

# Improvement of Physico-Mechanical Properties of Calcium Carbonate filled Natural Nubber and Low Density Polyethylene Blends with Titanate Coupling Agent

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**Abstract**—Nonblack particulate fillers most used with thermoplastic and rubber are calcium carbonate, silica, talc and alumina hydrates. The main characteristics, which control the effectiveness and the dispersion of filler in the polymer, are structure, surface area and chemical activity of filler. The mechanical behavior of rubber-thermoplastic blends depends greatly on interactions and compatibility that develop between the two polymers and the filler. The main objective of this study is to improve physico-mechanical properties of calcium carbonate ( $\text{CaCO}_3$ ) filled natural rubber (NR) and low density polyethylene (LDPE) blends using a titanate coupling agent. Two series of NR/LDPE blends, with and without titanate coupling agent, were prepared by varying LDPE loading from 10% to 90% at 10% intervals. 20 parts by weight of  $\text{CaCO}_3$  per 100 parts of combined polymer was incorporated into every blend composition. The blends were prepared using a Brabender plasticorder by melt mixing at a temperature of 130 °C, and at a rotor speed of 60 rpm. Physico-mechanical properties such as tensile properties, hardness, tear strength and morphology of the blends were studied. These properties were determined according to ISO standards. Morphology of the tensile fracture surface of blends was observed using a transmitted light microscopy. Tensile strength, tear strength and hardness of NR/LDPE blends increase with increase in LDPE loading while elongation at break decreases. NR/LDPE blends with titanate coupling agent exhibited enhanced properties at every LDPE loading. NR/LDPE blends having 30% of LDPE loading showed highest tensile strength. In this blend, NR was dispersed in LDPE matrix with good adhesion between NR and LDPE.

**Keywords**— *natural rubber/low density polyethylene blends; titanate coupling agent; physico-mechanical properties; morphology*

## I. INTRODUCTION

Polymer composite blends are being increasingly employed in the rubber industry because of their good strengths and low densities [1]. Especially, the reinforced rubber-thermoplastic blends are widely used in many fields including aircraft, aerospace and automotive industry [2]. The blending of natural

rubber with thermoplastics leads to a reduction in cost of the compound and makes it easier to fabricate complex shapes [3].

Fillers are incorporated into both rubbers and thermoplastics to reduce cost by increasing volume, to reinforce the polymer and thereby to improve performance of the final product. Calcium carbonate, silica, talc and alumina hydrates are the commonly used nonblack particulate fillers or mineral fillers, in thermoplastics and rubbers. Calcium carbonate is a natural product from sedimentary rocks and is separated into chalk, limestone, and marble. In some cases, calcium carbonate is treated to improve bonding with thermoplastics [4]. Main characteristics, which control effectiveness and dispersion of filler within polymer matrix, are structure, surface area and chemical activity of filler. Filler particles can be agglomerated without homogeneously dispersed throughout the polymer matrix. Therefore high shear mixers are to be used to break up agglomerates and to ensure good wetting and dispersion of the filler in the polymer matrix [5].

Physical properties of polymer blends are controlled mainly by nature of component polymers, blend composition, and interfacial adhesion between polymers [6]. The practical utility of a polymer blend is determined by the compatibility of component polymers, which is considered as the fundamental property. It has been observed that majority of rubber-thermoplastic blends, including NR/LDPE blends are incompatible [7], thus producing inferior properties.

Mechanical properties of a polymer can be improved through use of filler by reducing its particle size and/or by treating it with a suitable coupling agent [7]. Incorporation of fillers into thermoplastic elastomers, a kind of rubber-thermoplastic blends, have been widely practiced in the polymer industry to enhance certain properties. Mechanical properties of polymer blends can be enhanced by using physical or chemical modifiers [6].

Coupling agents are molecular bridges at the interface between the two substrates; an inorganic filler and organic polymer matrix. Silica based coupling agents are widely used

in rubbers especially when incorporating silica as filler [8] Titanium based coupling agents are added to thermoplastics, including polyethylene, when CaCO<sub>3</sub> fillers are incorporated [9]. However, titanium based coupling agents are not commonly used in rubbers.

The mechanical properties of polymer blends with CaCO<sub>3</sub> are dependent on interfaces where the polymer matrix and filler are in contact. As inorganic filler, CaCO<sub>3</sub> particles mostly polar, hydrophilic and has high free energy surfaces. Thus, filler particles might be incompatible with polymer matrices having non-polar, more hydrophobic and relatively low free energy surfaces. In order to overcome that possible incompatibility, titanium based coupling agent are introduced in this research.

Titanium based coupling agents are unique in their reaction with protons at the inorganic interface that results in the formation of organic monomolecular layers on the inorganic surface [9]. Titanate-treated inorganic fillers are hydrophobic, organophilic and organofunctional. When incorporated into thermoplastics, titanate-treated inorganic fillers often promote adhesion improve dispersion, and impact strength thus reducing brittleness, and make able to incorporate higher filler loading [10].

This study aims to develop CaCO<sub>3</sub> filled NR/LDPE blends using a titanium based coupling agent called titanate coupling agent. Major objective is to investigate the effect of titanium based coupling agent on physico-mechanical properties of NR/LDPE blends.

## II. EXPERIMENTAL

### A. Materials

Commercially available LDPE and ribbed smoke sheet (RSS) Grade-2 NR was used as the two polymers in this blend compounds. LDPE having melt flow index, density and crystalline melting temperature of 2.4 g/10 min., 0.923 g/cm<sup>3</sup> and 115 °C, respectively was supplied by Deluxe Plastics Ltd., Sri Lanka. RSS-2 having plasticity retention index of 64 was supplied by Rubber Research Institute of Sri Lanka.

Titanate coupling agent, a kind of neoalkoxy organotitanate of trade name of "Lica 12" in pellet from Kenrich Petrochemical Incorporation, having the chemical formulation of Titanium IV 2, 2 (bis 2-propenolatomethyl) butanolato, tris(dioctyl) phosphato-O was supplied by Pheonix industries, Sri Lanka. The coupling agent was used as received without any further purification. The respective chemical structure is presented in Fig. 1.

CaCO<sub>3</sub> having mean particle size of 2 µm and density of 0,56 g/cm<sup>3</sup> was used as the filler. It was obtained from Lanka Minerals & Chemicals (Pvt.), Sri Lanka. Other compounding ingredients, sulphur and dicumyl peroxide (DCP) as the vulcanizing gents, stearic acid and zinc oxide (ZnO) as the organic and inorganic activators, and BKF (2, 2'-methylene bis (4-methyl-6-tert butyl phenol)) as the antioxidant (A/O) are

industrial grade chemicals and were purchased from GloChem industries, Sri Lanka.

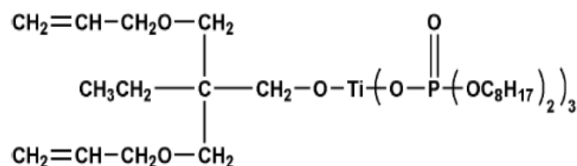


Fig. 1. Titanium IV 2,2 (bis 2- propenolatomethyl) butanolato, tris(dioctyl) phosphato-O

### B. Preparation of Blends

Two series of CaCO<sub>3</sub> filled NR/LDPE blend compounds were prepared with and without titanate coupling agent by varying LDPE loading from 10 % to 90% by weight at an interval of 20%. The formulation of the blend with the coupling agent is 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 14 minutes. Mixing cycle used in preparation of NR /LDPE blend compounds is given in Table II.

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 standards. Tensile properties, and tear strength, of NR/LDPE blends were determined using Instron tensile testing machine according to BS ISO 37:2010 and BS ISO 34-1:2010, respectively. Dumbbell tensile specimens and angle test tear specimens were used. Hardness of the blends was determined using dead load hardness tester according to BS ISO 48:2010.. Morphology of tensile fracture surfaces of the blends was suited using a transmitted light microscope.

TABLE I. FORMULATION OF THE BLENDS

Ingredient	Parts by weight					
	0	10	30	50	70	90
NR						
LDPE	100	90	70	50	30	10
Zinc oxide	5					
Stearic acid	2					
A/O	1					
CaCO <sub>3</sub>	20					
Coupling agent	0.5					
TBBS	1.0					
DCP	0.5					
Sulphur	0.5					

TABLE II. MIXING CYCLE

Time, min	Added ingredient
0	LDPE
4	NR
6	ZnO + Stearic acid +A/O
7	$\frac{1}{2}$ CaCO <sub>3</sub>
8	$\frac{1}{2}$ CaCO <sub>3</sub>
9	Coupling agent
11	TBBS
12	Sulphur + DCP
14	Dumping the compound

### III. RESULTS AND DISCUSSION

#### A. Physico-mechanical properties of the blends

Stress-strain curves for NR/LDPE blends without titanate coupling agent exhibited behavior of semi-crystalline thermoplastic material from 30% to 90% of LDPE loading. NR/LDPE blend having 10% of LDPE loading exhibited behavior of a highly elastic and soft material. Stress-strain curves for NR/LDPE blends with titanate coupling agent are also exhibited similar behaviors which are shown in Fig. 2. Stress-strain curves for NR/LDPE blends having LDPE loading from 50% to 90% and pure LDPE show behavior a semi-crystalline thermoplastic material. NR/LDPE blends having 10% and 30% shows a behaviour of a rubber. This change in behaviour suggests that a phase change of the blends would occur from 30% to 50% of LDPE loading. Tensile properties obtained from stress-strain curves for NR/LDPE blends with and without coupling agent are shown in Fig. 3 and Fig.4. Tensile strength of NR/LDPE blends without coupling agent show an initial increase up to 50% of LDPE loading, and then reaches a plateau. Tensile strength of the NR/LDPE blends with coupling agent increases up to 30% of LDPE loading and then decreases. The increase in tensile strength is relatively more pronounced with the blends containing CaCO<sub>3</sub> with titanate coupling agent. The resulting reinforcement is a function of the extent of CaCO<sub>3</sub> dispersion within the polymer matrix, and the potential of interaction of titanate coupling agent with the polymers. Strong interactions between filler particles and macromolecular chains of the polymeric matrix through a coupling agent will lead to deep changes at the interfacial zone [5].

Tensile strength of NR/LDPE blend having 30% LDPE loading is 6.9 MPa and the same with coupling agent is 18.8 MPa. 172% increase of tensile strength suggests that the added 20 wt% of CaCO<sub>3</sub> provide maximum reinforcement at that LDPE loading. Titanate coupling agent at the loading of 0.5 wt% develops adhesion between NR, LDPE and CaCO<sub>3</sub> and improves dispersion of CaCO<sub>3</sub> so that agglomerations causing compactness can be eliminated. The gradual decrease in tensile strength after 30% LDPE loading is associated with poor dispersion of CaCO<sub>3</sub>. As LDPE loading increases, dispersion of CaCO<sub>3</sub> becomes less efficient due to high compactness and thereby inhibiting function of the titanate coupling agent. Consequently, higher LDPE loading tend to reduce activity of titanate coupling agent.

Fig. 4 shows that elongation at break decreases gradually with increase in LDPE loading for NR/LDPE blends with and

without titanate coupling agent. This decrease in elongation is due to replacement of highly elastic NR by semi-crystalline LDPE. However, NR/LDPE blends with coupling agent exhibit higher elongations at every LDPE loading. Further, this increase is highly significant at lower LDPE loadings. This implies that poor adhesion between NR and LDPE phases and/or poor dispersion of CaCO<sub>3</sub> occurred with NR and LDPE in absence of coupling agent. Dispersion of inorganic fillers and their adhesion to an organic substrate is difficult as most thermoplastics and rubbers are non-polar. Titanates are well established as adhesion promoters for non-polar materials [9]. The coupling of titanate to inorganic/organic substrate in monolayers allows for elimination of air voids, enhanced hydrophobicity, and a complete continuous phase for stress/strain transfer [9]. Fig. 5 shows how filler is dispersed in a polymer matrix with and without titanate coupling agent.

Tear strength of NR/LDPE blends with and without coupling agent are illustrated in Fig. 6. Tear strength increases significantly with LDPE loading for both series of blends. This is attributed to replacement of NR with semi-crystalline LDPE and further to the phase change suggested. Higher tear strengths of blends with coupling agent at every LDPE loading is due to improvement of interfacial adhesions between NR, LDPE and CaCO<sub>3</sub> promoted with the activity of titanate coupling agent.

Hardness of NR/LDPE blends with and without coupling agent is shown in Fig. 7. Hardness up to 50% of LDPE loading shows a gradual increase with replacement of soft NR by hard and semi-crystalline LDPE. At higher LDPE loadings, hardness remains constant and is similar to pure LDPE. This constant and higher hardness of NR/LDPE blends having LDPE loading above 50% confirms that LDPE is the matrix phase in these NR/LDPE blends. This reconfirms that a phase change has occurred from 30% to 50% of LDPE loading. Increased hardness of the NR/LDPE blends with coupling agent is due to good adhesion of CaCO<sub>3</sub> with NR and LDPE and to good dispersion of CaCO<sub>3</sub> in NR and LDPE. Density of NR/LDPE blends decreases gradually with increase in LDPE loading due to replacement of high density NR from low density LDPE. Density of NR/LDPE blends lie in the range of 1.02 to 1.06 g/cm<sup>3</sup>.

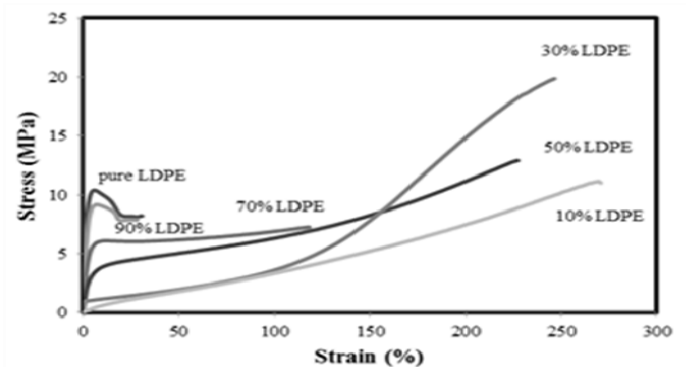


Fig. 1. Stress/strain curves for NR/LDPE blends with coupling agent

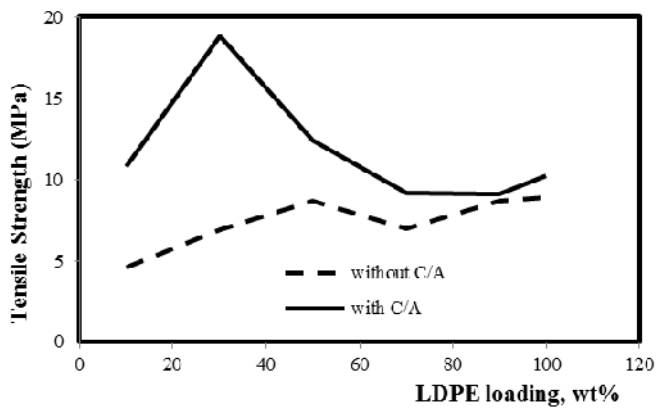


Fig. 2. Tensile strength of NR/LDPE blends, with and without coupling agent

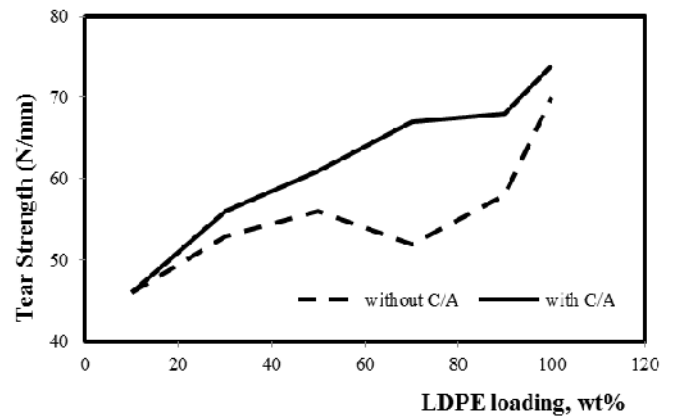


Fig. 5. Tear strength of NR/LDPE blends, with and without coupling agent

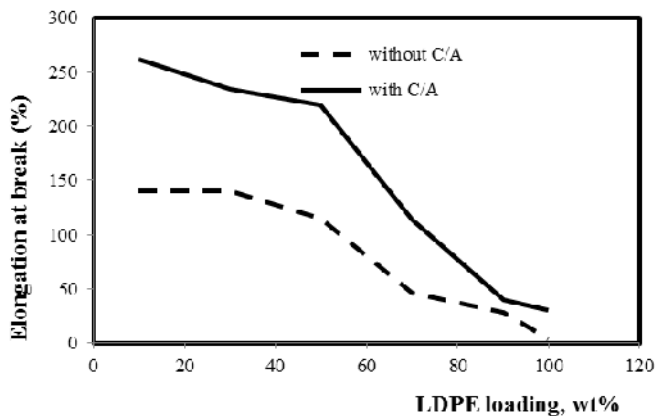


Fig. 3. Elongation at break of NR/LDPE blends, with and without coupling agent

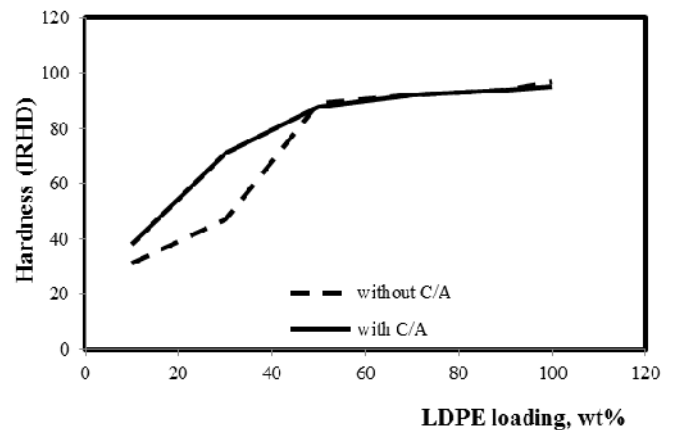


Fig. 6. Hardness of NR/LDPE blends, with and without coupling agent

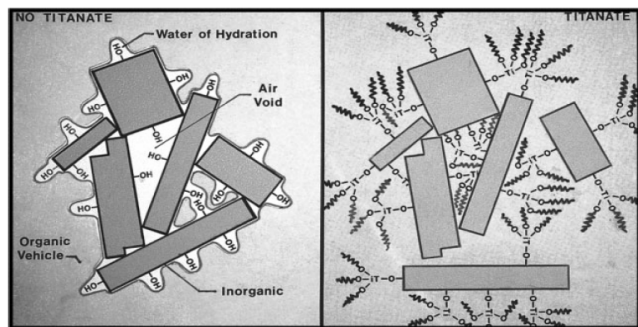


Fig. 4. Mechanism of filler dispersion in matrix with and without titanate [9]

#### B. Formation of network between NR, LDPE and $\text{CaCO}_3$ in presence of titanate coupling agent

Fig. 8 shows possible reactions for formation of a network with covalent bonds between  $\text{CaCO}_3$  and LDPE through titanate coupling agent. Crosslinking could also lead to a stabilization of the morphology improving the long-term properties compared to non-cross-linked blends. Moreover, crosslinked blends also give possibility of utilizing mixtures of polymer eventually leading to useful materials [11].  $\text{CaCO}_3$  attached NR will then form a strong interface with LDPE improving mechanical properties as observed in Fig. 3, Fig. 4, Fig 6 and Fig 7. Crosslinking of NR and DCP could also lead to stabilization of the morphology improving long-term properties compared to non-cross-linked blends [11]. The enhanced properties can be clearly from the stress-strain curve for NR/LDPE blend having 30% of LDPE loading with coupling agent, which is shown in Fig 9. According to Fig. 9, 70% loading of NR has good reaction with 20%  $\text{CaCO}_3$  and then with LDPE due to formation of covalent bonds between  $\text{CaCO}_3$  and titanate coupling agent. These morphological results are well matched with the tensile strength results given in Fig 3.

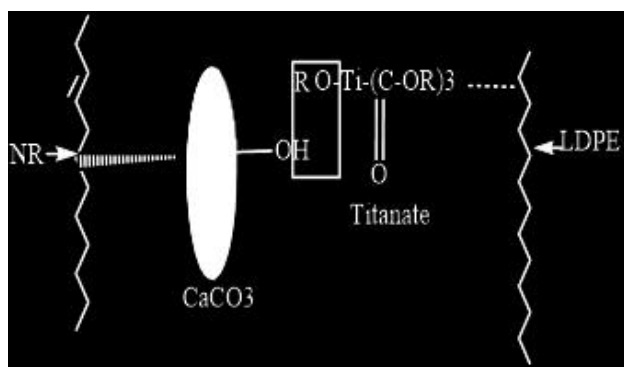


Fig. 7. Formation of a network with covalent and/or hydrogen bonding between NR and LDPE through CaCO<sub>3</sub> and titanate coupling agent

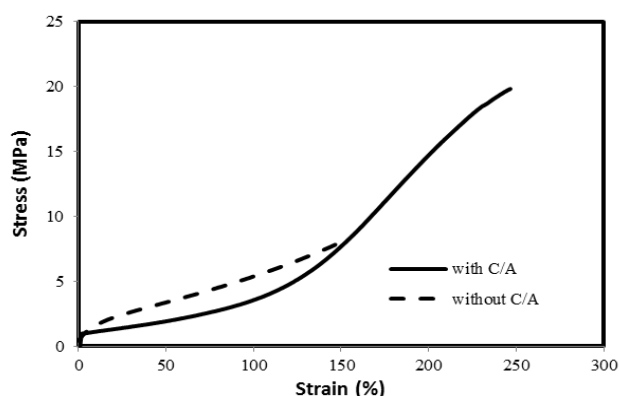


Fig. 8. Stress-strain curves for NR/LDPE blends having 30% of LDPE loading, with and without coupling agent

### C. Morphology

Fig. 10 shows transmission light microscopic images of tensile fracture surfaces of NR/LDPE blends with and without coupling agent. All images showed two phase morphology. The blend heterogeneity or the evidence of domains is reported for NR/LDPE/Silica blends also [12]. Fig. 10(a) and (c) show fine phase morphology with good adhesion characteristics of NR and LDPE. Fig 10(b) and (d) show coarse phase morphology. Further, Fig. 10 (b) clearly shows NR agglomerates resulted from poor mixing and dispersion characteristics. These results explain that good interfacial adhesions between NR and LDPE phases are formed when CaCO<sub>3</sub> is added with titanate coupling agent. This variation in phase morphology is in accordance with formation of network proposed in Fig. 8. In absence of titanate coupling agent, CaCO<sub>3</sub> does not make proper interactions with LDPE, although it is attached with NR. This phase separation indicates incompatibility of NR and LDPE that results in poor mechanical properties. Fig. 10(c) shows failure in NR phase revealing that NR/LDPE blend having 50% of LDPE loading was not properly dispersed compared to NR/LDPE blend having 30% of LDPE loading.

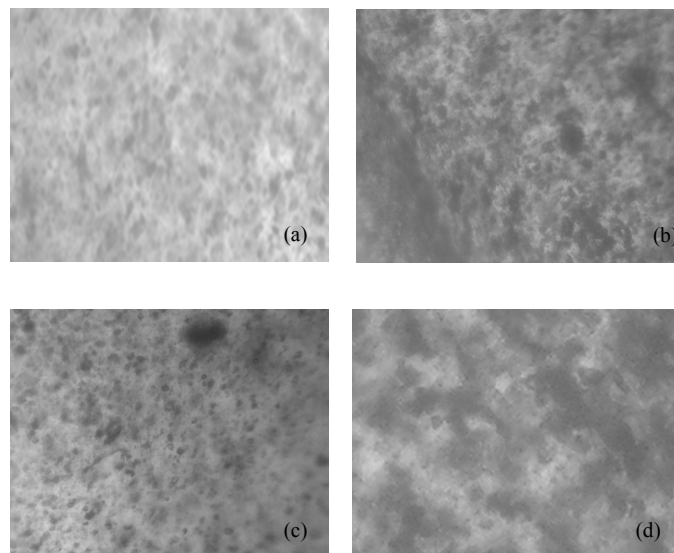


Fig. 9. Transmitted light microscopic images of tensile fracture surfaces of NR/LDPE blends at magnification 400 (a) 30% LDPE loading with coupling agent (b) 30% LDPE loading without coupling agent (c) 50% LDPE loading with coupling agent (d) 50% LDPE loading without coupling agent

### IV. CONCLUSIONS

Stress-strain curves for NR/LDPE blends proposed a phase change from elastic material to semi-crystalline material from 30% to 50% of LDPE loading. Tensile strength and tear strength of NR/LDPE blends without coupling agent increases with LDPE loading while elongation at break decreases. NR/LDPE blends with titanate coupling agent improved all measured mechanical properties at every LDPE loading. This is associated with the development of interfacial adhesions between NR, LDPE through CaCO<sub>3</sub> in presence of titanate coupling agent as explained by crosslinking formation reactions. Hardness increase with LDPE loading and reaches a plateau from 50% of LDPE loading and is with the change of matrix phase from NR to LDPE. Density decreases with increase in LDPE loading. Morphology of phases in NR/LDPE blends filled with CaCO<sub>3</sub> is strongly depended on CaCO<sub>3</sub> filler incorporation routes. Morphology of NR/LDPE blends having 30% of LDPE loading with titanate coupling agent shows fine regular shape NR dispersed phase with good homogeneity. Due to proper interfacial adhesions and/or good dispersion of CaCO<sub>3</sub> in NR and LDPE phases generated through titanate coupling agents in NR/LDPE blends having 30% of LDPE loading showed the best mechanical properties. This confirms that the added 20 wt% of CaCO<sub>3</sub> and 0.5 wt% of titanate coupling agent is more effectively formed strong covalent bonds that are required to improve physico-mechanical properties.

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## REFERENCES

- [1] W.Z. Nie, J. Li and Y.F. Zhang, "Tensile properties of surface treated carbon fibre reinforced ABS/PA6 composites", *Plast. Rubber Compos.*, vol. 39, no. 1, pp. 16–20, 2010.
- [2] S. Mohar, S. Rosenberger, J. Gulyás and B. Pukánszky, "Structure and impact resistance of short carbon fiber reinforced polyamide 6 composites" *J. Macromol. Sci. B*, vol. 38, no. 5-6, pp. 721–735, 1999.
- [3] A. Ahmad, D. H.Mohd, and I. Abdullah, "Mechanical properties of filled NR/LLDPE blends," *Irani. Polym. J.*, vol.13, no. 3, pp. 173–178, 2004.
- [4] A.W. Bosshard and H.P. Schlumpf, "Fillers and reinforcements in plastics additives 2/e", R. Gachter and H. Muller, Eds., Hanser Publishers, New York, 1987, pp 407-420.
- [5] R. Doufnoune and N. Haddaoui, "Effects of coupling agents on the tensile properties of calcium carbonate LDPE compatibilized with maleic anhydride-g-LDPE", *Int. Jour. Polym. Mat.*, vol. 57, pp. 295-318, 2008.
- [6] C. France, P.J. Hendra, W.F. Maddams and H.A. Willis, "Studies on thermoplastic elastomers blend on polyethylene elastomer blends", *Polymer*, vol. 28, no.5, p-710, 1987.
- [7] G. Jeanette, A. Carmen, I. Miren and D. Berenice, "Effect of coupling agents on mechanical and morphological behavior of the PP/HDPE blends with two different CaCO<sub>3</sub>", *Eur. Polym. J.*, vol. 38, pp. 2465-2475, 2002.
- [8] "Modern Plastics Handbook", C.A.Harper, Ed, McGraw-Hill, Inc., 2000, pp 5.1 – 5.125.
- [9] S.J. Monte, Titanate Coupling Agents, in "Functional Fillers for Plastics", Wiley-Vch Verlag GmbH & Co. KGaA, Weinheim, 2005.
- [10] S.J. Monte, "Ken-React Reference Manual—Titanate, Zirconate and Aluminate Coupling Agents", American Chemical Society, Washington DC, 1995.
- [11] I. Chodak, "Properties of crosslinked polyolefin-based materials", *Prog. Polym. Sci.*, vol. 20, no. 6, pp. 1185-1192, 1995.
- [12] P.Y. Teoh, M. Abdulbasset, "Effect of filler incorporation routes on mechanical properties of LDPE/NR/Silica composites", *Appl. Mech. Mater.*, vol. 679 pp 154-157, 2014.