

Property improvements of natural rubber and low density polyethylene blends through dynamic vulcanization

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Abstract

Polymer blends are prepared by melt mixing, solution or latex blending. Thermoplastic vulcanizates (TPVs) are generally produced by melt mixing. TPVs can be co-injected or co-extruded to produce complex articles built from very soft/hard components. Dynamic vulcanization would give rise to a uniform and fine distribution of rubber and thermoplastic phases. The aim of this study was to identify a suitable dynamic vulcanization system to produce natural rubber (NR)/low-density polyethylene (LDPE) blends with improved chemical, ageing and morphological properties. Three 50:50 NR/LDPE blends were prepared by varying the vulcanizing agent as sulphur, dicumyl peroxide (DCP) and 50:50 sulphur: DCP. A control was prepared without any vulcanizing agent. All these blends were prepared by melt mixing. The blends were characterized using FTIR spectroscopy and SEM analysis of tensile fracture surfaces. Water absorption, swelling and ageing behaviour of the blends were investigated.

Water absorption percentage of blends prepared with DCP and the mixed curing system was zero. Analysis of gel content indicated a higher crosslink density for the blend prepared with the mixed curing system compared to the other blends. Also, the former blend showed the highest retention of strength properties and elongation at break compared to the other two blends prepared with vulcanizing agents. SEM analysis showed a fine and smooth textured morphology for this blend. Results in overall indicated that the 50:50 NR/LDPE blend prepared with the mixed curing system would be suitable to manufacture heat and solvent resistant products.

Key words: ageing properties, dynamic vulcanization, morphology, NR/LDPE blends, swelling properties

Introduction

Polymer blends may be categorized in general into two broad classes: immiscible and miscible blends. Immiscible blends are those which exist

in two distinct phases, but they are practically still very useful materials, e.g., toughened plastics. Miscible blends are those, which exist in a single homogeneous phase and may exhibit

synergistic properties, different from the pure components (Utracki, 1990). Thermoplastic elastomers (TPEs) may be divided into the following classes according to their chemistry and morphology such as (soft) triblock copolymers, (hard) multi block copolymers and blends of rubbers with thermoplastics and application of dynamic vulcanization. The thermoplastic vulcanizates (TPVs) based on PP/EPDM blends by dynamic vulcanization exhibit superior tensile properties including higher tensile strength and greater elongation and also exhibit better processability (Koning *et al.*, 1998). In dynamic cross-linking, the rubber and thermoplastic are pre-mixed with the curative and other additives are then added. The rubber crosslinks *in-situ* to give typically a form of semi-interpenetrating polymer network, which is subsequently capable of being molded or extruded (Wu, 1987).

The morphology of a material is organized on a supra-molecular scale, *i.e.*, the curing agent, size and orientation of crystallites, domains, the structure of groups of molecules of the components and of their boundaries, and the degree of crystallinity. The morphology of polymer blends is understood as the mostly qualitative description of the spatial arrangement of the blend-component phases (Reijnders, 1989). However, in the case of dynamic vulcanization an inverse phase morphology characterized by a matrix phase representing the minor content. Therefore, no shear deformation as the main mixing mechanism, but mainly elongation deformations are required

as a precondition for an effective dispersion process (Coran and Patel, 1996).

Several crosslinking agents have been employed to crosslink the EPDM phase in PP/EPDM blends: co-agent assisted peroxides; activated phenol-formaldehyde resins, commonly known as resol-resins; platinum catalyzed hydro siloxane; vinyltrialkoxo silane/moisture; catalyzed quinine dioxime and bithiols; *etc.* (Naskar, 2004). Special crosslinking agent like benzene-1,3-bis (sulfonyl) azide for the preparation of TPVs was investigated by Lopez Manchado and Kenny, 2001. They concluded that the sulfonyl-azide group can act as an effective crosslinking agent for the elastomeric phase and also as a coupling agent between the elastomeric and thermoplastic phases. The cure rate, the final crosslink density, the thermal stability of the crosslinks formed, the safety, health and environmental characteristics of the chemicals used and the cost price are relevant parameters for the final choice of the crosslinking system (Naskar *et al.*, 2004).

Sulfur vulcanization of EPDM rubber and other elastomers is normally performed in the presence of activator and accelerators. It is proven, that the mechanism of sulfur vulcanization of EPDM is more or less similar to the mechanism, which is normally accepted for polydiene elastomers (Chapman and Porter, 1998). Sulfur/accelerator combinations have in principle been demonstrated to be applicable to dynamic vulcanization of PP/EPDM

blends by Coran and Patel, 1980. They observed improvement of tensile properties of PP/EPDM blends. However, sulfur crosslinking systems are not applied in commercial PP/EPDM TPVs, since PP has a relatively high melting point and the crosslinks lack in thermal and UV-stability. Moreover, the production and processing of these TPVs suffer from severe problems (Koning *et al.*, 1998).

Peroxide cure can be used to vulcanize both unsaturated and saturated elastomers. Vulcanization of the latter is not possible with sulphur. Nevertheless, there are some polymers which cannot be crosslinked by peroxide vulcanization. The efficiency of the total crosslinking reaction depends mainly on the type of peroxide and polymer radicals formed during the process. The relationship between peroxide structure and crosslinking efficiency has been described by Endstra, (1985). However, when peroxide is added to a PP/EPDM blend, two competing processes may take place simultaneously: EPDM-crosslinking and PP-degradation. It is generally accepted that degradation proceeds through β -chain scission by abstraction of tertiary hydrogen atoms from the main chain of the olefin polymer (Coran *et al.*, 1982).

In peroxide vulcanization, the crosslinks formed consist of carbon-carbon bonds between the polymer chains, while in sulphur vulcanisation the crosslinks between the chains consist of sulphur bridges: carbon-sulphur and sulphur-sulphur bonds (Dluzneski, 2001). The carbon-carbon bond is more rigid and

stable (bond energy is 351 kJ/mol) than the carbon-sulphur (285 kJ/mol) and sulphur-sulphur (267 kJ/mol) bonds. This difference in network structure gives the two vulcanisation systems their different characteristic properties, since the lower the bond energy the easier the breakage of bonds under influence of mechanical or thermal energy (Dluzneski, 2001). This will be reflected, for instance, in ageing properties: peroxide vulcanisates have much better heat ageing characteristics than sulphur cured elastomers, due to the fact that the carbon-carbon bonds are more stable than the sulphur bridges. Brodsky, (1994) reported combined sulphur/accelerator and peroxide cure for a blend of EPDM/BR/NR. He used a variety of mixed peroxide-sulphur curing systems and tested to study the mechanical properties of the vulcanizates. In regard to the curing behaviour, the results show that the mixed curing system leads to compounds with low scorch safety and low cure rate when compared to the usual sulphur/accelerator system. On the other hand, the mixed vulcanizates show a reduced reversion, proportional to the amount of peroxide used. In regard to physical properties, it was observed that vulcanizates produced with the mixed curing system have improved tensile strength and similar tear resistance. Ageing resistance, compression set and fatigue life of vulcanizates prepared with the mixed curing system was also found to be improved when compared to those of the sulphur/accelerator cured rubber. Vulcanization of EPDM with sulphur

and peroxide in two curing steps was studied by van der Burg (Van, 1998). The vulcanisates were found to have lower crosslink density and intermediate tear strength and compression set. The cross-linking of the NR and LDPE in our work was carried out using sulphur and peroxide individually and with 50:50 sulphur : peroxide (mixed) systems. Therefore, aim of this study was to identify a suitable dynamic vulcanization system to produce NR/LDPE blends. Because of the high incompatibility between the two components, compatibilization is necessary to improve the mechanical performance for commercial applications.

Materials and Methodology

Commercially available low density polyethylene (LDPE) and ribbed smoke sheet rubber (RSS 2) were used in the preparation of the blend compounds. LDPE having melt flow index, density and crystalline melting temperature of 2.4 g/10 min., 0.923 g/cm³ and 115 °C, respectively was supplied by Deluxe Plastics Ltd., Sri Lanka. RSS 2 having a plasticity retention index (PRI) of 64

was obtained from the Rubber Research Institute of Sri Lanka. Other compounding ingredients, sulphur and dicumyl peroxide (DCP) as the vulcanizing agents and BKF (2, 2'-methylene bis (4-methyl-6-tert butyl phenol)) as the antioxidant are industrial grade chemicals and were purchased from Glorchem Enterprises, Sri Lanka.

Blend preparation

Four 50:50 NR/LDPE blends were prepared with and without vulcanizing agents and the formulations are given in Table 1. The blends were prepared by melt mixing using a Brabender plasticorder operated at a temperature of 130 °C, and at a rotor speed of 60 rpm. Total mixing time was kept constant at 10 minutes. The mixing cycle used in the preparation of NR/LDPE blend compounds is also given in Table 1. NR/LDPE blend compounds were compressed in an electrically heated hydraulic press at 150 °C under 3.5 bar pressure for 15 minutes to produce 2 mm thick sheets. Test specimens were cut from these sheets according to the standard.

Table 1. Formulation and mixing cycle of 50:50 NR/LDPE blends

Ingredient	Parts by weight				Total mixing time (min.)
	Control	Sulphur system	DCP system	Mixed system	
LDPE	50	50	50	50	0
NR	50	50	50	50	4
Antioxidant	1	1	1	1	5
TBBS	0	1	0	0.5	6
Sulphur	0	1	0	0.5	8
DCP	0	0	1	0.5	10

Chemical properties of 50:50 NR/LDPE blends**Swelling behavior**

ISO 1817:2011 describes methods of evaluating the resistance of vulcanized and thermoplastic rubbers to the action of liquids by measurement of properties of the rubbers before and after immersion in test liquids. Two test pieces (30mm x 10mm x 2mm) from each of the treatments were tested. The test pieces were immersed in p-xylene for 72 hours in closed lid bottles and the swollen weight was obtained. Calculated the degree of swelling according to the formulation given below.

$$Q (\%) = (m - m_0/m_0) \times 100$$

Where, m_0 and m are the masses of the sample before and after swelling in p-xylene, respectively.

Gel content

Three test pieces approximately 1cm x 3cm x 0.2cm in size from each of the samples were tested. The test pieces were measured to the nearest 0.1 mg and covered with a mesh, then placed in boiled p-xylene solution for 16 hours according to ASTM D2240. Thereafter, the samples were taken out and the final weight was measured. Then the test pieces were oven aged at 70 °C and the weight after each hour was measured until the readings became constant.

FTIR spectra of gel samples

FTIR is a powerful technique to qualitatively identify organic materials and to determine molecular structure. The test pieces which were obtained from the gel content test were used to obtain the FTIR spectra. Nicolet 380 FTIR spectrometer was used for the testing.

Water absorption

Water absorption data was obtained by immersing 72 hours in water at 27 °C. Upon removal, specimens were dried and weighed immediately. The readings were taken after each hour until the weight was constant. The increase in weight was reported as a percentage.

Ageing properties of 50:50 NR/LDPE blends

Tensile and tear properties were evaluated after ageing. Ageing was carried out in an air circulating oven at 70 °C for 72 hours according to BS ISO 37:2010 (E) and BS ISO 34-1:2010 (E).

Morphology of 50:50 NR/LDPE blends

Surface morphology of tensile fracture surfaces of NR/LDPE blends was examined by a ZEISS EVO LS 15 Scanning Electron Microscope (SEM). The specimens for SEM observation were prepared by lay down the as-spun NR/LDPE fine droplet on a copper stub. Each sample was coated with a thin layer of gold prior to observation under SEM.

Results and Discussion

Chemical properties of 50:50

NR/LDPE blends

The swelling behaviour of a thermoplastic material defines the chemical or liquid absorption capacity of it or compound. If the compound shows a higher percentage of swelling it can absorb a high amount of chemical/liquid without dissolving in the same. The mobility of the penetrant through the polymer chains depends upon the free volume in the matrix. According to free volume theory (Harogopad and Aminabhavi, 1991), the rate of diffusion depends upon the ease with which polymer chain segments exchange their positions with penetrant molecules.

Figure 1 shows that percentage of swelling is highest in the 50:50 NR/LDPE blend prepared with sulphur as the curing agent. C-C bonds in a peroxide vulcanizate is more rigid and stable compared to C-S in a sulphur vulcanizate (Dluzneski, 2001). Also, C-C crosslinks are shorter than sulphur crosslinks and hence penetration of solvent molecules through a peroxide vulcanized network would be difficult than through a sulphur vulcanized network and this results in a higher

swelling value for the latter. A higher swelling value reflects a lower gel content. The Control shows a value less than 100 for the percentage of swelling and this indicates that the blend dissolves into p-xylene because non-crosslinked materials do not exhibit good resistance towards organic solvents.

According to the above figure, blends prepared with peroxide and the mixed curing system have good solvent resistance compared to the blend prepared with sulphur and the Control.

The gel content test is used for defining the solvent resistance of a thermoplastic, plastic or rubber compound. Crosslink density of a material is proportionate to the gel content. When the gel content is high, percentage swelling will be reduced. Figure 2 shows that the gel content of the blend prepared with peroxide is markedly higher than that of the blend prepared with sulphur as the curing agent. The blend prepared with the mixed curing system has the highest gel content and indicates the highest crosslink density due to good chemical interaction with NR and LDPE.

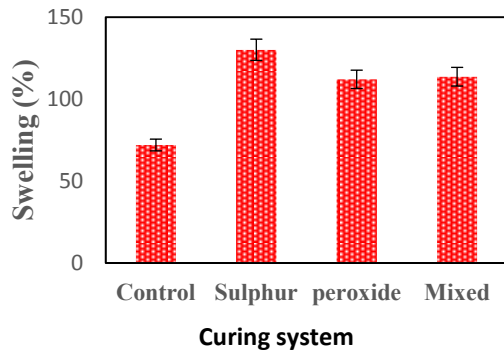


Fig. 1. Swelling behavior of 50:50 NR/LDPE blends prepared with different curing systems

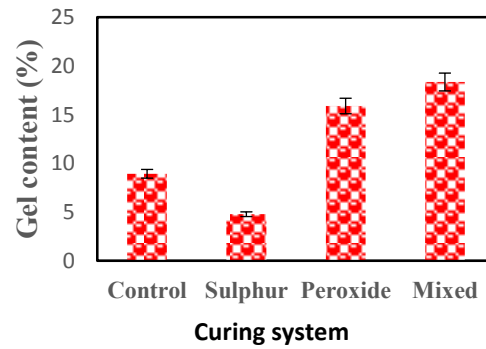


Fig. 2. Gel content of 50:50 NR/LDPE blends prepared with different curing systems

Figure 3, shows the FTIR spectra of NR/LDPE blends prepared with DCP and the mixed curing system. Both these NR/LDPE blends have a strong plastic stretching absorption around 1376 cm⁻¹. This peak confirms the presence of gel

and it is evidence for the amount of crosslinks present in the LDPE phase of the blend. In addition, the peak at 840 cm⁻¹ corresponding to natural rubber appears to be weak in both the blends.

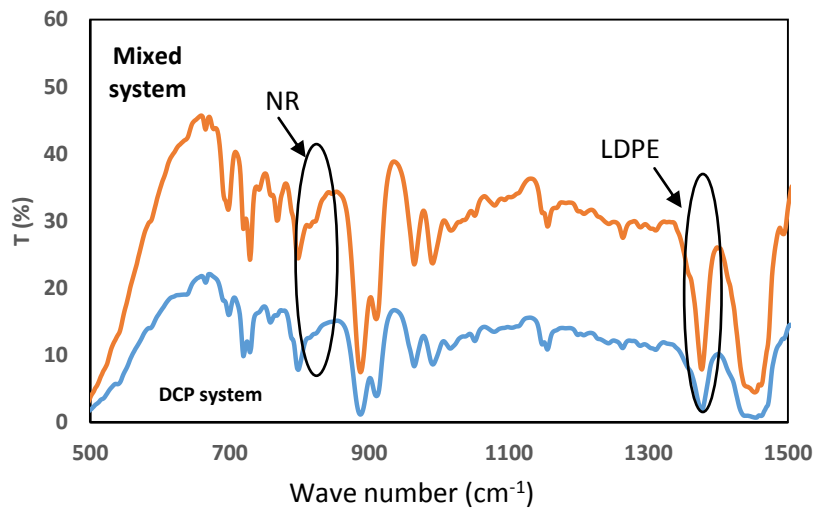


Fig. 3. FTIR spectra of 50:50 NR/LDPE blends prepared with DCP and the mixed curing system

Water absorption of 50:50 NR/LDPE blends

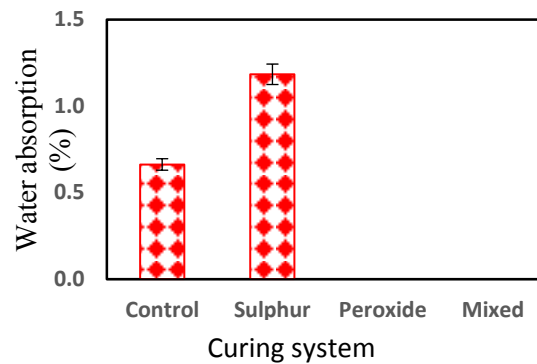


Fig. 4. Water absorption of 50:50 NR/LDPE blends prepared with different curing systems

According to Figure 4, blends prepared with DCP and the mixed curing system show a zero water absorption indicating higher water resistance. Under dynamic vulcanization, 50/50 NR/LDPE phase changed from co-continuous to plastic phase and plastics have good water resistance compared to rubber (Wang *et al.*, 2005).

Ageing properties of 50:50 NR/LDPE blends

The curves in Figure 5, which was obtained from tensile testing of aged test pieces shows almost a similar pattern of variation. However, the blend prepared with the mixed curing system shows a semi crystalline behavior compared to the other three composites. The highest strain value elucidates from the former blend and hence it indicates good heat resistance compared to the others.

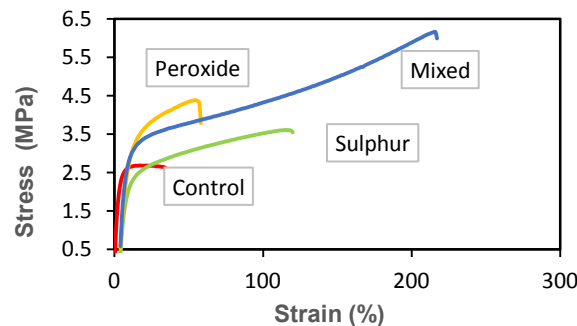


Fig. 5. Stress – strain curves of 50:50 NR/LDPE blends, after ageing

Table 2. *Percentage retention of properties of 50:50 NR/LDPE blends, after ageing*

System	Retention of tensile strength (%)	Retention of elongation at break (%)	Retention of tear strength (%)
Control	65	22	82
Sulphur	44	24	87
Peroxide	35	12	85
Mixed	54	40	90

All the blends show low retention of tensile strength and elongation at break, but high retention of tear strength. Therefore, these blends are not at the required level in regard to resistance to thermal degradation. According to Table 2, peroxide loaded blend shows very low ageing properties and indicates the initiation of radical reaction between C-C under the ageing condition. Carig and white (2006) has reported the changes in the polymer properties under the different environmental and processing conditions are termed ageing. Polymers have been known to demonstrate two kinds of ageing: chemical and physical. Chemical ageing is thermal degradation, photo oxidation, etc. and the changes are connected with degradation and lead to molecular chain scission and/or crosslinking. The result is cracking and chemical disintegration of polymers. Therefore, percentage retention of properties after ageing is generally less than 100.

Morphology of 50:50 NR/LDPE blends

Figure 6, (c) and (d) show smoother and fine fracture surface compared to (a)

and (b) and indicate good interfacial adhesion between NR and LDPE. Figure 6, (a) and (b) show coarse phase morphology. Figure (a) shows a clear separation of NR and LDPE phases, probably due to poor interfacial adhesion between the phases due to the absence of any crosslinks. This phase separation indicates incompatibility between NR and LDPE, which results in poor mechanical properties. The morphological analysis shows that interfacial adhesion between NR and LDPE phases is at the highest level when a mixture of sulphur and peroxide is added as the curing system. Further, the 50:50 NR/LDPE blend prepared with this mixed curing system shows a higher gel content, which means there is good interaction between the NR and LDPE phases. This blend is the least heterogeneous according to its phase morphology shown in Figure 6 (d). Results in overall indicate that the 50:50 NR/LDPE blend prepared with the mixed curing system would be suitable to manufacture heat and solvent resistant products.

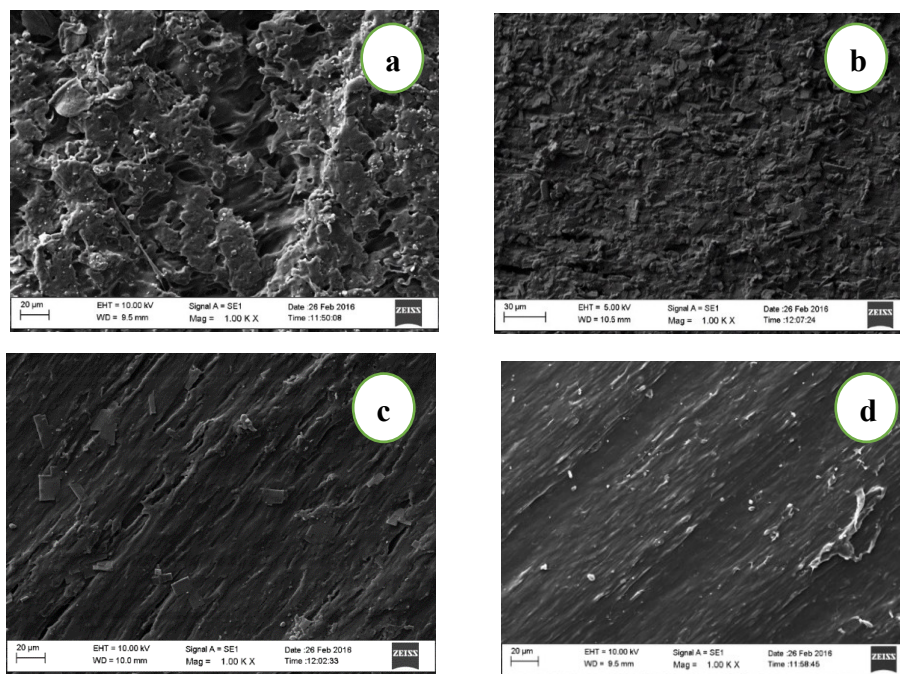


Fig. 6. Scanning electron micrographs of tensile fracture surfaces of 50:50 NR/LDPE blends at x1000 magnification (a) control (b) vulcanized with sulphur (c) vulcanized with DCP (d) vulcanized with the mixed curing system

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References

Brodsky, G J (1994). Mixed peroxide-sulfur rubber curing system. *Rubber World* **210** (5), 31-76.
 Chapman, A V and Porter, M (1988). Sulphur vulcanization chemistry. *Natural Rubber Science and Technology*.

AD Roberts (Ed.), Oxford University Press, Oxford.

Coran, A Y and Patel, R P (1996). Thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends. Hanser Publishers, Munich.

Coran, A Y and Patel, R (1980). *Rubber Chemistry and Technology* **53**, 141.

Coran, A Y, Patel R and Williams, D (1982). *Rubber Chemistry and Technology* **55**, pp.116.

Craig, I H and White, J R (2006). Mechanical properties of photo-degraded recycled photo degraded polyolefin. *Journal of Materials Science* **41** (3), 993-1006.

- Dluzneski, P R (2001). Peroxide vulcanization of elastomers. *Rubber Chemistry and Technology* **74**(3), 451-492.
- Endstra, W C (1985). Proceedings of SRC Conference on "Organic peroxides for Crosslinking applications", June 10-12, Copenhagen, Denmark.
- Harogopad, S B and Aminabhavi, T M (1991). Interactions of substituted benzenes with elastomers. *Polymer* **32**(5), 870-876.
- Koning, C, Van Duin, M, Pagnouille, C and Jerome, R (1998). Strategies for compatibilization of polymer blends. *Progress in Polymer Science* **23**(4), 707-757.
- López Manchado, M A and Kenny, J M (2001). Use of benzene-1, 3-bis (sulfonyl) azide as crosslinking agent of TPVs based on EPDM rubber-polyolefin blends. *Rubber Chemistry and Technology* **74**(2), 198-210.
- Naskar, K (2004). *Dynamically vulcanized PP/EPDM thermoplastic elastomers: exploring novel routes for crosslinking with peroxides*. University of Twente.
- Reijden-Stolk, C (1989). *A study on deformation and break-up of dispersed particles in elongational flow* (Doctoral dissertation, PhD Thesis, Technical University of Delft).
- Utracki, L A and Sammut, P (1990). Rheology of polycarbonate/linear low density polyethylene blends. *Polymer Engineering and Science* **30**(17), 1027-1040.
- Van Bevervoorde-Meilof, E W E (1998). *Improving mechanical properties of EPDM rubber by mixed vulcanisation*.
- Wang, S, Yu, J and Yu, J (2005). Compatible thermoplastic starch/polyethylene blends by one-step reactive extrusion. *Polymer International* **54**(2), 279-285.
- Wu, S (1987). Formation of dispersed phase in incompatible polymer blends: Interfacial and rheological effects. *Polymer Engineering and Science* **27**(5), 335-343.

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