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# APPINDICES

# APPENDIX A

## Overall Compositions of Rubbers

**Table A-1** Properties of natural rubber latex concentrated

| Properties | Test Results |
|---|---|
| Total solids content, % | 61.88 |
| Dry rubber content, % | 60.14 |
| Non rubber solids, % | 1.824 |
| Ammonia content (on total weight), % | 0.669 |
| Ammonia content (on water phase), % | 1.756 |
| pH value | 10.39 |
| KOH number | 0.679 |
| Volatile fatty acid number (VFA) | 0.027 |
| Mechanical stability at 55% TS. Sec | 830 |
| Specific gravity at 25 °C | 0.943 |
| Viscosity (60% TS, spindle no.1.60 rpm),cps | 78.50 |
| Coagulum content (80 mesh), ppm | 27.00 |

All tests are performed according to relevant ISO 2004-1997(E) specification.

**Table A-2** Properties of dry natural rubber (STR5L)

| Properties | Test Results |
|---|---|
| Dirt content (%wt) | 0.04 |
| Ash content (%wt) | 0.40 |
| Volatile matter (%wt) | 0.80 |
| Nitrogen (%wt) | 0.60 |
| Plasticity retention index | 60.0 |
| Mooney viscosity | 59.2 |

**Table A-3** Properties of nitrile rubber (Krynac®3345F).

| Properties | Test Results |
|---|---|
| Mooney Viscosity, ML(1+4) at 100°C MU | 45±5 |
| ACN, % | 33±1 |
| Volatile matter | Max. 0.5 |
| Ash content | Max. 0.7 |
| Density, g/cm$^3$ | 0.97 |

# APPENDIX B

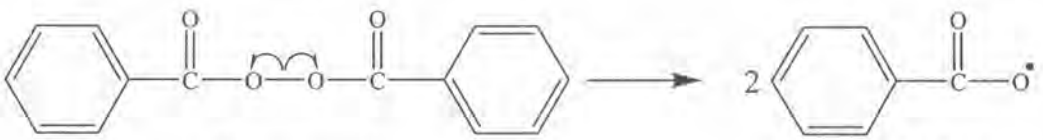
## Mechanism of Graft Copolymerization

The following reaction scheme is proposed for the graft copolymerization of vinyl monomers onto natural rubber by the free radical method:

**(a) Initiation**

The initiators generate free radicals for stating the polymerization process. The radicals interact with the monomer or the rubber molecule leading to the formation of the actual active sites for polymerization (Eawsuwan, 2003).

1. Benzoyl peroxide

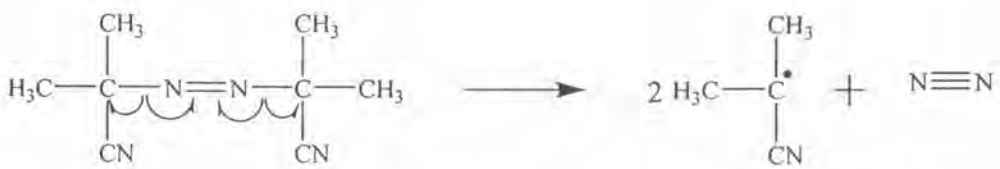


Benzoyl peroxide



Benzoyl radicals

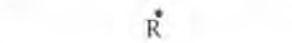
2. 2, 2'-Azobisisobutyronitrile



2, 2'-Azobisisobutyronitrile



Cyanpropyl radicals

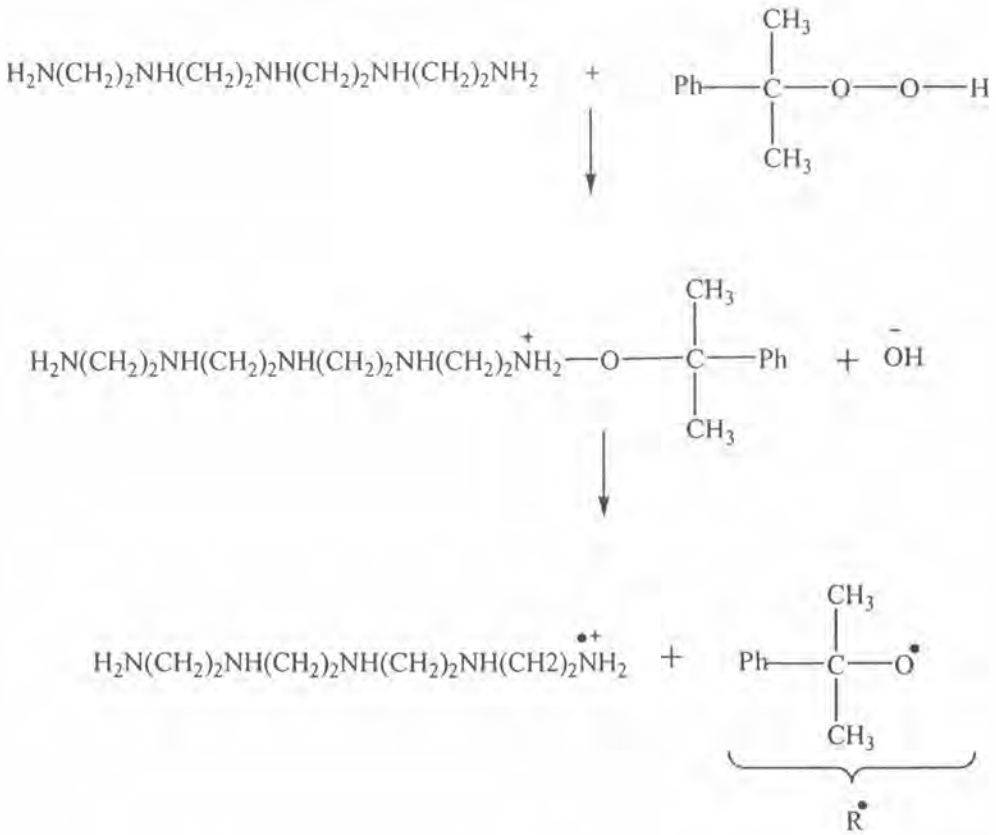


3. Potassium persulfate

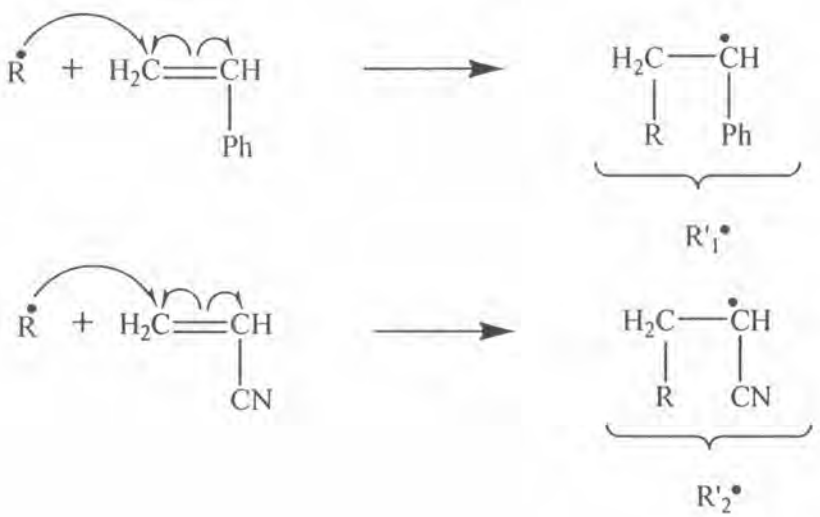
Persulfate

Sulfate radicals

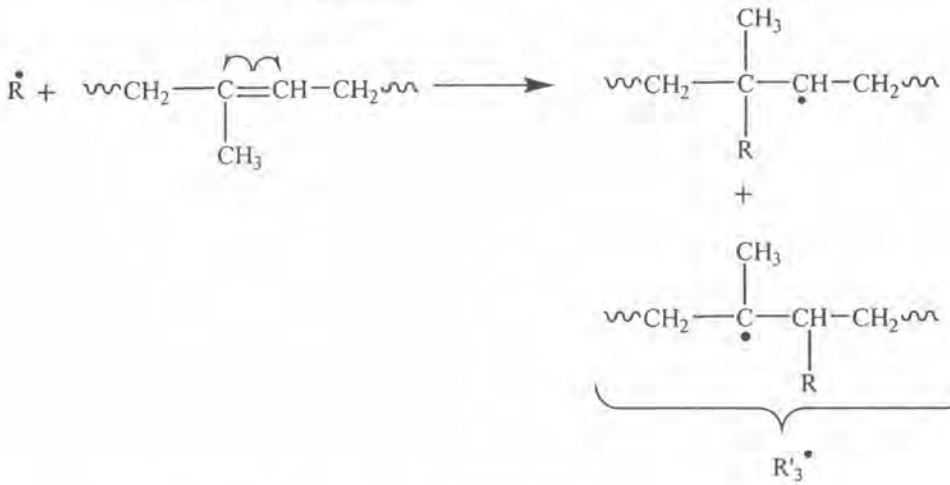
4. Cumene hydroperoxides/tetraethylene pentamine

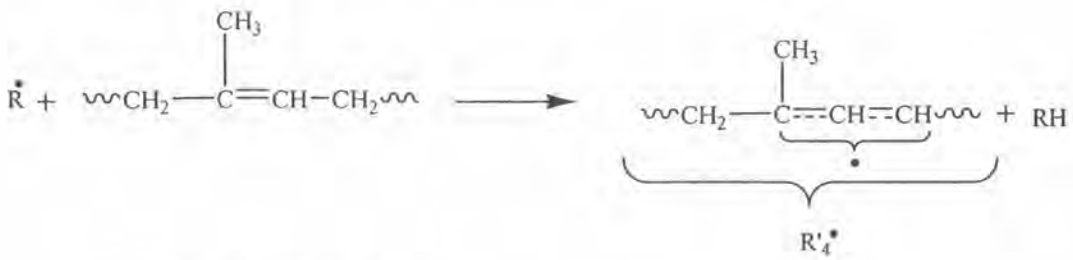


i) Attacking monomer



ii) Attacking rubber



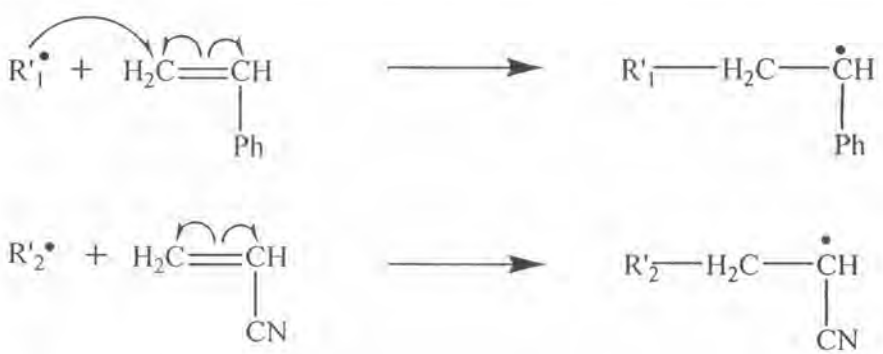


**(b) Propagation**

Both free and grafted chains are in the same environment and are presumed to grow at equivalent rates as described by:

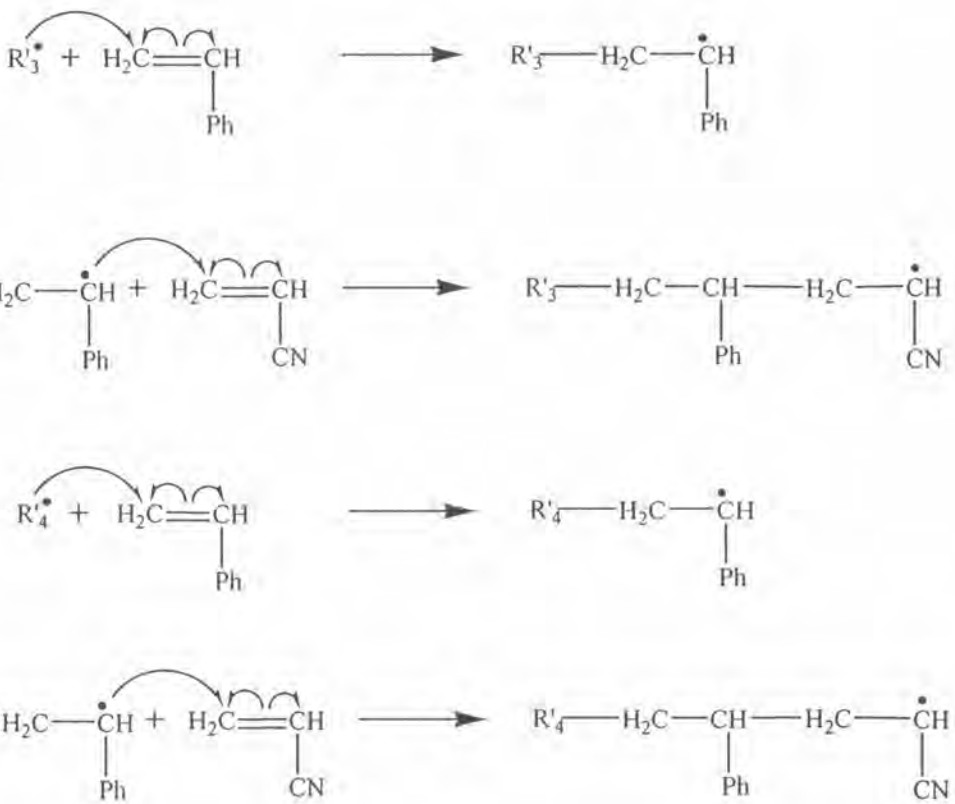
i) Propagation of free copolymerization:

Polymerization of monomer itself, both styrene and acrylonitrile can be occurred. It is proposed that the radical initiate double bond of the monomer to give the radical (styryl or ACN radical) which then react with other styrene or acrylonitrile monomers.



ii) Propagation of graft copolymerization

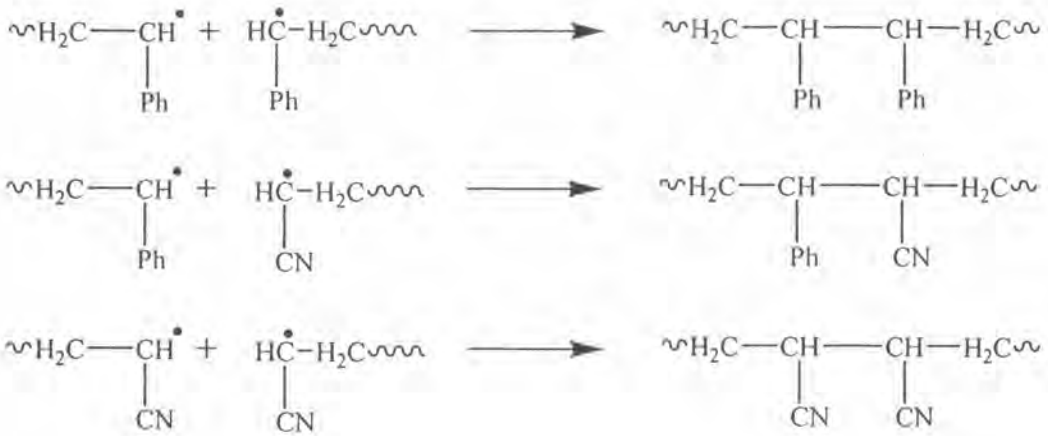
In the styrene polymerization, the polyisoprenyl radical can be completed for styrene monomer to form graft copolymers because the reactivity of the polystyryl radicals is similar to the polyisoprenyl radical. For the comparison of the reactivity ratio between ST and ACN ($r_{ST}$ = 0.4 and $r_{ACN}$ = 0.04) (Immergutand and Brandrup, 1989), the styryl radicals have higher reactivity than ACN radicals. Moreover, ACN had more difficulty to graft onto NR structure compared to ST due to the highly different polarity between ACN and NR. Thus, ST was expected to react first with NR macroradicals and then the resulting styryl radicals copolymerized with ACN.



**(c) Termination**

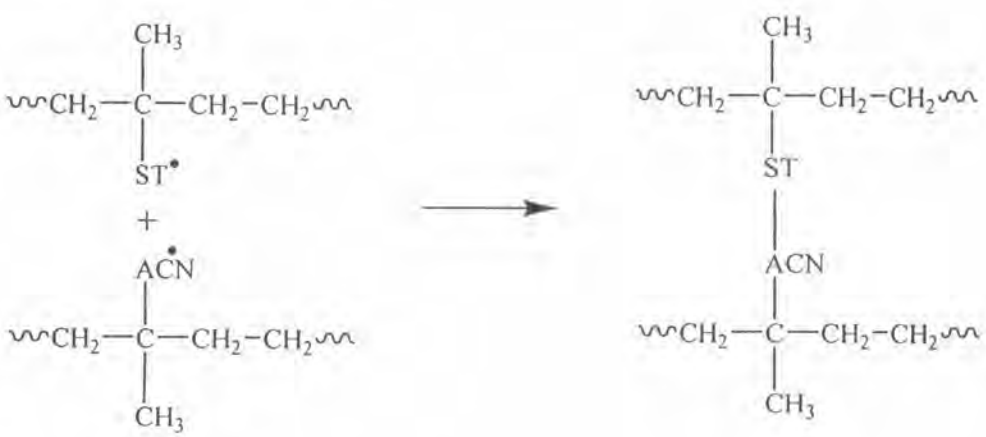
A termination reaction always involves recombination of two radicals. In the former case, a bond is formed between two growing radicals, whereby the polymer molecule is the summation of the sizes of the radicals upon termination.

i) Termination of free copolymerization:

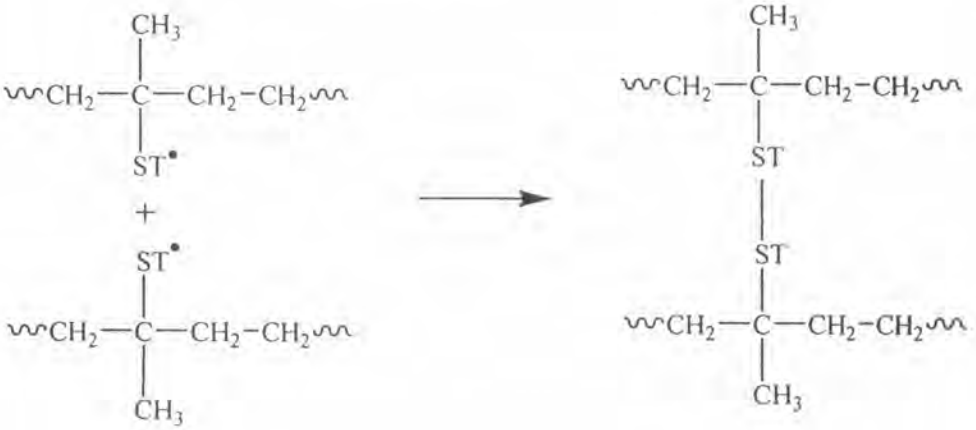


ii) Termination of graft copolymerization:

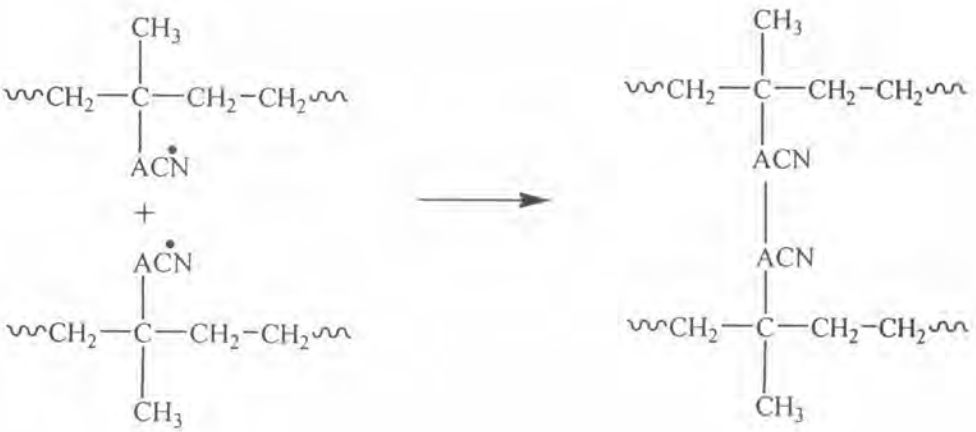
- Recombination between styryl and ACN macroradicals



• Recombination between styryl macroradicals



• Recombination between ACN macroradicals



# APPENDIX C

## Data of Graft Copolymerization

**Table C-1** Effect of initiator concentration, reaction temperature and $N_2$ pressure on the %conversion, %grafting efficiency (%GE),% free SAN, % free NR and %graft copolymer obtained from emulsion graft copolymerization initiated by CHPO/TEPA

| Exp. | Initiator Conc. (phr) | Temp. (°C) | $N_2$ Pressure (bar) | NR (g) | Product (g) | DRC (%) | NR Content (g). | Conv. (%) | Sample (g) | wt.A* | wt.B* | Graft copolymer (%) | Free SAN (%) | Free NR (%) | Total SAN | Free SAN | Graft SAN | GE (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 70 | 2 | 100.0 | 104.9 | 60.14 | 60.16 | 74.83 | 3.390 | 2.326 | 2.238 | 66.03 | 2.593 | 31.38 | 44.90 | 2.720 | 42.18 | 93.94 |
| 2 | 2 | 70 | 2 | 100.1 | 114.6 | 60.14 | 60.22 | 90.93 | 3.478 | 2.794 | 2.734 | 78.61 | 1.725 | 19.67 | 54.56 | 1.977 | 52.58 | 96.38 |
| 3 | 3 | 70 | 2 | 100.2 | 105.9 | 60.14 | 60.25 | 76.46 | 5.455 | 3.893 | 3.699 | 67.79 | 3.563 | 28.64 | 45.87 | 3.773 | 42.10 | 91.78 |
| 4 | 2 | 60 | 2 | 100.1 | 109.5 | 60.14 | 60.21 | 82.42 | 3.324 | 2.449 | 2.376 | 71.49 | 2.193 | 26.32 | 49.45 | 2.401 | 47.05 | 95.15 |
| 5 | 2 | 70 | 2 | 100.1 | 114.6 | 60.14 | 60.22 | 90.93 | 3.478 | 2.794 | 2.734 | 78.61 | 1.725 | 19.67 | 54.56 | 1.977 | 52.58 | 96.38 |
| 6 | 2 | 80 | 2 | 100.1 | 114.4 | 60.14 | 60.19 | 90.57 | 3.134 | 2.585 | 2.466 | 78.70 | 3.804 | 17.50 | 54.34 | 4.349 | 49.99 | 92.00 |
| 7 | 2 | 70 | 1 | 100.1 | 100.0 | 60.14 | 60.19 | 66.68 | 3.900 | 2.544 | 2.468 | 63.27 | 1.956 | 34.77 | 40.01 | 1.956 | 38.05 | 95.11 |
| 8 | 2 | 70 | 2 | 100.1 | 114.6 | 60.14 | 60.22 | 90.93 | 3.478 | 2.794 | 2.734 | 78.61 | 1.725 | 19.67 | 54.56 | 1.977 | 52.58 | 96.38 |
| 9 | 2 | 70 | 4 | 100.2 | 112.8 | 60.14 | 60.25 | 88.07 | 4.224 | 3.447 | 3.286 | 77.78 | 3.818 | 18.40 | 52.84 | 4.309 | 48.53 | 91.85 |
| 10 | 2 | 70 | 6 | 100.1 | 114.9 | 60.14 | 60.21 | 91.63 | 5.939 | 5.208 | 4.901 | 82.52 | 5.176 | 12.30 | 54.98 | 5.951 | 49.03 | 89.18 |

*wt.A = Grafted product was extracted by light petroleum ether for 24 hrs.

*wt.B = Grafted product was extracted by light petroleum ether for 24 hrs and then extracted by dimethyl formamide for 24 hrs.

**Table C-2** Effect of initiator concentration, reaction temperature and $N_2$ pressure on the %conversion, %grafting efficiency (%GE),% free SAN, % free NR and %graft copolymer obtained from emulsion graft copolymerization initiated by $K_2S_2O_8$

| Exp. | Initiator Conc. (phr) | Temp. (°C) | $N_2$ Pressure (bar) | NR (g) | Product (g) | DRC (%) | NR Content (g) | Conv. (%) | Sample (g) | wt.A* | wt.B* | Graft copolymer (%) | Free SAN (%) | Free NR (%) | Total SAN | Free SAN | Graft SAN | GE (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 70 | 2 | 100.2 | 105.6 | 60.14 | 60.24 | 75.99 | 3.240 | 2.241 | 2.171 | 67.02 | 2.154 | 30.83 | 45.59 | 2.275 | 43.32 | 95.01 |
| 2 | 2 | 70 | 2 | 100.2 | 113.7 | 60.14 | 60.27 | 89.56 | 3.669 | 2.940 | 2.856 | 77.83 | 2.292 | 19.88 | 53.73 | 2.607 | 51.13 | 95.15 |
| 3 | 3 | 70 | 2 | 100.2 | 99.3 | 60.14 | 60.23 | 65.57 | 2.646 | 1.586 | 1.554 | 58.72 | 1.217 | 40.07 | 39.34 | 1.209 | 38.14 | 96.93 |
| 4 | 2 | 60 | 2 | 100.1 | 110.8 | 60.14 | 60.19 | 84.72 | 3.273 | 2.448 | 2.405 | 73.46 | 1.326 | 25.21 | 50.83 | 1.469 | 49.36 | 97.11 |
| 5 | 2 | 70 | 2 | 100.0 | 113.7 | 60.14 | 60.16 | 89.56 | 3.669 | 2.940 | 2.856 | 77.83 | 2.292 | 19.88 | 53.73 | 2.607 | 51.13 | 95.15 |
| 6 | 2 | 80 | 2 | 100.1 | 109.3 | 60.14 | 60.18 | 82.20 | 4.397 | 3.486 | 3.131 | 71.21 | 8.062 | 20.73 | 49.32 | 8.814 | 40.51 | 82.13 |
| 7 | 2 | 70 | 1 | 100.1 | 100.3 | 60.14 | 60.21 | 67.16 | 4.958 | 3.271 | 3.164 | 63.83 | 2.160 | 34.01 | 40.29 | 2.167 | 38.13 | 94.62 |
| 8 | 2 | 70 | 2 | 100.1 | 113.7 | 60.14 | 60.22 | 89.56 | 3.669 | 2.940 | 2.856 | 77.83 | 2.292 | 19.88 | 53.73 | 2.607 | 51.13 | 95.15 |
| 9 | 2 | 70 | 4 | 100.1 | 111.0 | 60.14 | 60.21 | 85.00 | 4.421 | 3.487 | 3.336 | 75.46 | 3.405 | 21.13 | 51.00 | 3.779 | 47.22 | 92.59 |
| 10 | 2 | 70 | 6 | 100.1 | 110.9 | 60.14 | 60.17 | 84.83 | 5.768 | 4.528 | 4.324 | 74.98 | 3.534 | 21.49 | 50.90 | 3.919 | 46.98 | 92.30 |

*wt.A = Grafted product was extracted by light petroleum ether for 24 hrs.

*wt.B = Grafted product was extracted by light petroleum ether for 24 hrs and then extracted by dimethyl formamide for 24 hrs.

**Table C-3** Effect of initiator concentration, reaction temperature and $N_2$ pressure on the %graft copolymer % free SAN, and % free NR obtained from solution graft copolymerization initiated by BPO

| Exp. | Initiator concentration (phr) | Temp. (°C) | $N_2$ Pressure (bar) | NR (g) | Product (g) | Sample (g) | wt.A* | wt.B* | Graft copolymer (%) | free SAN (%) | free NR (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 70 | 2 | 20.00 | 15.90 | 3.045 | 1.872 | 1.855 | 60.93 | 0.542 | 38.53 |
| 2 | 5 | 70 | 2 | 20.11 | 16.26 | 2.945 | 2.522 | 2.505 | 85.07 | 0.560 | 14.37 |
| 3 | 10 | 70 | 2 | 20.13 | 15.84 | 3.024 | 2.458 | 2.433 | 80.47 | 0.843 | 18.69 |
| 4 | 15 | 70 | 2 | 20.15 | 17.39 | 3.143 | 2.546 | 2.504 | 79.67 | 1.323 | 19.00 |
| 5 | 20 | 70 | 2 | 20.09 | 16.45 | 3.009 | 2.131 | 1.595 | 53.02 | 17.796 | 29.18 |
| 6 | 5 | 60 | 2 | 20.09 | 5.402 | 5.402 | ND | ND | ND | ND | ND |
| 7 | 5 | 70 | 2 | 20.13 | 16.26 | 2.945 | 2.522 | 2.505 | 85.07 | 0.560 | 14.37 |
| 8 | 5 | 80 | 2 | 20.11 | 18.19 | 3.246 | 2.572 | 2.461 | 75.83 | 3.411 | 20.76 |
| 9 | 5 | 90 | 2 | 20.11 | 13.87 | 2.895 | 2.280 | 1.966 | 67.93 | 10.822 | 21.25 |
| 10 | 5 | 70 | 1 | 20.12 | 14.74 | 3.012 | 1.341 | 1.116 | 37.07 | 7.447 | 55.49 |
| 11 | 5 | 70 | 2 | 20.14 | 16.25 | 2.945 | 2.522 | 2.505 | 85.07 | 0.560 | 14.37 |
| 12 | 5 | 70 | 4 | 20.09 | 16.17 | 2.786 | 2.388 | 2.305 | 82.76 | 2.980 | 14.26 |
| 13 | 5 | 70 | 6 | 20.10 | 16.34 | 3.036 | 2.294 | 2.143 | 70.60 | 4.961 | 24.44 |

*wt.A = Grafted product was extracted by light petroleum ether for 24 hrs. ND = Not Determined.

*wt.B = Grafted product was extracted by light petroleum ether for 24 hrs and then extracted by dimethyl formamide for 24 hrs.

**Table C-4** Effect of initiator concentration, reaction temperature and $N_2$ pressure on the %graft copolymer % free SAN, and % free NR obtained from solution graft copolymerization initiated by AIBN

| Exp. | Initiator concentration (phr) | Temp. (°C) | $N_2$ Pressure (bar) | NR (g) | Product (g) | Sample (g) | wt.A* | wt.B* | Graft copolymer (%) | Free SAN (%) | Free NR (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 80 | 2 | 20.13 | 16.03 | 3.593 | 2.444 | 2.422 | 67.40 | 0.615 | 31.98 |
| 2 | 3 | 80 | 2 | 20.12 | 16.25 | 2.592 | 2.134 | 2.102 | 81.12 | 1.235 | 17.65 |
| 3 | 5 | 80 | 2 | 20.13 | 17.18 | 2.022 | 1.609 | 1.564 | 77.33 | 2.260 | 20.41 |
| 4 | 10 | 80 | 2 | 20.21 | 17.26 | 3.358 | 2.171 | 2.042 | 60.81 | 3.845 | 35.34 |
| 5 | 3 | 60 | 2 | 3.098 | 3.098 | 3.098 | ND | ND | ND | ND | ND |
| 6 | 3 | 70 | 2 | 20.03 | 16.04 | 1.595 | 0.673 | 0.031 | 1.912 | 40.26 | 57.82 |
| 7 | 3 | 80 | 2 | 20.12 | 16.25 | 2.592 | 2.134 | 2.102 | 81.12 | 1.235 | 17.65 |
| 8 | 3 | 90 | 2 | 20.10 | 17.13 | 3.014 | 0.035 | 0.016 | 0.530 | 0.647 | 98.82 |
| 9 | 3 | 80 | 1 | 20.07 | 15.84 | 3.846 | 1.158 | 1.080 | 28.07 | 2.031 | 69.90 |
| 10 | 3 | 80 | 2 | 20.12 | 16.25 | 2.592 | 2.134 | 2.102 | 81.12 | 1.235 | 17.65 |
| 11 | 3 | 80 | 4 | 20.03 | 14.24 | 1.880 | 0.259 | 0.149 | 7.948 | 5.836 | 86.22 |
| 12 | 3 | 80 | 6 | 20.12 | 15.38 | 0.880 | 0.058 | 0.009 | 1.068 | 5.479 | 93.45 |

*wt.A = Grafted product was extracted by light petroleum ether for 24 hrs. ND = Not Determined.

*wt.B = Grafted product was extracted by light petroleum ether for 24 hrs and then extracted by dimethyl formamide for 24 hrs.

# APPENDIX D

## Determination of Compositions of Graft Copolymer Using CHN Analyzer

Example of calculation

1) For NR-*g*-(ST-*co*-ACN): from graft copolymerization condition 70 °C, 2 bar of $N_2$ pressure and 5phr of initiator concentration.

| | | | | |
|---|---|---|---|---|
| Assume A:I:S | | = | a:b:c mole% | |
| ($C_3H_3N$) Acrylonitrile | | = | a[$C_3H_3N$] | |
| ($C_5H_8$) Isoprene | | = | b[$C_5H_8$] | |
| ($C_8H_8$) Styrene | | = | c[$C_8H_8$] | |
| From CHN method | C: H: N | = | 85.38 : 10.36 : 0.84 | |
| Carbon | C = [3a + 5b +8c] x 12 | = | 85.38 gm | (1.1) |
| Hydrogen | H = [3a +8b +8c] x 1 | = | 10.36 gm | (1.2) |
| Nitrogen | N = [a] x 14 | = | 0.84 gm | (1.3) |
| From Eq 1.3 | a | = | 0.06 | |
| From Eq 1.1 | 0.18 + 5b + 8c | = | 7.12 | |
| From Eq 1.2 | 0.18 + 5b + 8c | = | 10.36 | |
| | 5b + 8c | = | 6.22 | (1.4) |
| | 8b + 8c | = | 10.18 | (1.5) |
| | 3b | = | 3.25 | (1.6) |
| | b | = | 1.01 | |
| From Eq 1.1 | 0.18 + 5(1.01) + 8c | = | 7.12 | |
| | c | = | 0.19 | |
| a + b +c = | 0.06 + 1.01+ 0.19 | = | 1.33 | |
| | a : b : c | = | 4.49 : 81.2 :14.3 mole % | |

**Table D-1** Compositions of graft copolymer obtained from CHN analyzer

| Initiator Conc (phr) | T (°C) | $P_{N_2}$ (bar) | C (wt%) | H (wt%) | N (wt%) | ACN (mole%) | ST (mole%) | Isoprene (mole%) | ACN (mole%) | | ST (mole%) | | Isoprene (mole%) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Ave. | S.D. | Ave. | S.D. | Ave. | S.D. |
| 1 | 70 | 2 | 86.2 | 11.2 | 0.27 | 1.37 | 4.14 | 94.5 | 1.62 | 0.35 | 94.6 | 0.08 | 3.83 | 0.43 |
| | | | 86.0 | 11.2 | 0.37 | 1.87 | 3.52 | 94.6 | | | | | | |
| 5 | 70 | 2 | 85.4 | 10.4 | 0.84 | 4.49 | 14.3 | 81.2 | 4.44 | 0.08 | 81.2 | 0.06 | 14.3 | 0.01 |
| | | | 86.6 | 10.5 | 0.83 | 4.38 | 14.3 | 81.3 | | | | | | |
| 10 | 70 | 2 | 86.0 | 10.5 | 0.60 | 3.20 | 13.5 | 83.3 | 3.33 | 0.19 | 83.7 | 0.49 | 13.0 | 0.69 |
| | | | 85.5 | 10.5 | 0.65 | 3.47 | 12.5 | 84.0 | | | | | | |
| 15 | 70 | 2 | 84.6 | 10.7 | 0.68 | 3.56 | 7.40 | 89.0 | 3.52 | 0.07 | 88.8 | 0.31 | 7.66 | 0.38 |
| | | | 85.0 | 10.7 | 0.67 | 3.47 | 7.93 | 88.6 | | | | | | |
| 20 | 70 | 2 | 85.6 | 10.9 | 0.68 | 3.51 | 6.60 | 89.9 | 3.51 | 0.00 | 90.0 | 0.08 | 6.54 | 0.08 |
| | | | 85.5 | 10.9 | 0.68 | 3.51 | 6.48 | 90.0 | | | | | | |
| 5 | 70 | 2 | 85.4 | 10.4 | 0.84 | 4.49 | 14.3 | 81.2 | 4.44 | 0.08 | 81.2 | 0.06 | 14.3 | 0.01 |
| | | | 86.6 | 10.5 | 0.83 | 4.38 | 14.3 | 81.3 | | | | | | |
| 5 | 80 | 2 | 85.7 | 10.8 | 0.78 | 4.05 | 8.61 | 87.3 | 3.96 | 0.13 | 87.5 | 0.28 | 8.50 | 0.16 |
| | | | 85.8 | 10.8 | 0.75 | 3.87 | 8.39 | 87.7 | | | | | | |
| 5 | 90 | 2 | 85.3 | 11.0 | 1.19 | 5.97 | 3.95 | 90.1 | 4.85 | 1.59 | 91.9 | 2.50 | 3.30 | 0.91 |
| | | | 85.2 | 11.1 | 0.74 | 3.72 | 2.66 | 93.6 | | | | | | |
| 5 | 70 | 1 | 86.0 | 11.4 | 0.44 | 2.19 | 0.61 | 97.2 | 1.97 | 0.31 | 96.5 | 1.05 | 1.57 | 1.35 |
| | | | 85.9 | 11.2 | 0.35 | 1.75 | 2.53 | 95.7 | | | | | | |
| 5 | 70 | 2 | 85.4 | 10.4 | 0.84 | 4.49 | 14.3 | 81.2 | 4.44 | 0.08 | 81.2 | 0.06 | 14.3 | 0.01 |
| | | | 86.6 | 10.5 | 0.83 | 4.38 | 14.3 | 81.3 | | | | | | |
| 5 | 70 | 4 | 86.0 | 11.0 | 0.42 | 2.14 | 5.75 | 92.1 | 2.80 | 0.97 | 91.1 | 1.48 | 6.10 | 0.52 |
| | | | 85.5 | 10.9 | 0.68 | 3.51 | 6.48 | 90.0 | | | | | | |
| 5 | 70 | 6 | 85.7 | 10.9 | 0.46 | 2.38 | 6.41 | 91.2 | 2.45 | 0.11 | 91.4 | 0.22 | 6.18 | 0.33 |
| | | | 85.5 | 10.9 | 0.49 | 2.53 | 5.95 | 91.5 | | | | | | |

# APPENDIX E

## Mechanical Properties and Oil Resistance of NR/NBR Vulcanizates Containing GNR.

**Table E-1** Tensile strength of GNR modified NR/NBR blends (50/50 wt%)

| Rubber blends | GNR content | %Graft copolymer | Tensile Strength (MPa) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | Ave. | S.D. |
| NR | - | - | 20.8 | 18.2 | 20.7 | 19.9 | 1.46 |
| NBR | - | - | 2.81 | 2.68 | 2.97 | 2.82 | 0.15 |
| NR/NBR | 0 | 0 | 5.21 | 4.22 | 4.57 | 4.67 | 0.50 |
| | 10 | 53 | 10.2 | 10.4 | 10.0 | 10.2 | 0.20 |
| | 10 | 70 | 10.9 | 12.4 | 10.7 | 11.4 | 0.93 |
| | 10 | 76 | 12.1 | 12.1 | 12.2 | 12.1 | 0.09 |
| | 10 | 85 | 13.9 | 10.7 | 11.8 | 12.1 | 1.61 |
| NR/NBR | 0 | 0 | 5.21 | 4.22 | 4.57 | 4.67 | 0.50 |
| | 5 | 85 | 11.9 | 11.8 | 12.4 | 12.0 | 0.32 |
| | 10 | 85 | 13.9 | 10.7 | 11.8 | 12.1 | 1.61 |
| | 15 | 85 | 10.9 | 11.1 | 10.8 | 10.9 | 0.31 |
| | 20 | 85 | 10.4 | 10.6 | 10.7 | 10.6 | 0.13 |

**Table E-2** Ultimate Elongation of GNR modified NR/NBR blends (50/50 wt%)

| Rubber blends | GNR content | %Graft copolymer | Ultimate Elongation (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | Ave. | S.D. |
| NR | - | - | 749 | 729 | 715 | 731 | 16.9 |
| NBR | - | - | 323 | 317 | 338 | 326 | 10.7 |
| NR/NBR | 0 | 0 | 359 | 346 | 388 | 364 | 21.4 |
| | 10 | 53 | 640 | 620 | 663 | 641 | 21.6 |
| | 10 | 70 | 600 | 624 | 609 | 611 | 12.3 |
| | 10 | 76 | 602 | 569 | 642 | 604 | 36.5 |
| | 10 | 85 | 564 | 510 | 546 | 540 | 27.4 |
| NR/NBR | 0 | 0 | 359 | 346 | 388 | 364 | 21.4 |
| | 5 | 85 | 598 | 586 | 584 | 590 | 7.38 |
| | 10 | 85 | 564 | 510 | 546 | 540 | 27.4 |
| | 15 | 85 | 686 | 633 | 687 | 668 | 27.6 |
| | 20 | 85 | 681 | 635 | 681 | 666 | 26.5 |

**Table E-3** Hardness of GNR modified NR/NBR blends (50/50 wt%)

| Rubber blends | GNR content | %Graft copolymer | Hardness | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 5 | Ave. | S.D. |
| NR | - | - | 46.5 | 44.5 | 46.0 | 45.0 | 44.5 | 45.3 | 0.91 |
| NBR | - | - | 54.5 | 55.0 | 55.5 | 55.0 | 55.5 | 55.1 | 0.42 |
| NR/NBR | 0 | 0 | 42.5 | 40.5 | 40.5 | 40.0 | 41.5 | 41.0 | 0.89 |
| | 10 | 53 | 41.5 | 41.5 | 41.0 | 42.5 | 41.5 | 41.6 | 0.55 |
| | 10 | 70 | 41.5 | 41.5 | 42.0 | 42.5 | 42.0 | 41.9 | 0.42 |
| | 10 | 76 | 42.5 | 43.0 | 42.0 | 42.5 | 42.5 | 42.5 | 0.35 |
| | 10 | 85 | 42.5 | 43.5 | 43.0 | 44.0 | 42.5 | 43.1 | 0.65 |
| NR/NBR | 0 | 0 | 42.5 | 40.5 | 40.5 | 40.0 | 41.5 | 41.0 | 0.89 |
| | 5 | 85 | 42.0 | 42.5 | 42.0 | 41.5 | 42.5 | 42.1 | 0.42 |
| | 10 | 85 | 42.5 | 43.5 | 43.0 | 44.0 | 42.5 | 43.1 | 0.65 |
| | 15 | 85 | 42.5 | 43.5 | 44.5 | 43.5 | 44.0 | 43.6 | 0.74 |
| | 20 | 85 | 43.5 | 44.0 | 45.0 | 44.0 | 44.5 | 44.2 | 0.57 |

**Table E-4** Volume fraction of GNR modified NR/NBR blends (50/50 wt%)

| Rubber blends | GNR content | %Graft copolymer | Volume fraction of rubber | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | Ave. | S.D. |
| NR | - | - | 0.241 | 0.248 | 0.242 | 0.244 | 0.003 |
| NBR | - | - | 0.328 | 0.315 | 0.318 | 0.320 | 0.007 |
| NR/NBR | 0 | 0 | 0.253 | 0.255 | 0.244 | 0.250 | 0.006 |
| | 10 | 53 | 0.260 | 0.261 | 0.272 | 0.264 | 0.007 |
| | 10 | 70 | 0.278 | 0.277 | 0.284 | 0.280 | 0.009 |
| | 10 | 76 | 0.296 | 0.280 | 0.292 | 0.289 | 0.009 |
| | 10 | 85 | 0.295 | 0.297 | 0.303 | 0.298 | 0.004 |
| NR/NBR | 0 | 0 | 0.253 | 0.255 | 0.244 | 0.250 | 0.006 |
| | 5 | 85 | 0.290 | 0.289 | 0.289 | 0.290 | 0.001 |
| | 10 | 85 | 0.295 | 0.297 | 0.303 | 0.298 | 0.004 |
| | 15 | 85 | 0.283 | 0.276 | 0.273 | 0.277 | 0.005 |
| | 20 | 85 | 0.252 | 0.262 | 0.257 | 0.257 | 0.005 |

**Table E-5** Oil swelling (%) of GNR modified NR/NBR blends (50/50 wt%)

| Rubber blends | GNR content | %Graft copolymer | Oil swelling (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | Ave. | S.D. |
| NR | - | - | 145.4 | 155.7 | 155.6 | 152.2 | 5.9 |
| NBR | - | - | 3.439 | 3.570 | 3.549 | 3.519 | 0.1 |
| NR/NBR | 0 | 0 | 119.4 | 120.0 | 104.7 | 114.7 | 8.7 |
| | 10 | 53 | 87.81 | 73.29 | 118.6 | 93.23 | 23.1 |
| | 10 | 70 | 75.52 | 104.99 | 71.72 | 84.08 | 18.2 |
| | 10 | 76 | 74.25 | 69.86 | 72.57 | 72.23 | 2.2 |
| | 10 | 85 | 76.65 | 65.71 | 65.99 | 69.45 | 6.2 |
| NR/NBR | 0 | 0 | 119.4 | 120.0 | 104.7 | 114.7 | 8.7 |
| | 5 | 85 | 80.59 | 80.59 | 80.59 | 80.59 | 0.0 |
| | 10 | 85 | 76.65 | 65.71 | 65.99 | 69.45 | 6.2 |
| | 15 | 85 | 78.46 | 104.14 | 87.90 | 90.17 | 13.0 |
| | 20 | 85 | 95.00 | 96.74 | 97.04 | 96.26 | 1.1 |

# VITA

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