 3 curve a). A mixture of 85 wt % of PP-3 and 15 wt % of PTMQ was also produced and analyzed under the same condition. Its DSC thermogram exhibits a trace assigned to PTMQ (Fig. 3 curve b).

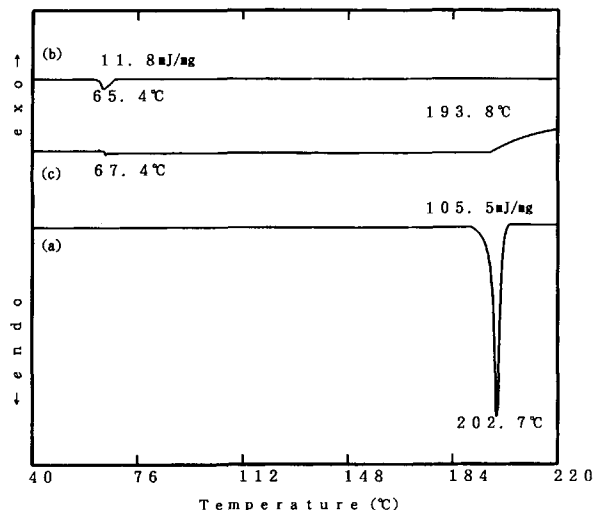The same weight of thin pieces of each compound were piled and sealed in an alu-

Figure 2 DSC thermogram of PM, PTMQ, and their mixture. (a) PM, (b) PTMQ, (c) the mixture.

minium pan and analyzed by DSC under the same conditions. Its thermogram exhibits an endothermal peak of 3.8 mJ/mg at 202.4°C assigned to PM and a slightly exothermal curve after that (Fig. 3 curve c). The partial disappearance of the peak assigned to PM suggests that an interaction occurred under the heating scan in molten PP also, even in the static condition.*

4. ETMQ does not crosslink the EPDM particles under the given condition (Table II B-02, C-02).

5. ETMQ/divinylbenzene system could not crosslink the EPDM particles under the given condition (Table II A-02). Since divinylbenzene is recognized as a polyfunctional monomer of high reactivity to carbon radical, this fact indicates that there is a peculiar interaction, which promotes the crosslinking reaction, between PM and the dihydroquinoline derivatives different from an interaction between PM and another polyfunctional monomer.

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* Based on this fact, it can also be concluded that PP and PM does not play a role in the production of free radicals in PP/ EPDM blends. The area of the peak is about 15% that of pure PM and the value of 15% is substantially equal to the content value of PM in PP. The peak also appears at substantially the same temperature as pure PM (105.5 mJ/mg at 202.7°C/Fig. 2 curve a). If PP and PM produced free radicals under the given dynamic crosslink conditions, PM would polymerize and reduce the area of the peak or shift the peak temperature.

6. PM/1-(3,4-dihydro-2-naphthyl)-pyrolizine (DNP) does not crosslink the EPDM particles under the given conditions (Table III C-14).

DNP (see Fig. 9. g) is a kind of 1,1-disubstituted-styrene and has a basic structure similar to ETMQ as a vinyl monomer (Fig. 1 b). The fact also indicates that there is a peculiar interaction between PM and ETMQ. The absence of the ability of accelerator can be explained by the effect of the pyrolizine group on the unsaturated bond. It has an electron-attractive character which reduces the electron density or the *e*-value and has a steric hinderance affect on the double bond. Both of the effects prevent formation of the charge-transfer complex.

Tree Mechanisms of PM Radical Production from the Charge-Transfer Complex. Three kinds of mechanisms of PM radical production from the charge-transfer complex can be considered;[20-22]

The first mechanism is a transference of a proton from a dihydroquinoline-derivative cation radical to a PM anion radical which produces two radicals as a result (Fig. 4). Though the conditions for the proton transference in a charge-transfer complex are not clear, it would be reasonable to suppose the large difference of *e*-value between PM and the dihydro-
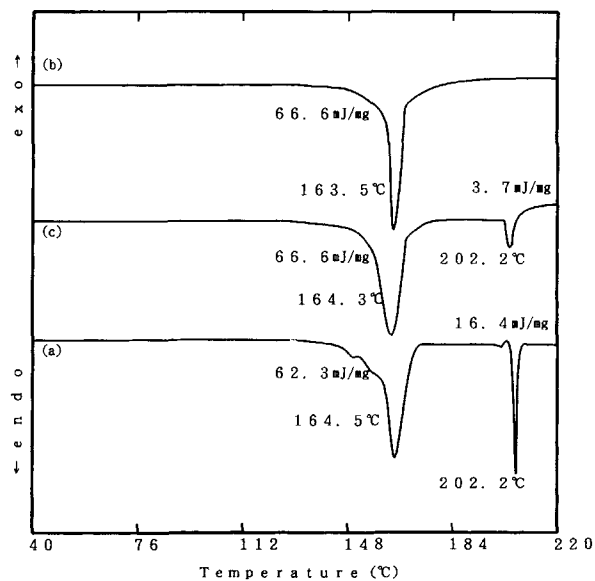

Figure 3 DSC thermogram of PM/PP blend, PTMQ/ PP blend, and their mixture. (a) PM/PP blend, (b) PTMQ/PP blend, (c) the mixture.

Table III   Effect of Inhibitors on the Developed PM Crosslink Reaction

Sample Designation	Composition Polyolefin/ Unsaturated-elastomer (80 wt %)/(20 wt %)	Crosslink System (wphr)	Xylene-insoluble Fraction (wt %)
C00	PP-3/EPDM-1	None	2.5
C-00		PM (0.3)	11.5
C-11		PM/HM (0.3/0.2)	5.0
C-12		PM/8HQN (0.3/0.2)	5.8
C-13		PM/QN (0.3/0.2)	1.4
C-14		PM/DNP (0.3/0.2)	< 1.0
C-15		PM/ODA (0.3/0.2)	< 1.0
C-16		PM/MBDA (0.3/0.2)	< 1.0
C-17		PM/SADA (0.3/0.2)	< 1.0

Abbreviations: PM = N,N'-m-phenylene-bis-maleimide; AD = octylated diphenylamine; CD = 4.4'-bis-(a,a'-dimethybenzyl)diphenylamine; TD = p-(p-toluene sulfonylamido)diphenylamine; H = hexamethylenetetramine; Q = quinoline; HQ = 8-hydroxyl quinoline; DNP = 1-(3,4-dihydro-2-naphthyl)-pyrolizine.

quinoline derivative a favorable condition for the transference.

Apparently the produced PM radical will accelerate the crosslinking reaction. On the other hand, the produced ETMQ radical or PTMQ radical probably is not involved with the crosslinking reaction, because they are trisubstituted cyclic vinyl monomer radicals and too bulky to react with other compounds. The most probable reaction would be a methyl-group rearrangement from the C-2 position to C-3 position to enable the radical to stabilize itself by resonance (Fig. 4-I).

The character difference between two resultant radicals produced from the proton transference, namely one a reactive polyfunctional radical and the other a stable radical, is considered to be necessary for the production of radicals in a charge-transfer complex which can accelerate the crosslinking reaction. The condition makes it easy to change a charge-transfer complex into two radicals, reducing the cage effect by suppressing the reaction between the produced radicals to permit the reactive radicals to diffuse into molten polymer effectively.

The second possible mechanism is an abstraction of a hydrogen ion from EPDM at the allylic position by the charge-transfer complex which also produces two kinds of radicals as a result.

Two kinds of abstraction are possible. One is the abstraction of a hydrogen anion by the dihydroquinoline derivative cation radical (Fig. 5). The other is the abstraction of a proton by PM anion radical (Fig. 6). The latter is less likely to occur than the former because the dihydroquinoline derivative cation radical is too bulky to react with a carbon in

EPDM. In the former it is notable that PM anion radicals will react with EPDM at allylic position directly. It is also notable that the two radicals produced are a reactive multifunctional radical and a stable radical (Fig. 4-II). The combination is the same as that of the proton transference mechanism.

The third possible mechanism is coupling of a cation radical and an anion radical in the charge-transfer complex to produce a diradical compound (Fig. 7). However, polymerization between a trisubstituted cyclic monomer, such as the dihydroquinoline derivative, and a disubstituted vinyl monomer, such as PM, seldom occurs and the resultant diradical seems to be too bulky and too stable as an initiator. This mechanism is less possible than other two mechanisms.

9,10-Dihydrophenanthrene and its acceleration mechanism. Although 9,10-dihydrophenanthrene (DHP) (Fig. 1d) is not able to form a charge-transfer complex with PM, it is found to be an accelerator for the PM crosslinking reaction (Table II C-05). The fact indicates that there is also another kind of peculiar interaction between PM and DHP to produce a PM radical.

The interaction is considered to be transference of a hydrogen radical from DHP at the C-9 or C-10 position to PM, which produce a PM radical. That is, DHP is a hydrogen radical donor and PM is a hydrogen radical acceptor (Fig. 8). It is notable that after the transference PM and DHP will become a reactive polyfunctional radical and a stable radical by resonance effect, respectively, also. The possi-
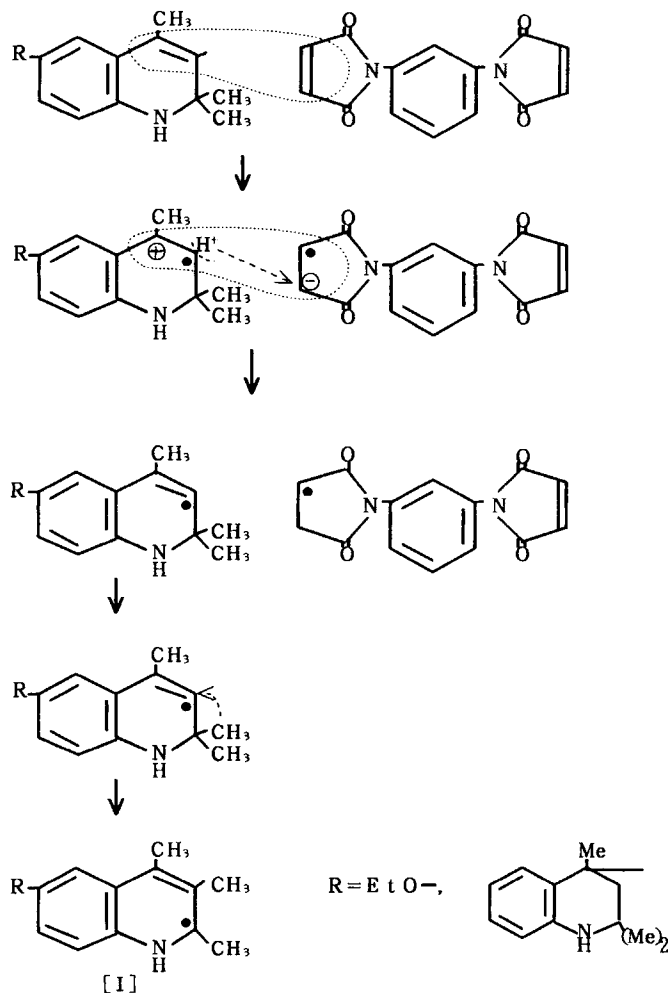
Figure 4 Proposed mechanism of radical production from an interaction between PM and dihydroquinoline derivatives (1). A proton transference from PM to dihydroquinoline derivative in the charge-transfer complex.

bility of this interaction may be supported by the mechanism of initiation of thermal polymerization of styrene presented by F. R. Mayo.[23,24] Mayo proposed that the initiation, a production of styrene monomer radical, is caused by a hydrogen transference from a styrene dimer produced by the Diels–Alder reaction to a styrene monomer. It is possible also that aromatic compounds, which are able to stabilize themselves by resonance after a hydrogen radical discharge,[25] will transfer a hydrogen radical to a compound involving a double bond.

Effects and Selectivity of the Crosslink Reactions

Following the xylene-insoluble fraction tests, the samples of high degree of crosslinking gave enough residue to be analyzed by DSC. All of the DSC ther-

mograms of the residue exhibit only a trace or a small peak assigned to PP and reveal that the crosslinking reaction proceeded in PP/EPDM blends at the EPDM particles selectively. The DSC thermograms of residue from the PP/PE/EPDM blend (Table II E-01) exhibit only a trace and a small peak assigned to PP and PE, respectively, to indicate that the selectivity is retained in the case of the matrix of the polyolefin mixture.

In addition to the results of the DSC analysis, the following facts shown in Table II also indicate that the crosslink reaction proceeded with selectivity:

1. From B-03 to B-08 in Table II, the xylene-insoluble fraction increased as the concen-
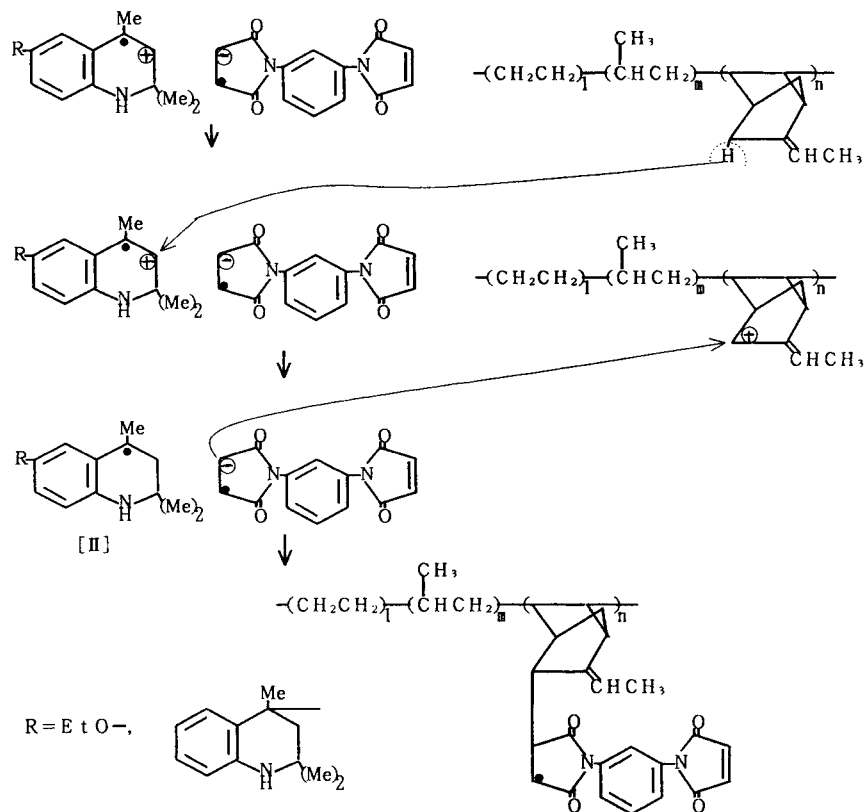
Figure 5 Proposed mechanism of radical production from an interaction between PM and dihydroquinoline derivatives (2). A hydrogen ion abstraction from EPDM by dihydroquinoline derivative cation radical in the charge-transfer complex.
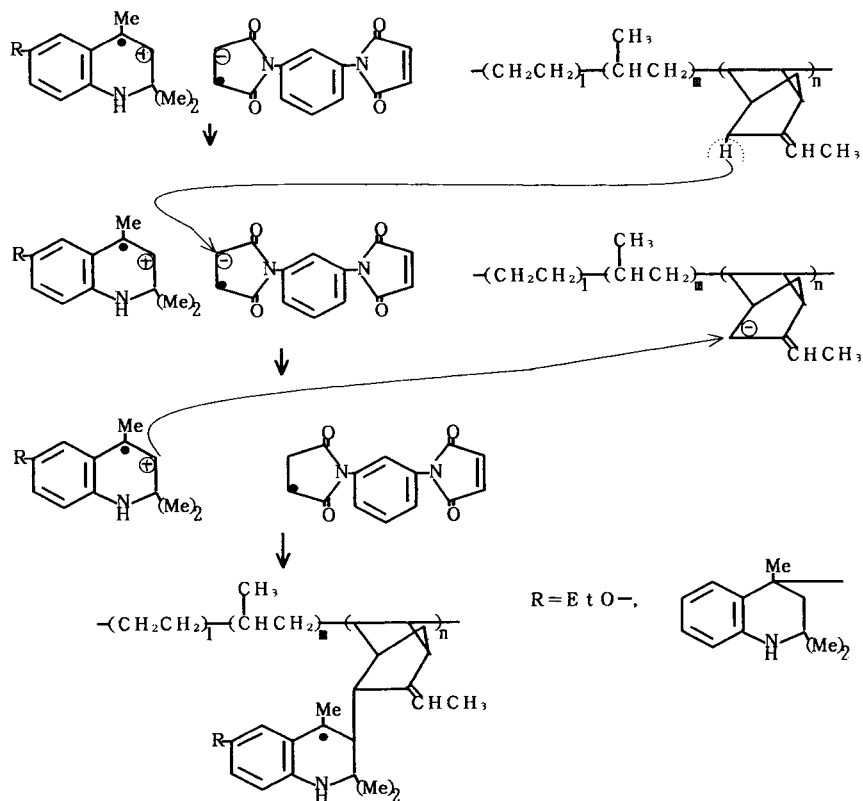

Figure 6 Proposed mechanism of radical production from an interaction between PM and dihydroquinoline derivatives (3). A hydrogen ion abstraction from EPDM by PM anion cation radical in the charge-transfer complex.
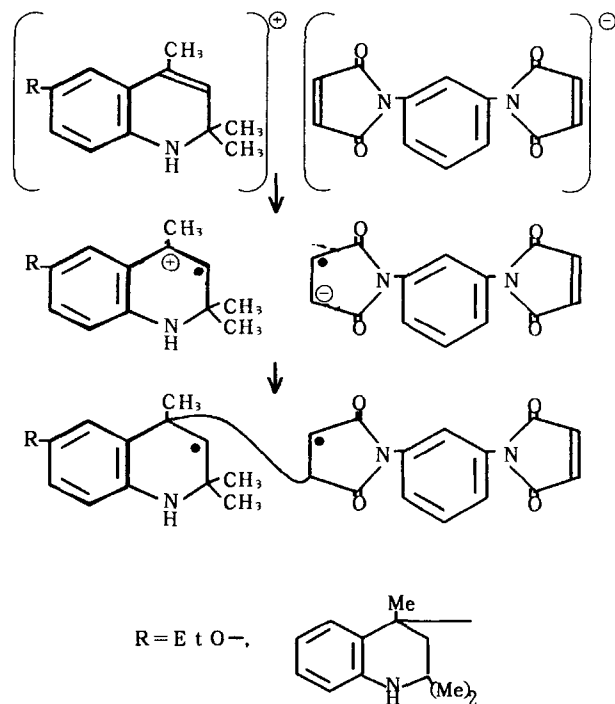
Figure 7 Proposed mechanism of radical production from an interaction between PM and dihydroquinoline derivatives (4). Production of the diradical by coupling in the charge-transfer complex.

[Ⅲ]

Figure 8 Proposed mechanism of radical production from an interaction between PM and DHP.

during the second extrusion process. Probably because the melt-blend conditions required for the dynamic crosslinking were severe, antioxidant contained in the raw materials was consumed during the first extrusion when the viscosity of molten blend is higher. However, the degree of increase of MFR is much less than that by peroxide/coagent crosslink system necessary to obtain the same degree of crosslinking.

tration of the crosslink system increased. However, when the value of the xylene-insoluble fraction became substantially equal to the value of the wt % of EPDM in the blend, further increase in the concentration of the crosslink system did not increase the value of the xylene-insoluble fraction. In all other samples, the value of xylene-insoluble fraction did not substantially exceed the value of wt % of the elastomer in the blend.

2. Increase of the vicat-softening temperature depends on the value of xylene-insoluble fraction.

3. Where crosslinking occurs in the EPDM particles exclusively and degradation of PP in matrix does not, the MFR of the blend will decrease. The decrease of MFR was observed in D-01, which involved PP of MFR of 23 as matrix.

On the other hand, in A-01, B-03, C-03, and C-04, which involved PP of MFR of 1.5, 1.5, 8, and 8, respectively, a slight increase of MFR was observed. It may be assumed that in the blends having PP of a lower MFR, slight degradation of PP matrix occurred
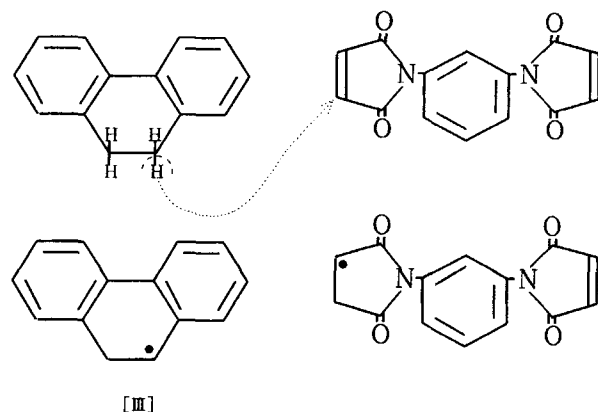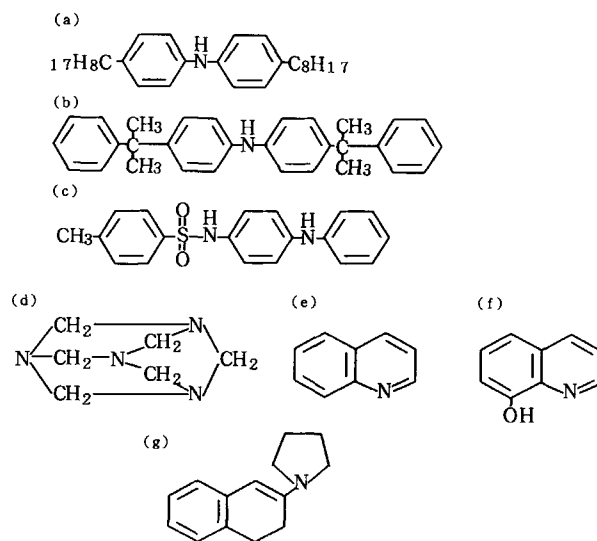

Figure 9 Structures of inhibitors of the developed PM crosslink reaction. (a) Octylated diphenylamine (AD); (b) 4,4'-*bis*-(*a,a'*-dimethybenzyl)diphenylamine (CD); (c) *p*(*p*-Toluene sulfonylamido)diphenylamine (TD); (d) hexamethylenetetramine (H); (e) quinoline (Q); (f) 8-hydroxyl quinoline (HQ); (g) 1-(3,4-dihydro-2-naphthyl)-pyrolizine (DNP).

Inhibitors of PM Crosslink Reaction

In this research some inhibitors for the PM crosslink reaction also are found. Figure 9 shows their structures and Table III shows their effect. Octylated diphenylamine (AD) (Fig. 9a), 4,4-bis-(α,α'-dimethybenzyl)-diphenylamine (CD) (Fig. 9b), and p-(p-toluene sulfonylamido)diphenylamine (TD) (Fig. 9c) are known as antioxidants for rubber and plastic materials. Their mechanism of antioxidation is considered to be a hydrogen radical transference from the nitrogen located between two aromatic rings to peroxide radical. In other words, the reaction is a hydrogen radical abstraction from secondary aromatic amine by a peroxide radical. However, PM radical, or carbon radical, is not considered to be active enough to abstract a hydrogen radical from the nitrogen. Therefore, it indicates that there is another mechanism for the inhibition.

If the lone pair electrons on the nitrogen react with PM at a carbon atom in carbonyl group to form a kind of complex, the crosslink reaction would be prevented because the formation of the complex reduces the e-value of PM, which is a main cause of its high reactivity to other radicals or compounds, and provides steric hinderance against the formation of charge-transfer complex. In order to confirm the effect of the lone pair electrons, the inhibition ability of hexamethylenetetramine (H) (Fig. 9d) as a tertiary amine, and 8-hydroxyl quinoline (HQ) (Fig. 9e) and quinoline (Q) (Fig. 9f) as aromatic amines

on the PM crosslinking reaction were investigated. The results shown in Table III reveal that they also have inhibition capability on the PM crosslinking reaction. (It should be mentioned that DNP discussed above is also a tertiary amine.)

The proposed mechanism of inhibition also suggests that ability of the inhibition will be dependant on the electron-density on the nitrogen in the compound and the degree of steric hinderance effect on the lone pair given by neighboring groups. From this point of view it can be explained that Q has the greatest effect among them and the effect of HQ is reduced because of the hydrogen bond between the hydrogen of hydroxyl group at C-8-position and the lone pair electron.

N. G. Gaylord also indicates that in the reaction of molten high-density polyethylene (HDPE) with maleic anhydride (MAH) using peroxide as catalyst the crosslinking reaction of the HDPE was prevented by the presence of electron donor compounds containing nitrogen atoms.[26]

It is interesting that ETMQ and PTMQ are conventionally considered to belong to the amine antioxidant group but have a quite different function during the PM crosslink reaction in the PP/EPDM blends. This may be explained by the difference of character of the lone pair of electrons on the nitrogen among them. It is difficult for ETMQ and PTMQ to form the complex with PM, because the neighboring alkyl group lowers the electron-density and sterically hinders the lone pair electron.

Table IV   Effects of the Developed PM Crosslinking Reaction of Various Polyolefin/Elastomer Blends

Sample Designation	Composition Polyolefin/ Unsaturated Elastomer (80 wt %)/(20 wt %)	Crosslink System (wphr)	MFR 2.16 kg Load 230°C (g/10 min)	Vicat-softening Temperature (°C)	Xylene-insoluble Fraction (wt %)
F-00	PP-4/SBS-1	None	13.5	134	1.6
F-01		ETMQ (0.2)	—	—	17.5
F-02		PM (0.3)	—	—	16.7
F-03	PP-4/SBS-2	PM/ETMQ (0.3/0.2)	6.3	138	21.9
G-00	PP-1/SIS-1	None	2.6	134	< 1.0
G-01		PM/ETMQ (0.3/0.2)	1.3	140	8.4
H-00	PE-1/PB-1[a]	None	—	64	1.4
H-01		PM/ETMQ (0.06/0.04)	1.3	81	36.5
J-00	PE-1/PB-2[a]	None	—	98	< 1.0
J-01		PM/ETMQ (0.06/0.03)	2.2	101	30.0

[a] Samples H and J comprise 60 wt % of PE and 40 wt % of PB, and, 70 wt % of PE and 30 wt % of PB, respectively.

Abbreviations: PM = N,N'-m-phenylene-bis-maleimide; ETMQ = 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline; PTMQ = polymerized-(2,2,4-trimethyl-1,2-dihydroquinoline); DHP = 9,10-dihydrophenanthrene.

Other Polyolefin/Unsaturated-Elastomer Blends

Table 4 shows the effect of the dynamic PM cross-linking systems on other kinds of polyolefin/un-saturate-elastomer blends.

Although the basic character of property changes after the crosslinking is virtually the same as that of the PP/EPDM blends, there are a few differences.

From the concentration of double bonds in the elastomer, it might be expected that PM in the absence of accelerator can crosslink the SBS particles in PP/SBS blends substantially up to 100% (Table IV F-03) but only 10% of the amounts of PM/ETMQ system in comparison to the amounts required in PP/EPDM blends can crosslink the PB particles in VLDPE/PB blend up to virtually 100% (Table IV H-01, J-01). On the other hand, it is rather surprising that the degree of crosslinking of the SIS in PP/SIS blend was low. This may be caused by partial thermal decomposition of SIS under the given conditions.

It is the most remarkable difference that ETMQ in the absence of PM crosslinked SBS particles in PP/SBS blend (Table IV F-01). It is proposed that ETMQ and a double bond of SBS form a charge-transfer complex to produce a free radical in the SBS which initiates the crosslinking reaction.

CONCLUSION

On the basis of the experiments carried out, the mechanism of the selective crosslink reaction of the developed PM/accelerator system can be pictured as follows:

1. Under intensive mixing of the dynamic crosslinking procedure free radicals are produced on carbon at the allylic position in un-saturated elastomer particle in saturated po-lyolefin matrix. The radical can react with certain polyfunctional monomers, such as N,N'-m-phenylene-bis-maleimide (PM), and initiate the crosslinking reaction.
2. 6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquino-line (ETMQ) or polymerized-(2,2,4-tri-methyl-1,2-dihydroquinoline) (PTMQ) ac-celerates the PM crosslink reaction. The PM/ETMQ or PM/PTMQ system is believed to form a charge-transfer complex and produces PM radicals, which accelerate the crosslinking reaction of the elastomer. The crosslinking reaction proceeds selectively without any significant crosslinking or degradation of the polyolefin matrix because the radicals produced from the system, unlike those from peroxides, do not abstract hydrogen radicals from the secondary or tertiary carbon in the polyolefin.
3. 9,10-Dihydrophenanthrene (DHP) accelerates the PM crosslink reaction of unsaturated elastomer particles in saturated polyolefin matrix under dynamic crosslinking conditions. It is believed that a transference of a hydrogen radical from DHP to PM occurs and produces PM radical, which accelerates the crosslinking reaction of the elastomer. The PM/DHP system crosslinks unsaturated elastomer particles selectively via the same mechanism as the PM/ETMQ and the PM/PTMQ systems.
4. The developed crosslink systems exhibit unique selectivity in polyolefin/unsaturated-elastomer blends. They are considered to be a useful technique to produce polyolefin/crosslinked elastomer blends when it is needed to retain the mechanical and the rheological properties of the polyolefin in the resulting blends.

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