

REFERENCES

- Abdou-Sabet, S., Puydak, R.C., and Rader, C.P. (1996) Dynamically vulcanized thermoplastic elastomers. Rubber Chemistry and Technology, 69, 476-494.
- Akiba, M., and Hashim, A.S. (1997) Vulcanization and crosslinking in elastomers. Progress in Polymer Science, 22(3), 475-521.
- Ali, F., Chang, Y.W., Kang, S.C., and Yoon, J.Y. (2009) Thermal, mechanical and rheological properties of poly(lactic acid)/epoxidized soybean oil blends. Polymer Bulletin, 62(1), 91-98.
- Boochathum, P., and Prajudtake, W. (2001) Vulcanization of cis- and trans-polyisoprene and their blends: cure characteristics and crosslink distribution. European Polymer Journal, 37(), 417-427.
- Choi, J.S., and Park, W.H. (2003) Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) plasticized by biodegradable soybean oils. Macromolecular Symposia, 197(1), 65-76.
- Choi, J.S., and Park, W.H. (2004) Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate). Polymer Testing, 23(4), 455-460.
- Drobny, J.G. (Ed.). (1999) Technology of Fluoropolymers. New Hampshire: CRC Press.
- "Fluoro PVDF." *The Plastics Today for the Technologies of Tomorrow*. PPC Polymer Plastics Corporation. 25 May. 2009
<http://www.polymerplastics.com/fluoro_pvdf.shtml>.
- Goodfellow. "Supplier Data - Polyhydroxybutyrate - (PHB) Biopolymer (Goodfellow)." *AZoM™ - The A to Z of Materials*. 4 Mar. 2003.
AZoM™.com Pty. Ltd. 18 Mar. 2009
<<http://www.azom.com/details.asp?ArticleID=1881>>.
- Hagen, R., Salmén, L., and Stenberg, B. (1996) Effects of the type of crosslink on viscoelastic properties of natural rubber. Journal of Polymer Science Part B: Polymer Physics, 34(12), 1997-2006.
- Hietala, S., Holmberg, S., Karjalainen, M., Näsman, J., Paronen, M., Serimaa, R., Sundholm, F., and Vahvaselkä, S. (1997) Structural investigation of

- radiation grafted and sulfonated poly(vinylidene fluoride), PVDF, membranes. Journal of Materials Chemistry, 7(5), 721–726.
- Holden, G., Kricheldorf, H.R., and Quirk, R.P. (Eds.). (2004) Thermoplastic Elastomers. Munich: Hanser Verlag, 143-146.
- Ibrahim, A., and Dahlan, M. (1998) Thermoplastic natural rubber blends. Progress in Polymer Science, 23(4), 665-706.
- Ikeda, Y., Yasuda, Y., Makino, S., Yamamoto, S., Tosaka, M., Senoo, K., and Kohjiya, S. (2007) Strain-induced crystallization of peroxide-crosslinked natural rubber. Polymer, 48(5), 1171-1175.
- Ismail, H., and Hairunezam, H.M. (2001) The effect of a compatibilizer on curing characteristics, mechanical properties and oil resistance of styrene butadiene rubber/epoxidized natural rubber blends. European Polymer Journal, 37(1), 39-44.
- Ismail, H., and Suzaimah, S. (2000) Styrene butadiene rubber/ epoxidized natural rubber blends: dynamic properties, curing characteristics and swelling studies. Polymer Testing, 19(8), 879–888.
- Javadi, A., Srithep, Y., Pilla, S., Lee, J., Gong, S., and Turng, L.S. (2010) Processing and characterization of solid and microcellular PHBV/coir fiber composites. Materials Science and Engineering: C, 30(5), 749–757.
- Jürdens, K. (2002) The pan-European strategic market study TPE 2000. TPE in der Prozesskette, VDI-Gesellschaft Kunststofftechnik, VDI-Verlag, Düsseldorf.
- Kaito, A. (2006) Unique orientation textures formed in miscible blends of poly(vinylidene fluoride) and poly[(R)-3-hydroxybutyrate]. Polymer, 47(10), 3548–3556.
- Koning, C., Duin, M.V., Pagnouille, C., and Jerome, R. (1998) Strategies for compatibilization of polymer blends. Progress in Polymer Science, 23(4), 707-757.
- “Kynar automotive applications.” (2005) Kynar polyvinylidene fluoride. Arkema Inc., 1-8.
- Li, Y., Oono, Y., Kadowaki, Y., Inoue, T., Nakayama, K., and Shimizu, H. (2006) A novel thermoplastic elastomer by reaction-induced phase decomposition from a miscible polymer blend. Macromolecules, 39(12), 4195-4201.

- Liu, J., and Jungnickel, B.J. (2007) Crystallization kinetical and morphological peculiarities in binary crystalline/crystalline polymer blends. Journal of Polymer Science Part B: Polymer Physics, 45(15), 1917-1931.
- Loan, L.D. (1972) Peroxide crosslinking reactions of polymers. Pure and Applied Chemistry, 30(1-2), 173-180.
- Magaraphan, R., and Yamoun, C. (2008) Dynamic vulcanization of fluoroelastomer and natural rubber. The 1st Thailand Natural Rubber Conference, 1, 152-163.
- Marega, C. and Marigo, A. (2003) Influence of annealing and chain defects on the melting behaviour of poly(vinylidene fluoride). European Polymer Journal, 39(8), 1713-1720.
- Miao, L., Qiu, Z., Yang, W., and Ikehara, T. (2008) Fully biodegradable poly(3-hydroxybutyrate-co-hydroxyvalerate)/ poly(ethylene succinate) blends: phase behavior, crystallization and mechanical properties. Reactive and Functional Polymers, 68(2), 446-457.
- Nakason, C., Nuansomsri, K., Kaesaman, A., and Kiatkamjornwong, S. (2006) Dynamic vulcanization of natural rubber/high-density polyethylene blends: Effect of compatibilization, blend ratio and curing system. Polymer Testing, 25(6), 782-796.
- Nakason, C., Wannavilai, P., and Kaesaman A. (2006) Effect of vulcanization system on properties of thermoplastic vulcanizates based on epoxidized natural rubber/polypropylene blends. Polymer Testing, 25(1), 34-41.
- Nakason, C., Worlee, A., and Salaeh, S. (2008) Effect of vulcanization systems on properties and recyclability of dynamically cured epoxidized natural rubber/polypropylene blends. Polymer Testing, 27(7), 858-869.
- Narayan, R. (1994) Polymeric materials from agricultural feedstocks. in Polymers from Agricultural Coproducts, ACS Symposium Series, 575, 2-28.
- Palys, L.H., and Callais, P.A. (2003) Understanding organic peroxides to obtain optimal crosslinking performance. Rubber World, December 1.
- Park, S.J., Jin, F.L., and Lee, J.R. (2004) Thermal and mechanical properties of tetrafunctional epoxy resin toughened with epoxidized soybean oil. Materials Science and Engineering A, 374(1-2), 109-114.

- “Polyhydroxybutyrate.” *Wikipedia, the free encyclopedia*. 15 Apr. 2009. Wikimedia Foundation, Inc.. 18 May. 2009
<<http://en.wikipedia.org/wiki/Polyhydroxybutyrate>>.
- “Polyhydroxybutyrate.” *Polyhydroxybutyrate – GreenPlastics*. 22 Dec. 2008. MeTracker, LLC. 18 Mar. 2009
<<http://www.greenplastics.com/reference/index.php?title=Polyhydroxybutyrate>>.
- “Polyvinylidene fluoride.” *Wikipedia, the free encyclopedia*. 18 May. 2009. Wikimedia Foundation, Inc.. 25 May. 2009
<<http://en.wikipedia.org/wiki/PVDF>>.
- “PVDF (polyvinylidene fluoride).” *Solvay Membranes*. 3 May. 2009. Solvay S.A. 25 May. 2009 <<http://www.solvaymembranes.com/products/fluoropolymers/solefpvdf/0,,592-2-0,00.htm>>.
- Qiu, Z., Fujinami, S., Komura, M., Nakajima, K., Ikehara, T., and Nishi, T. (2004) Spherulitic morphology and growth of poly(vinylidene fluoride)/poly(3-hydroxybutyrate-co-hydroxyvalerate) blends by optical microscopy. *Polymer*, 45(13), 4355–4360.
- Scharnowski, D. (2005) Characterisation of the influence of cooling rates on structure and properties of dynamic vulcanizates. Dissertation: Halle (Saale), Martin-Luther-Universität, Halle-Wittenberg, Germany, 1-134.
- Taguet, A., Ameduri, B., and Boutevin, B. (2005) Crosslinking of vinylidene fluoride-containing fluoropolymers. Advances in Polymer Science, 184, 127–211.
- “Thermoplastic elastomer.” *Wikipedia, the free encyclopedia*. 5 May. 2009. Wikimedia Foundation, Inc.. 25 May. 2009
<http://en.wikipedia.org/wiki/Thermoplastic_elastomer>.
- Thitithammawong, A., Nakason, C., Sahakaroa, K., and Noordermeer, J. (2007) Effect of different types of peroxides on rheological, mechanical, and morphological properties of thermoplastic vulcanizates based on natural rubber/polypropylene blends. Polymer Testing, 26(4), 537–546.

- Unnikrishnan G., and Thomas, S. (1997) Sorption and diffusion of aliphatic hydrocarbons into crosslinked natural rubber. Journal of Polymer Science Part B: Polymer Physics, 35(5), 725-734.
- Varghese, S., Alex, R., and Kuriakose, B. (2004) Natural rubber-isotactic polypropylene thermoplastic blends. Journal of Applied Polymer Science, 92(4), 2063 – 2068.
- Varkey, J.T., Rao, S.S., and Thomas, S. (1996) Effect of prevulcanization on the rheological behavior of natural rubber/styrene butadiene rubber latex blends. Journal of Applied Polymer Science, 62(12), 2169-2180.
- Wang, S., Ma, P., Wang, R., Wang, S., Zhang, Yo., and Zhang, Yi. (2008) Mechanical, thermal and degradation properties of poly(d,l-lactide)/poly(hydroxybutyrate-co-hydroxyvalerate)/poly(ethylene glycol) blend. Polymer Degradation and Stability, 93(7), 1364–1369.
- Wang, S., Song, C., Chen, G., Guo, T., Liu, J., Zhang, B., and Takeuchi, S. (2005) Characteristics and biodegradation properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organophilic montmorillonite (PHBV/OMMT) nanocomposite. Polymer Degradation and Stability, 87(1), 69-76.
- You, J.W., Chiu, H.J., and Don, T.M. (2003) Spherulitic morphology and crystallization kinetics of melt-miscible blends of poly(3-hydroxybutyrate) with low molecular weight poly(ethylene oxide). Polymer, 44(15), 4355–4362.

APPENDICES

Appendix A Cure Characteristic Data

Data of cure characteristic result shown in chapter IV were obtained from Moving Die Rheometer (MDR). They conclude the data of compounded NR vulcanize by EV system at Acc:S ratio of 12, DCP system at DCP content of 3 phr, and DBPH system at DBPH content of 3 phr. These data are shown in Tables A1-A3.

Table A1 Parameter results of compounded NR with EV system at Acc:S ratio of 12

Sample ID	ML (lbf in)	MH (lbf in)	ts2 (min:sec)	tc90 (min:sec)
EV ratio 12, 150 °C	0.33	11.33	02:50.9	09:04.2
EV ratio 12, 160 °C	0.29	9.02	01:52.9	04:57.0
EV ratio 12, 170 °C	0.21	4.61	01:36.7	03:39.6
EV ratio 12, 180 °C	0.12	1.86	>(30:00.0)	02:09.6
EV ratio 12, 190 °C	0.08	1.57	>(30:00.0)	01:21.6
EV ratio 12, 200 °C	0.09	1.45	>(30:00.0)	00:57.6

Table A2 Parameter results of the compounded NR by DCP system at DCP content of 3 phr

Sample ID	ML (lbf in)	MH (lbf in)	ts2 (min:sec)	tc90 (min:sec)
3 DCP, 150 °C	2.79	10.27	03:49.8	23:20.4
3 DCP, 160 °C	2.12	9.82	02:19.2	16:15.6
3 DCP, 170 °C	1.10	4.12	04:17.4	10:00.6
3 DCP, 180 °C	0.91	2.38	>(30:00.0)	02:54.0
3 DCP, 190 °C	0.85	2.16	>(30:00.0)	01:33.6
3 DCP, 200 °C	0.80	2.01	>(30:00.0)	00:55.2

Table A3 Parameter results of the compounded NR by DBPH system at DBPH content of 3 phr

Sample ID	ML (lbf-in)	MH (lbf-in)	ts2 (min:sec)	tc90 (min:sec)
3 DBPH, 150 °C	0.82	3.30	08:54.0	25:33.6
3 DBPH, 160 °C	0.81	4.91	08:51.0	23:56.4
3 DBPH, 170 °C	0.81	5.69	03:48.0	16:52.8
3 DBPH, 180 °C	0.80	5.34	01:48.6	07:13.2
3 DBPH, 190 °C	0.87	4.89	01:02.4	02:48.0
3 DBPH, 200 °C	0.82	4.39	00:41.5	01:13.8

Data of cure characteristic result shown in chapter V were also obtained from Moving Die Rheometer (MDR). They conclude the data of compounded NR vulcanize by CV and EV system and the data of 50NR/50 PVDF thermoplastic vulcanizates. The Acc:S ratio of 0.5 and 2 were used to vulcanize compounded NR in CV and EV system, respectively. DBPH system was used in vulcanization of 50NR/50PVDF thermoplastic vulcanizates at 180 °C and the content of DBPH was varied at 1, 3, 5, and 7 phr. These data are shown in Table A4-A5.

Table A4 Parameter results of the compounded NR by CV and EV systems

Sample ID	ML (lbf-in)	MH (lbf-in)	tc50 (min:sec)	tc90 (min:sec)
CV system, 150 °C	1.27	12.42	04:25.8	08:08.4
EV system, 150 °C	0.89	14.19	04:37.8	08:10.2
CV system, 180 °C	0.25	2.14	01:06.0	01:40.8
EV system, 180 °C	0.17	2.89	01:13.2	01:43.2

Table A5 Parameter results of the thermoplastic vulcanizates with the NR/PVDF composition of 50/50 vulcanized by peroxide system at 180 °C

Sample ID	ML (lbf in)	MH (lbf in)	tc50 (min:sec)	tc90 (min:sec)
DBPH 1 phr	0.31	1.31	02:43.2	08:19.8
DBPH 3 phr	0.88	4.22	02:09.0	06:13.8
DBPH 5 phr	0.68	6.94	02:09.6	06:10.8
DBPH 7 phr	0.91	8.13	01:55.8	05:37.8

Appendix B Calculations of Crystallinity Percentage

The calculated crystallinity percentages include percents crystallinity of PVDF; PHBV; 80PVDF/20PHBV thermoplastic blend; and 50NR/40PVDF/10PHBV at various ESO content of 0, 1, 2, 5, 7, and 10 phr. The used enthalpies of melting per gram of 100 % crystalline are 109 J/g for PHBV, and 104.7 J/g for PVDF. All calculations are shown below.

$$\text{From } X_c (\%) = \frac{\Delta H_{sample}^*}{\Delta H_{ref}^0} \times 100,$$

ΔH_{sample}^* is the measured enthalpy of sample, and ΔH_{ref}^0 is the enthalpy of melting per gram of 100 % crystalline of sample.

Percent Crystallinity of PVDF

From the result, ΔH_{PVDF}^* is 34.4 J/g and ΔH_{PVDF}^0 is 104.7 J/g.

$$\begin{aligned} \text{Percent crystallinity of PVDF} &= \frac{\Delta H_{PVDF}^*}{\Delta H_{PVDF}^0} \times 100, \\ &= \frac{34.4}{104.7} \times 100, \\ &= 32.8 \%. \end{aligned}$$

Percent Crystallinity of PHBV

From the result, ΔH_{PHBV}^* is 98.7 J/g and ΔH_{PHBV}^0 is 109 J/g.

$$\begin{aligned} \text{Percent crystallinity of PHBV} &= \frac{\Delta H_{PHBV}^*}{\Delta H_{PHBV}^0} \times 100. \\ &= \frac{98.7}{109} \times 100, \\ &= 90.6 \%. \end{aligned}$$

For the blend, the relative percent crystallinity was calculated relatively to the composition of PVDF/PHBV which was 80/20 from the following equation:

$$X_{Blend}(\%) = \frac{\Delta H_{Blend}^*}{(0.8 \times \Delta H_{PVDF}^0) + (0.2 \times \Delta H_{PHBV}^0)} \times 100,$$

X_{Blend} is the relative percent crystallinity of the blend samples. ΔH_{Blend}^* is the measured enthalpy of the blend samples. ΔH_{PVDF}^0 is 104.7 J/g, and ΔH_{PHBV}^0 is 109 J/g.

Relative Percent Crystallinity of 80/20 PVDF/PHBV Blend

From the result, ΔH_{Blend}^* is 57.9 J/g,

$$\begin{aligned} X_{Blend}(\%) &= \frac{\Delta H_{Blend}^*}{(0.8 \times \Delta H_{PVDF}^0) + (0.2 \times \Delta H_{PHBV}^0)} \times 100, \\ &= \frac{57.9}{(0.8 \times 104.7) + (0.2 \times 109)} \times 100, \\ &= 54.9 \%. \end{aligned}$$

For thermoplastic vulcanizates (TPV), The crystallization was occurred from only PVDF and PHBV. The relative percent crystallinity was calculated relatively to the composition of PVDF and PHBV in NR/PVDF/PHBV blend which were 40 and 10, respectively. The equation used in calculation relative percent crystallinity of thermoplastic vulcanizate is shown below:

$$X_{TPV}(\%) = \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100.$$

X_{TPV} is the relative percent crystallinity of the TPV samples. ΔH_{TPV}^* is the measured enthalpy of the TPV samples. ΔH_{PVDF}^0 is 104.7 J/g, and ΔH_{PHBV}^0 is 109 J/g. The calculations of relative percent crystallinity of TPVs are shown as follow.

Relative Percent Crystallinity of 50/40/10 TPV at ESO content 0 phr

From the result, ΔH_{TPV}^* of TPVs at ESO 0 phr is 16.9 J/g.

$$\begin{aligned} X_{TPV}(\%) &= \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \\ &= \frac{16.9}{(0.4 \times 104.7) + (0.1 \times 109)} \times 100, \\ &= 32.0 \%. \end{aligned}$$

Relative Percent Crystallinity of 50/40/10 TPV at ESO content 1 phr

From the result, ΔH_{TPV}^* of TPVs at ESO 1 phr is 15.2 J/g.

$$\begin{aligned} X_{TPV}(\%) &= \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \\ &= \frac{15.2}{(0.4 \times 104.7) + (0.1 \times 109)} \times 100, \\ &= 28.8 \%. \end{aligned}$$

Relative Percent Crystallinity of 50/40/10 TPV at ESO content 2 phr

From the result, ΔH_{TPV}^* of TPVs at ESO 2 phr is 15.4 J/g.

$$\begin{aligned} X_{TPV}(\%) &= \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \\ &= \frac{15.4}{(0.4 \times 104.7) + (0.1 \times 109)} \times 100, \\ &= 29.2 \%. \end{aligned}$$

Relative Percent Crystallinity of 50/40/10 TPV at ESO content 5 phr

From the result, ΔH_{TPV}^* of TPVs at ESO 5 phr is 15.5 J/g.

$$\begin{aligned} X_{TPV}(\%) &= \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \\ &= \frac{15.5}{(0.4 \times 104.7) + (0.1 \times 109)} \times 100, \\ &= 29.4 \%. \end{aligned}$$

Relative Percent Crystallinity of 50/40/10 TPV at ESO content 7 phr

From the result, ΔH_{TPV}^* of TPVs at ESO 7 phr is 15.7 J/g.

$$\begin{aligned} X_{TPV}(\%) &= \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \\ &= \frac{15.7}{(0.4 \times 104.7) + (0.1 \times 109)} \times 100, \\ &= 29.8 \%. \end{aligned}$$

Relative Percent Crystallinity of 50/40/10 TPV at ESO content 10 phr

From the result, ΔH_{TPV}^* of TPVs at ESO 10 phr is 14.3 J/g.

$$\begin{aligned} X_{TPV}(\%) &= \frac{\Delta H_{TPV}^*}{(0.4 \times \Delta H_{PVDF}^0) + (0.1 \times \Delta H_{PHBV}^0)} \times 100. \\ &= \frac{14.3}{(0.4 \times 104.7) + (0.1 \times 109)} \times 100, \\ &= 27.1 \%. \end{aligned}$$

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Presentations:

1. Phothiphon, K.; and Magaraphan, R. (2010, April 6-10) Effect of Blend Composition of Natural Rubber/ Poly(vinylidene fluoride) via Dynamic Vulcanization on Properties of Rubber Used in Fuel System. Poster Presentation of the International Polymer Conference POLYCHAR 18, Siegen, Germany.
2. Phothiphon, K.; and Magaraphan, R. (2010, April 22) Functionalized Natural Rubber: Rubber Parts for Gasohol Resistance. Poster Presentation of the 1st National Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and the 16th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

