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An investigation on chloroprene-compatible acrylonitrile butadiene rubber/high density polyethylene blends



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ABSTRACT

Blends of acrylonitrile butadiene rubber/high density polyethylene (NBR/HDPE) compatibilized by Chloroprene rubber (CR) were prepared. A fixed quantity of industrial waste such as marble waste (MW, 40 phr) was also included. The effect of the blend ratio and CR on cure characteristics, mechanical and swelling properties of MW-filled NBR/HDPE blends was investigated. The results showed that the MW-filled NBR/HDPE blends revealed an increase in tensile strength, tear, modulus, hardness and cross-link density for increasing weight ratio of HDPE. The minimum torque (M_L) and maximum torque (M_H) of blends increased with increasing weight ratio of HDPE while scorch time (t_{s2}) cure time (t_{c90}), compression set and abrasion loss of blends decreased with increasing weight ratio of HDPE. The blends also showed a continuous reduction in elongation at break as well as swelling coefficient with increasing HDPE amount in blends. MW filled blends based on CR provided the most encouraging balance values of overall properties.

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Introduction

Acrylonitrile-butadiene rubber (NBR) is well-known unsaturated copolymers for about five decays [1,2]. It has been used in many industrial required purposes as hoses, O-ring seals, insulation base product and other many packaging materials [3].

The main components of technically related NBR composed of 24–30 wt% of acrylonitrile and include some benefits in contrast to other elastomer like polymers, such as, good processability, resistance to oils as well as hydrocarbons, especially resistance to hydrocarbons and oils, and NBR has wide region of service temperature (from $-35\text{ }^{\circ}\text{C}$ up to $100\text{ }^{\circ}\text{C}$) [4,5]. High density polyethylene (HDPE) is a semi-crystalline with outstanding chemical resistance as well as simple processability. Acrylonitrile butadiene rubber (NBR) is a simply processable, tough, and flexible rubber.

The knowledge of thermoplastic elastomers (TPEs) from blends of NBR and HDPE has occurred as a valuable implement in tailoring polymers to require of end users. A various articles as well as books were published on this issue [6–10], and the theoretical studies performed generally on engineering

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thermoplastics covered the approaches for industrial applications Coran and Patel [11] accounted the technological compatibilization of PP/NBR and PE/NBR blends. They have reported the effect of addition of graft copolymer and dynamic vulcanization on mechanical properties of these blends. Recently, Liu et al. [12] studied the effectiveness of various basic functional groups in polypropylene as compatibilizers in a PP/NBR system using morphological and impact property measurements. Commonly, it is simple to blend of similar polarities and solubility of rubber and plastic to make a valuable thermoplastic elastomer, for example PP/ethylene-propylene–diene copolymer (EPDM), epoxidized natural rubber (ENR) with polyvinyl chloride (PVC), PVC/NBR) and nylon/NBR. However, it is obscured to fabricate a TPE via an elastomer and plastic composing different polarities as well as solubility.

This is due to large interfacial tension between these two polymers. This intricacy could be solved by the use of a compatibilizer to get better interfacial relation between two phases [13–16]. Accordingly, the objective of this research was to study cure characteristics, mechanical as well as swelling properties in the blends of NBR with HDPE which was chosen as blend constituents, because these NBR and HDPE are available in great amounts, possess outstanding properties and are paced among the most frequent polymers applied for the fabrication of commercially existing NBR/HDPE based blends.

The aim of the study expressed in this article was to compatibilize NBR with HDPE by using Chloroprene (CR) as compatibilizer that gets better compatibility of NBR/HDPE blends through interfacial chemical response. Cure time, scorch time as well as torque measurements, mechanical and swelling properties of these blends were also evaluated.

Experimental

Materials

Acrylonitrile–butadiene rubber (NBR 3310, acrylonitrile, 35 wt%) Chloroprene rubber (CR) as compatibilizer and HDPE used in this study is a commercial product from the local market of Karachi. The melt flow index (MFI) of HDPE is 5.64 g/10 (190 °C, 2.16 kg), and density is 0.953 g/cm³. Marble waste (MW) was arranged from marble industry.

The MW was desiccated in oven for 24 h at 80 °C, then mashed and passed through 37 µm sieve. The other constituents were Zinc oxide delivered by M/S S. Chemicals Industries Ltd. Pakistan. Stearic acid was purchased from Nimir (Pvt.) Ltd., Lahore, Mercaptobenzothiazole (MBT), Tetramethylthiuram disulfide (TMTD) as accelerators, 3-Dimethylbutyl-N-phenyl-p-phenylenediamine and sulfur were obtained from commercial market.

Preparation of NBR/HDPE blends

Locally existing NBR, HDPE and CR, as above, were purposed for compatibilized blends. The concentrations for NBR/HDPE blends are expressed in Table 1. The NBR/HDPE blends were fabricated via two-step mixing process. To prepare the blends, the NBR, HDPE and fillers were fed into a Brabender internal mixer (Brabender Instruments,

Table 1 The main compositions of studied MW filled NBR/HDPE.

Ingredients	Designation NBR:HDPE blends					
	100:00	85:15	70:30	55:45	40:60	25:75
NBR	100	85	70	55	40	25
HDPE	00	15	30	45	60	75
ZnO	5.00	5.00	5.00	5.00	5.00	5.00
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
TMTD	0.8	0.68	0.56	0.44	0.32	0.2
MBT	1.2	1.02	0.84	0.66	0.48	0.3
Antioxidant	1.00	1.00	1.00	1.00	1.00	1.00
Sulfur	2.00	1.7	1.4	1.1	0.8	0.5
Processing oil	4.0	4.0	4.0	4.0	4.0	4.0
MW	40	40	40	40	40	40
CR	5.00					

Germany), along with other ingredients at 160° C and 60 rpm for 10 min. The Brabender mixer, equipped with a pair of Banbury blades, has a total volume of 50 ml and it was filled to 70% of the total volume, as recommended by Brabender, for all sample preparations. After blending, the blended mixture was cooled down and sulfur was added on two-roll mill (16 × 33 cm) according to ASTM D 3182 (2001). Eventually, when mixing finished, the compounds were kept at room temperature for as minimum 24 h before their cure characteristics were measured. Test specimens were obtained by compression molding at 160° C and a pressure of 20 MPa for the respective optimum cure time (t₉₀) obtained from rheographs. After curing, the vulcanized sheet was taken out of the mold and immediately cooled under tap to stop further curing. All samples were cured at this temperature and stored in a cool dark place for 24 h.

Cure characteristics

The cure characteristics of blends were epitomized (ASTM method D 2084 at 160 °C) as in our prior research works [17,18].

Physical properties

Analysis of all physical mechanical properties (ASTM-412, ASTM D-624 Hardness according to ASTM D 2240) swelling and aging properties was conducted as ASTM D 573) of chloroprene compatibilized NBR/HDPE blend was performed as depicted before employing standard procedures [19–21].

Compression set (as per ASTM D 395-61) is generally empathized as percentage (%) of applied deformation, i.e., but can be stated as % of original thickness. The assessment of set is enormously effective quality control analysis as it is a comparatively easy test as well as the results is susceptible to state of cure.

Abrasion loss was also measured by abrasion check tester (Gibitre Italy), according to DIN 53516/ASTM D 5963, where all tests performed a room temperature.

Equilibrium swelling

The equilibrium swelling of blends was evaluated as in our former research works [22–24].

Thermal aging

All samples for thermal aging were put in an air circulating oven at 100 °C for 72 h, after that the aging properties were calculated. Property retention was then determined as the percentage of the value after aging divided by the value before aging.

Results and discussion

The total component of MW was explored by XRF spectrometer (Table 2). The components observing of MW illustrated the existence of Oxide of Calcium (68.6%), Oxide of Magnesium (22.13%) as core constituents closes with Silica (3.89%), Oxide of Aluminum (2.785%), Oxide of Iron (0.603%), Oxide of Chromium (0.24%) Oxide of Zinc (0.20%) in addition to Oxide of Titanium (0.549%). observably the component of MW show that compound of calcium as well as magnesium in huge quantity whereas silica, oxide of aluminum and iron as well in little.

Rheological characteristics

Cure/rheological characterization of rubber or their blends and composites traditionally have engaged qualitative and frequently measurements of the changes in flow-capability of reacting material systems during cure. Moving die rheometers have been common use in the rubber industry as a development and quality control tool. Typical torque response curves for NBR/HDPE blends are shown in Table 3. The results show the changes in elastic and viscous response of the material during the initial 20 min of cure.

It could be observed that the addition of HDPE to NBR, the minimum torque was increased, which caused to increase

in the maximum torque. This result is attributed to the fact that the rigidity of the NBR/HDPE blends increasing with the addition of HDPE, leading to the higher torque. Generally, the maximum torque can be taken as the maximum viscosity of the rubber compound.

The incorporation of HDPE in NBR, the scorch time (t_{s2}), and the optimum cure time (t_{c90}) are decreased, while the cure rate index (CRI) is increased. The scorch time and cure time decrease due to the constraint of the mobility of the NBR with the introduction of HDPE in the blends. The decrease in the curing time was pointed to the peak energy input and higher heat upsurge through compounding due to greater viscosity of the blends with addition of HDPE. Consequently, the cure rate of the blend increases with decreasing content of NBR. It includes more unsaturation side than HDPE, and usually produces higher crosslink side for three dimensional structure in NBR/HDPE systems.

The decrease in cure time is extremely beneficial because it increases the product rate. Table 2 demonstrates the influence of blend ratio as well as CR as compatibilizer on the maximum torque estimated from the rheographs. The compatibilizer loading was 5 phr. An increase in ML and MH values has been examined for all the specimens after the CR addition. The higher values of torques revealed by the mixes having higher content of HDPE can be attributed to increase the crystallinity in blends.

HDPE, being semi-crystalline, can urge restraint to the mobility of the molecular chains escorting to higher values of torque. The scorch time and cure time (t_{90}) do not show any significant change after addition of CR in the MW filled NBR/HDPE blends. However the CRI values increase with an increase in HDPE content for all blends due to the prominent decrease in cure time and scorch time. This obviously shows that NBR is the cure activating part in NBR/HDPE blends. The higher CRI values of NBR affluent mixes are due to having unsaturated part in NBR.

Mechanical properties

The variation in tensile strength with the addition of HDPE to NBR in the MW filled NBR/HDPE blends is shown in Fig. 1. It is observed that the tensile strength value increases by increasing HDPE content in the NBR/HDPE blends. The tensile strength of NBR/HDPE blends increases gradually with HDPE loading and an increase of 134% is observed at 75 pph loading. The stiffness of the blends usually increases due to the inclusion of the plastic segment (HDPE) in the rubber (NBR) matrix. The mechanical properties of blends are

Table 2 Quantitative analysis of marble sludge using WDX-ray fluorescence spectrometer.

Constituent	Weight %
CaO	68.6
MgO	22.13
SiO ₂	3.89
Al ₂ O ₃	2.785
Fe ₂ O ₃	0.603
Cr ₂ O ₃	0.24
ZnO	0.20
TiO	0.549

Table 3 Cure characteristics of examined MW filled NBR/HDPE blends.

Blend designation	Cure characteristic at 160 °C									
	ML, dN m		MH, dN m		t_{s2} , min		t_{90} , min		CRI, min ⁻¹	
	–	CR	–	CR	–	CR	–	CR	–	CR
100:00	1.87	1.94	6.13	6.32	1.98	1.90	10.3	9.87	11.9	12.5
85:15	2.05	2.16	6.27	6.61	1.81	1.74	10.1	9.71	12.1	12.5
70:30	2.32	2.48	6.62	7.07	1.67	1.56	9.56	8.94	12.7	13.5
55:45	2.47	2.65	7.33	7.86	1.53	1.42	9.00	8.36	13.4	14.4
40:60	2.61	2.79	7.85	8.40	1.45	1.34	8.24	7.63	14.7	16.0
25:75	2.93	3.17	9.05	9.81	1.33	1.25	7.53	7.10	16.1	17.1

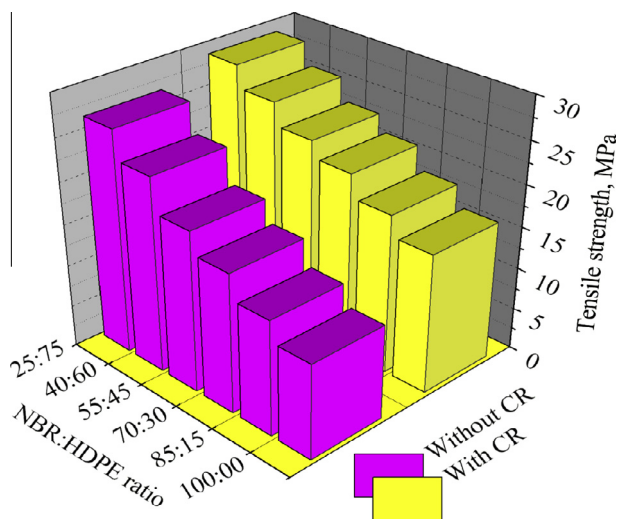


Fig. 1 Dependence of tensile strength of the blends on HDPE and CR.

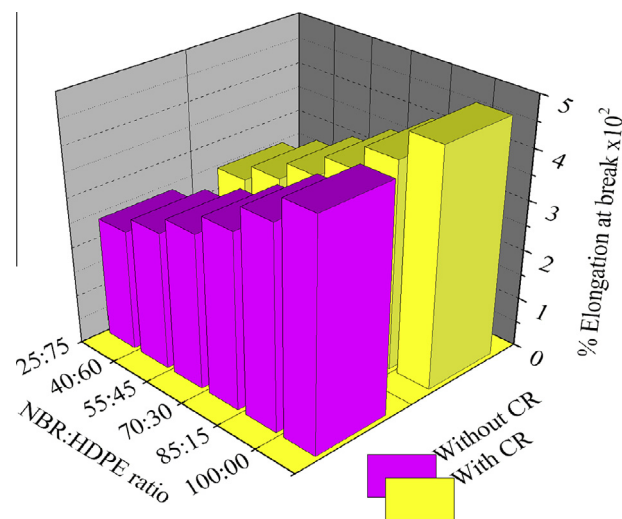


Fig. 3 Dependence of % elongation at break of the blends on HDPE and CR.

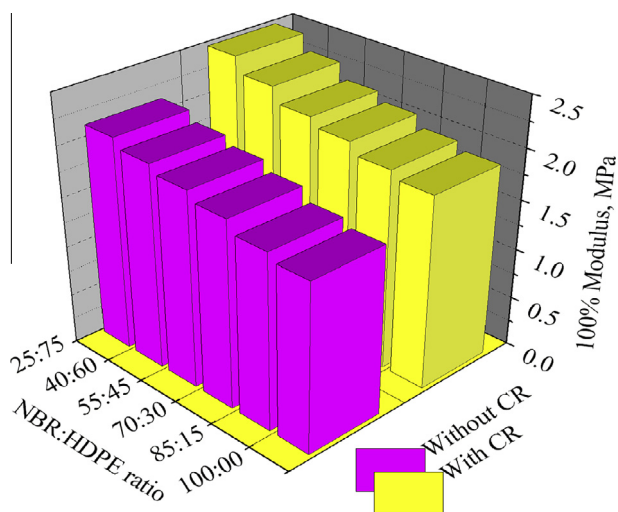


Fig. 2 Dependence of 100% modulus of the blends on HDPE and CR.

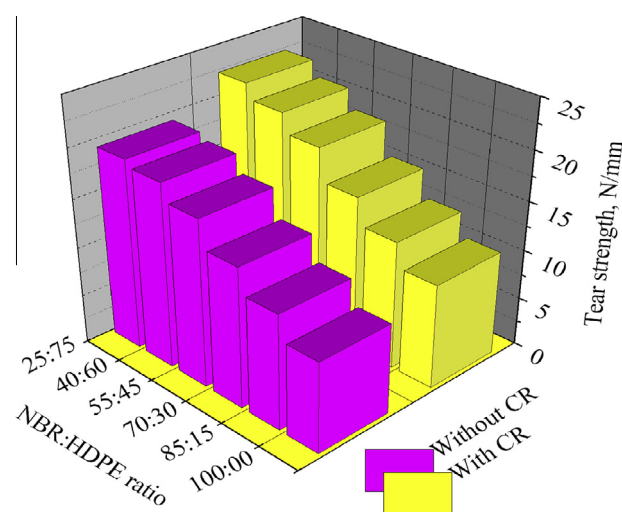


Fig. 4 Dependence of tear strength of the blends on HDPE and CR.

generally determined by the thermoplastic matrix, and the increasing HDPE loading in the NBR phase obviously decreases the rubber matrix content in the filled NBR/HDPE blends, leading to the increased mechanical properties.

Fig. 2 shows the modulus of the MW filled NBR/HDPE blends. It can be observed that the modulus of the blends increases with increasing HDPE content. At higher HDPE content, the elastomer phase remains as dispersed particles. The HDPE phase contributes to the higher modulus of NBR/HDPE blends. It was found that increasing the HDPE content in the blends results in decrease in elasticity. The effect of HDPE content on the elongation at break of MS filled NBR/HDPE blends is shown in Fig. 3. The considerable decrease in elongation at break is also seen to the increasing of HDPE content.

The variation in tear strength with the addition of HDPE to NBR is shown in Fig. 4. It is evidently seen that the assimilation of HDPE in NBR leads to increase in the tear strength.

This can be attributed to the presence of HDPE (hard fraction) in NBR. Conversely such hard fraction plays a role of filler and therefore, the eventual tear strength is increased. In other words, the toughness of rubber vulcanizates generally increases due to the assimilation of HDPE in the NBR [25]. The tensile strength, 100% modulus, and tear strength were enhanced due to the increased in hardness.

Shore hardness of the MW filled NBR/HDPE blends is shown in Fig. 5. It can be examined that increasing the amount of HDPE in MW filled NBR/HDPE blends showed an increasing trend. The increment of hardness was due to the dominant of HDPE, on the other hand such hard segments play just like filler and thus, the hardness of blends gradual increased. In other words, the rigidity of rubber vulcanizates generally increases due to the inclusion of HDPE in the NBR.

Compression set is assessing the capability of rubber and their blends to keep their elastic properties after extended

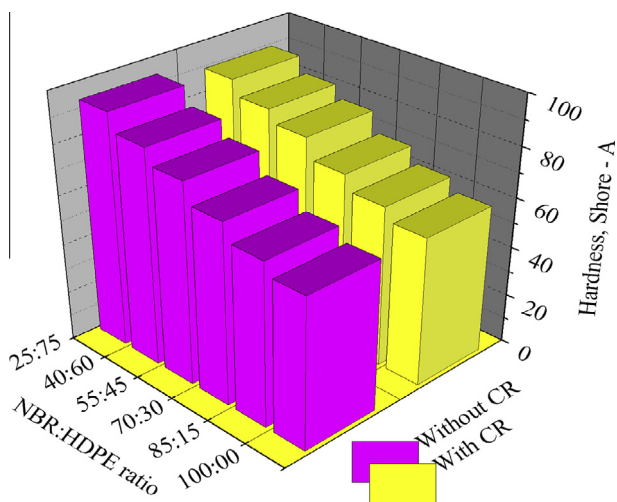


Fig. 5 Dependence of hardness of the blends on HDPE and CR.

compression at fixed strain under a precise set of state. The deprived performance of rubber compound in terms of compression set is attributed to un-crosslinked shackles that do not contribute to the permanent network and are able to relax during the compression stage. Compression set result of MW filled NBR and NBR/HDPE blends are present in Fig. 6. The results of NBR/HDPE blends show variation in their results. The compression set of NBR/HDPE blend is obviously decreased with increasing HDPE content in blend ratio.

When the HDPE content increases in blends from 15 to 75 wt%, the value of compression set decreases from 20.3% to 12.1%, which is 59.6% lower than that for NBR. It is due to the effective network chain or crosslink in the deformed state. The lower values of blends indicate the best material for the compression state. No distinguished effect found with having 5 pph CR incorporation NBR/HDPE blends.

The abrasion loss (Gibitre Italy) of NBR/HDPE blends with different amounts of HDPE with, and without CR is shown in Fig. 7. The results disclose that the abrasion loss of NBR/HDPE blend is noticeably decreased with increasing

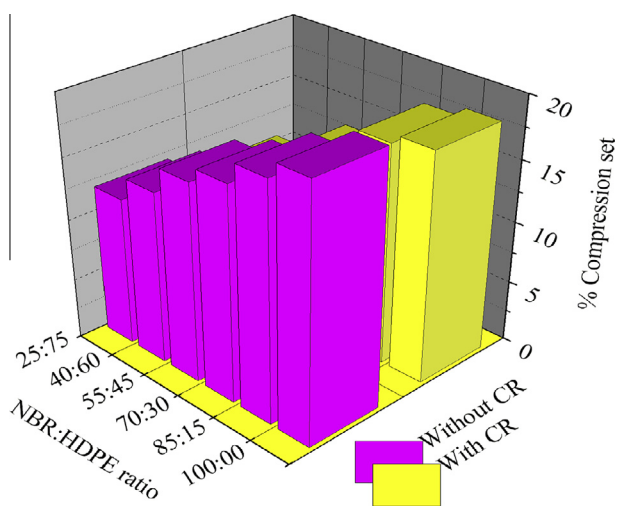


Fig. 6 Dependence of % compression set of the blends on HDPE and CR.

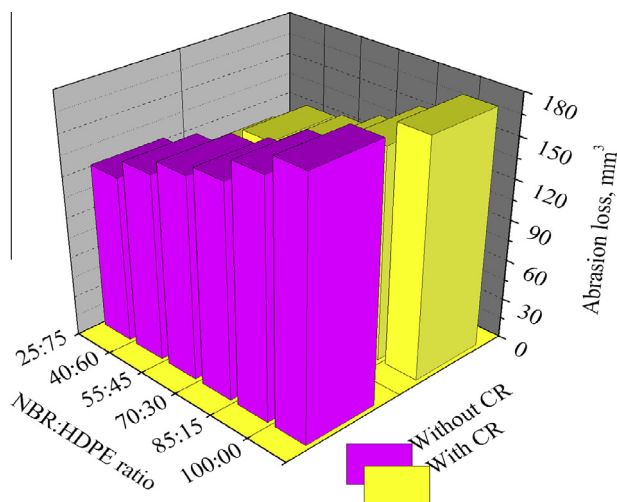


Fig. 7 Dependence of abrasion loss of the blends on HDPE and CR.

HDPE content in blend ratio. When the HDPE increases from 15 to 75 wt%, the value of abrasion loss decreases from 186 to 123 mm^3 , which is 66.13% lower than that for MW, filled NBR. It can be recognized that the HDPE can enhance the abrasion resistance of NBR greatly. It is well known that the abrasion resistance of HDPE is outstanding. The HDPE blended with NBR preserves the outstanding abrasion resistance. The abrasion resistance improvement of NBR after incorporation of HDPE is frequently because of the excellent abrasion resistance of the HDPE. Compared with those of the NBR/HDPE blend, the abrasion loss of blends with 5 pph CR incorporation was improved indicating the strong influence on the improvement of interface interaction.

Chloroprene rubber of 5 phr is used here for compatibilizing NBR/HDPE blends. Figs. 1–7 also show the influence of CR content on different properties and it increases significantly with the addition of CR amount. It is clear that the highly polar CR molecules may share electrons to some extent with NBR or HDPE, which pulls on and weakens the C–H and C–Cl bonds, and improves the overall properties of the blends. The interaction between chlorines of CR and the CN groups in NBR can delay the detachment of the labile chlorine atoms.

Swelling studies

The swelling characteristic of the NBR/HDPE blends in toluene is shown in Table 4. The percentage of toluene uptake was decreased after addition of HDPE to NBR rubber. This can be attributed to the certainty that the existence of HDPE in the NBR/HDPE restricts the penetration of solvent into the intermolecular gaps and consequently decreases the swelling percentage [26].

It was noticed that, the toluene immersion of NBR/HDPE blends compounds, the solvent molecules must enter in the NBR phase and depart more or less around the HDPE phase. The HDPE phase could escort to very circuitous path for toluene molecules going through the NBR/HDPE blend.

The equilibrium swelling of NBR/HDPE blends in toluene was analyzed to estimate the extent of cross-linking. The cross-link density values are also given in Table 4. One can see, as the equilibrium swelling values decrease, the degree of crosslink

Table 4 Swelling parameters of investigated MW filled NBR/HDPE in toluene.

Blend designation	Swelling parameters			
	Equilibrium swelling, %		Crosslink density $\times 10^{-4}$ mole/cc	
	Without CR	With CR	Without CR	With CR
100:00	138	135	0.16	0.18
85:15	130	124	3.52	3.64
70:30	123	116	3.84	4.08
55:45	115	108	4.22	4.53
40:60	110	103	4.72	4.97
25:75	103	92	5.06	5.56

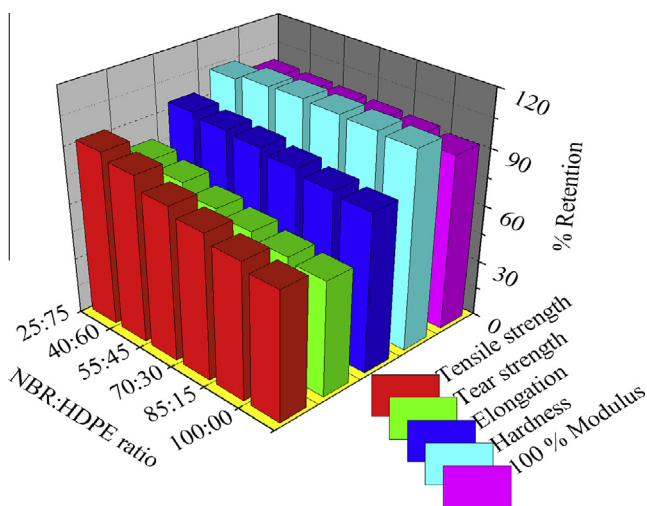
increase. It is also clear that the accumulation of HDPE in place of NBR obviously decreases the values of equilibrium swelling. To investigate the effect of HDPE on the crosslink density of the NBR/HDPE vulcanizates, consider the HDPE as additional filler.

Properties of MW filled NBR/HDPE blends after thermal aging

Fig. 8 shows the percentage retention of aged tensile strength, tear strength and elongation at break of the MW filled NBR/HDPE blends increase by increasing the HDPE content. However, the hardness slightly decreases and no notable alter in the modulus. Thus, the thermal stability of MW filled NBR/HDPE blend is improved with the addition of HDPE.

Influence of CR on the properties of MW filled NBR/HDPE Blends

Table 3, illustrates the cure characteristic behavior of MW filled NBR/HDPE blends compatibilized by CR. As shown in Table 3 with the addition of CR, the scotch time, cure time and cure rate index slightly increased while the minimum and maximum torque is decreased. All results of cure characteristics show the representative elastomeric nature of being soft and hard. Compared with CR compatibilized NBR/HDPE blends, the NBR/HDPE blends had higher scotch time, cure time and cure rate index values.

**Fig. 8** Dependence of % retention of the blends on HDPE and CR.

Figs. 1–7 illustrate influence of CR on the Mechanical Properties of MW filled NBR/HDPE Blends. The results of all properties such as tensile as well as tear strength, elongation at break, modulus, hardness, compression set and abrasion loss of the NBR/HDPE compatibilized with CR are improved due to the CR has fine compatibility with NBR and HDPE because the polarity of CR is less than NBR but greater than HDPE. During vulcanization, the CR mainly dispersed in the NBR matrix resulting in considerably improved the interface interaction between NBR and HDPE, leading to the enhancing the mechanical properties such as tensile strength, tear strength, elongation at break, however, the CR additions had slight influence on the cure characteristics, modulus, compression set, abrasion loss and flame propagation rate. Compared with those of the NBR/HDPE blend, the tensile strength, elongation at break and tear strength of NBR/HDPE blends with 5 pph CR containing were improved, indicating the strong influence of CR incorporation on the improvement of interface interaction % retention after aging of the NBR/HDPE and CR compatibilized NBR/HDPE blends is shown in Fig. 8. With CR additions had small effect on percentage retention values compared with without compatibilizer NBR/HDPE blend. Compatibilization of NBR/HDPE also influence on swelling properties.

Conclusions

5 pph of CR compatibilized NBR/HDPE blends have been successfully prepared incorporated various composition with fixed amount of MW. The role of CR as compatibilizer in the NBR/HDPE blend system has been investigated. HDPE obviously increases the mechanical properties of NBR blends, and the incorporation of CR further improves the mechanical properties of MW filled NBR/HDPE blends. The CR combined with the probable conception resulted improved the compatibility and interfacial adhesion between NBR and HDPE phases, which contributed to the enhanced cure characteristics, mechanical and swelling properties.

Conflict of Interest

The author has declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

References

- [1] Klinkender CR. Handbook of speciality elastomers. CRC Press; 2008, p. 289–403.
- [2] George J, Varguhese KT, Thomas S. Dynamically vulcanized thermoplastic elastomer blends of polyethylene and nitrile rubber. *Polymer* 2000;41(4):1507–17.
- [3] Feldman D, Barbalata A. Synthetic polymers technology, properties, applications. London: Chapman & Hall; 1996, p. 53–155.
- [4] Khalaf AI, Yehia AA, Ismail MN, El-Sabbagh H. High performance oil resistant rubber. *Op J Org Polym Mater* 2012;2(4):88–93.
- [5] El-Nemr FK. Effect of different curing systems on the mechanical and physical–chemical properties of acrylonitrile butadiene rubber vulcanisates. *Mater Des* 2011;32(6):3361–9.
- [6] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press; 1979.
- [7] Bucknall CB. Toughened plastics. London: Applied Science Publishers; 1977.
- [8] Paul DR, Bucknall CB. Polymer blends: formulation. New York: Wiley; 2000.
- [9] Zhen XZ, Chen CH, Gao XW, Kim JK, Xin ZX. A study on the compatibility and physical properties of chlorinated polyethylene rubber/nitrile rubber blends. *J Appl Polym Sci* 2011;120(2):1180–5.
- [10] Walsh DJ, Higgins JS, Maconnachie A. Polymer blends and mixtures. Dordrecht: Martinus Nijhoff Publishers; 1985.
- [11] Coran AY, Patel R. Rubber-thermoplastic compositions. Part VIII. Nitrile rubber Polyolefin blends with technological compatibilization. *Rubb Chem Technol* 1983;56(5):1045–60.
- [12] Liu NC, Xie HQ, Baker WE. Comparison of the effectiveness of different basic functional groups for the reactive compatibilization of polymer blends. *Polymer* 1993;34(22):4680–7.
- [13] Mathew M, Thomas S. Compatibilization of heterogeneous NBR/PS blends by the addition of styrene acrylonitrile copolymer: effect on morphology and mechanical properties. *Polymer* 2003;44(4):1295–307.
- [14] Marcia G, Oliveira B, Soares G. Mercapto-modified copolymers in polymer blends. III. The effect of functionalized ethylene–propylene–diene rubber (EPDM) on curing and mechanical properties of NBR/EPDM blends. *J Appl Polym Sci* 2001;82(1):38–52.
- [15] Shaltout AN. Effect of electron beam irradiation and ethylene vinyl acetate copolymer on the properties of NBR/HDPE blends. *J Macromol Sci Part A* 2009;47(2):160–5.
- [16] Chuanhui X, Liming F, Chen Y. *In situ reactive compatibilized polypropylene/nitrile butadiene rubber blends by zinc dimethacrylate: preparation, structure, and properties.* *Polym Eng Sci* 2014;54(10):2321–31.
- [17] Ahmed K, Nizami SS, Raza NZ, Mahmood K, Kamaluddin S. An assessment of rice husk ash modified, marble sludge loaded natural rubber hybrid composites. *J Mater Environ Sci* 2013;4(2):205–16.
- [18] Ahmed K, Nizami SS, Raza NZ. Characteristics of natural rubber hybrid composites based on marble sludge/carbon black and marble sludge/rice husk derived silica. *J Ind Eng Chem* 2013;19(4):1169–76.
- [19] Ahmed K. Hybrid composites prepared from Industrial waste: mechanical and swelling behavior. *J Adv Res* 2015;6(2): 225–32.
- [20] Ahmed K, Nizami SS, Raza NZ, Habib F. The effect of silica on the properties of marble sludge filled hybrid natural rubber composites. *J King Saud Univ (Sci)* 2013;25(2):331–9.
- [21] Ahmed K. Properties of natural rubber composite incorporated with industrial waste/carbon black hybrid filler. *Chem Lett* 2013;42(5):1105–7.
- [22] Ahmed K, Nizami SS, Raza NZ, Mahmood K. Characterization of mechanical properties of marble sludge/natural rubber composites. *J Chem Soc Pak* 2012;33(6):1468–76.
- [23] Ahmed K, Nizami SS, Raza NZ, Mahmood K. Effect of micro sized marble sludge on physical properties of natural rubber composites. *Chem Ind Chem Eng Quart* 2013;19(2) :281–93.
- [24] Ahmed K, Nizami SS, Raza NZ. Reinforcement of natural rubber hybrid composites based on marble sludge/Silica and marble sludge/rice husk derived silica. *J Adv Res* 2014;5(2):165–73.
- [25] Utracki LA. Polymer alloys and blends; thermodynamics and rheology. Munich: Hanser; 1989.
- [26] Setua DK, Soman C, Bhowmick AK, Mathur GN. Oil resistant thermoplastic elastomers of nitrile rubber and high density polyethylene blends. *Polym Eng Sci* 2008;42(1):10–8.