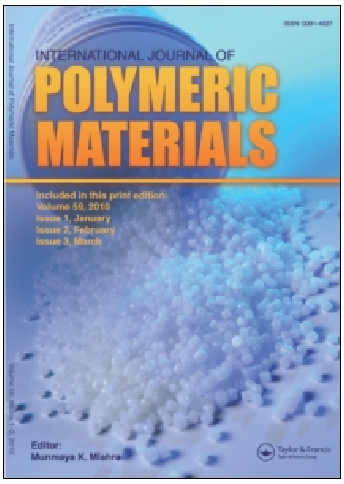

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A Study on Grafting of Natural Rubber and Nitrile Rubber on Thermoplastic Low Density Polyethylene Using Maleic Anhydride and Acrylic Acid

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LDPE/NR and LDPE/NBR blends were prepared by conventional mixing on two-roll mill. Modified blends were prepared by grafting (reactive blending). Grafting was carried out using acrylic acid and maleic anhydride. Compression-molded sheets were prepared out of the compounds and properties were evaluated. Mechanical properties like tensile strength, ultimate modulus, elongation at break, and hardness were determined. Effect of heat aging and effect of chemicals were estimated. The blends were characterized using FTIR spectrum. The electrical properties, abrasion resistance, solubility tests, and flammability tests for the compounds were also conducted. In all experiments results are found to be much higher for grafted compounds compared to ungrafted blends.

Keywords: grafting, polymer blends, LDPE, NR, NBR, rubber plastics blends, reactive blending

INTRODUCTION

Polymer blending is mostly carried out by mechanical mixing of the molten polymers [1–2]. During mechanical mixing of molten polymer, mixing energy and shear flow can have major effects on domain size and structure. This will affect properties of blends [1]. Simple mechanical blends of incompatible polymers do not usually show the desired

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properties. This is because of macroscopic phase separation and weak connectivity at the phase boundary [3–4]. In a blend, less viscous phase will tend to be the continuous phase or matrix and more viscous phase will tend to form dispersed domains. The simplest shape of the dispersed domain is spherical, which is trying to minimize its surface energy [5]. Generally increasing attraction between phases tends to decrease the size of the spheres and increase the practical compatibility [6–8]. Compatible blends posses a broad transition region. This will modulates property gradient and has ability to resist stress. This is referred as interphase [9–11]. Therefore, reactive blending of the polymer components has been actively studied. Block or graft copolymers are formed in-situ during mixing process, which act as effective compatibilizer [12–13]. In reactive blending connectivity of polymer components can be improved by covalent bond formation [14–16]. Control over phase morphology can be achieved by chemical or polymerization reactions. In reactive blending reaction occurs between the functionalized components and the unfunctionalized components in the polymers. Grafting [12,17–18] can be done by melt blending; two-roll mill, banbary mixer, brabender plasticoder and twin-screw extruder [19–21].

EXPERIMENTAL

Materials Used

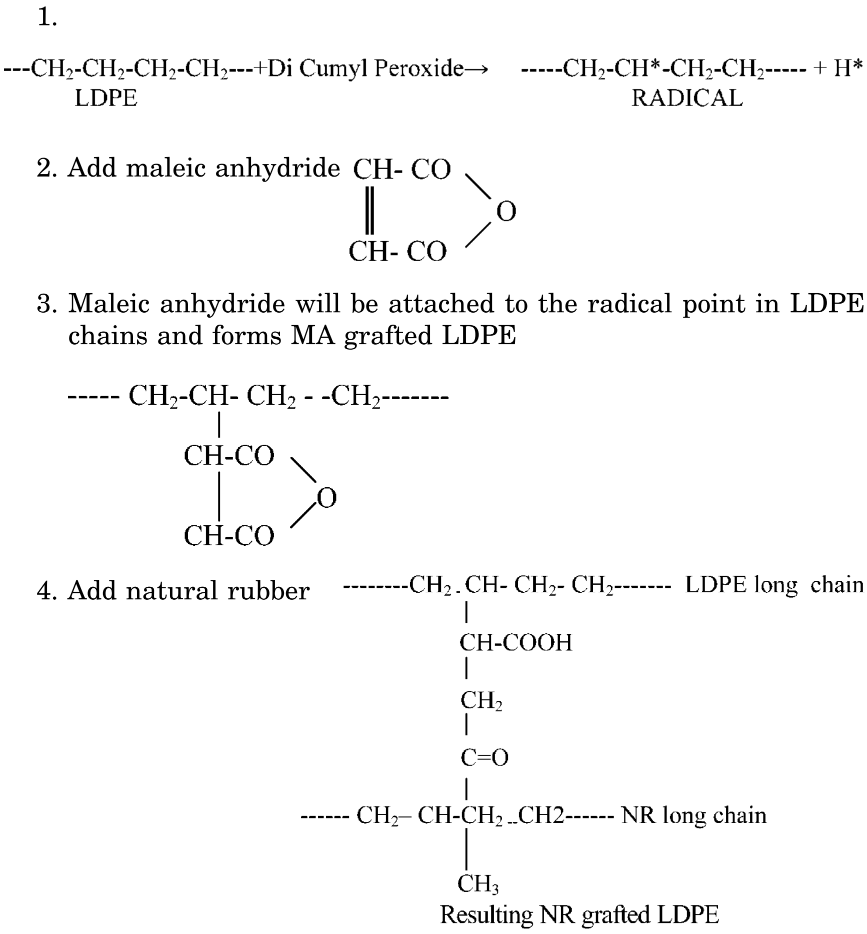
Natural rubber (NR), ISNR 5 ML (1 + 4) @ 100°C 82 was supplied by Rubber Research Institute, Kottayam. Nitrile rubber (NBR), ML (1 + 4) @ 100°C 45 was supplied by Apar Polymers, Gujarat, Low density polyethylene (LDPE) 16 MA 400 was supplied by Reliance Industries, Baroda. Dicumyl peroxide (DCP), acrylic acid (AA), maleic anhydride (MA), and so on are laboratory grade.

Mixing Process

Compounds were prepared as per the formulation given in Table 1. Mixing was done on laboratory two-roll mill (6 × 12 inch). Temperature of rear roll was kept at 120°C and front roll was at 70°C. A close nip gap was selected and granules were added. When LDPE became softer, DCP was added as an initiator. This is for the generation of free radicals, which is to produce free radicals sites on LDPE chains. Acrylic acid or maleic anhydride was added at this stage, which was joined with LDPE chains. Temperature was increased to 140°C and mixing continued for 10 min. The mixture was taken out from the rollers and cooled. For the reaction mechanism, see Scheme 1.

TABLE 1 Formulation of Compounds

Ingrediants, Phr	A1	B1	C1	D1
Low density polyethylene	80	80	80	80
NR	20	20		
Nitrile rubber			20	20
Dicumyl peroxide	0.2	0.2	0.2	0.2
Acrylic acid	4		4	
Maleic anhydride		4		4



1.

---CH_2-CH_2-CH_2-CH_2---+Di Cumyl Peroxide→ -----CH_2-CH^*-CH_2-CH_2----- + H^*

LDPE RADICAL

2. Add maleic anhydride

3. Maleic anhydride will be attached to the radical point in LDPE chains and forms MA grafted LDPE

4. Add natural rubber

Similar reactions are occurring in AA grafted LDPE.
Nitrile rubber is also attached to LDPE using both acrylic acid and maleic anhydride.

SCHEME 1 Reaction mechanism.

Molding Technique

Compression-molded sheets were prepared out of the grafted compounds. The press platens with the mold were preheated to 120°C. When temperature attained compounds were kept inside the mold with the help of aluminum foils to prevent sticking to the molds. Proper degassing was given and platens closed using a pressure of 50 kg/cm^2. Pressure was applied for 10 min and pressure released, the mold opened, cooled to room temperature, and sheets were taken out. The aluminum foil was removed before testing the specimens.

Testing Methods

a. *Tensile testing*: Specimens were punched out from the compression-molded sheets and tested on a universal testing machine (UTM) as per ASTM D 638 with a testing speed of 50 mm/min. Tensile strength, ultimate modulus, and percentage elongation were calculated.
b. *Aging*: Tensile specimens were kept in an air oven at 70°C for 16 h as per ASTM D 794 and after aging the specimens were taken out, cooled to room temperature, and tested for the strength on a universal testing machine as before.
c. *Volume and surface resistivity*: Electrical resistance of the samples was measured using a mega ohmmeter as per ASTM D 257. Volume resistivity is the resistance through the cross-section of the sample. Surface resistivity is the resistance through the surface of the sample.
d. *Chemical resistance*: Immersion tests were performed as per ASTM D 543 in different mediums like toluene, HCl, NaOH, and caster oil. Specimens were kept immersed for 24 h and any physical changes like swelling, color change, loss of gloss, crazing, bubbling cloudiness, and tackiness were observed.
e. *Hardness*: Hardness of the specimens was estimated using durometer with shore A and shore D methods as per the standard ASTM D 785.
f. *Abrasion resistance*: Abrasion loss was measured using a Tabor abrader with 500 gm load and for 1,000 cycles as per ASTM D 1044.
g. *Flammability test*: A rectangular specimen of 50 × 5 cm was taken and a 20 cm mark was given on it. The specimen was kept over a Bunsen burner and allowed to catch fire. Time taken for reaching the flame up to the mark was noted. This test was performed according to ASTM D 635.
h. *Solubility test*: Solubility was checked in organic solvents and water.

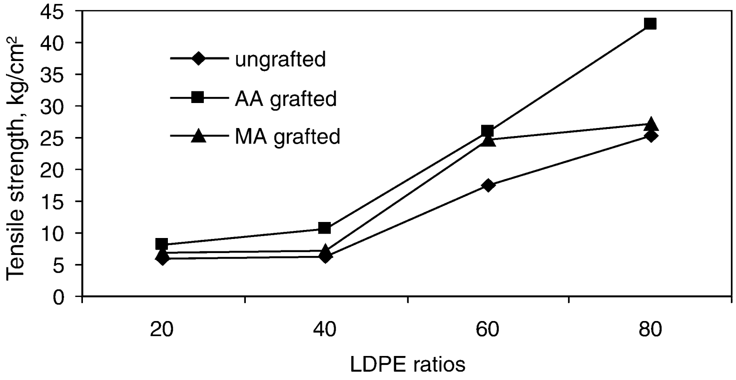


FIGURE 1 Tensile strength of LDPE/NR blends.

i. *FTIR*: The grafted compounds were characterized using FTIR spectroscopy to estimate the extend of grafting. FTIR of ungrafted blend of NBR/LDPE and MA grafted NBR/LDPE were taken on a Perkin Elmer spectrum GXFTIR, with a scan range 15600 cm^{-1} to 30 cm^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows tensile strength values of ungrafted AA and MA grafted natural rubber with respect to LDPE ratios. As the amount of LDPE increases the tensile strength increases in all types of compounds. Among them acrylic acid grafted compounds give higher strength than other types of grafting. Similar types of phenomenon are observed in NBR grafted compounds also shown in Figure 2. The

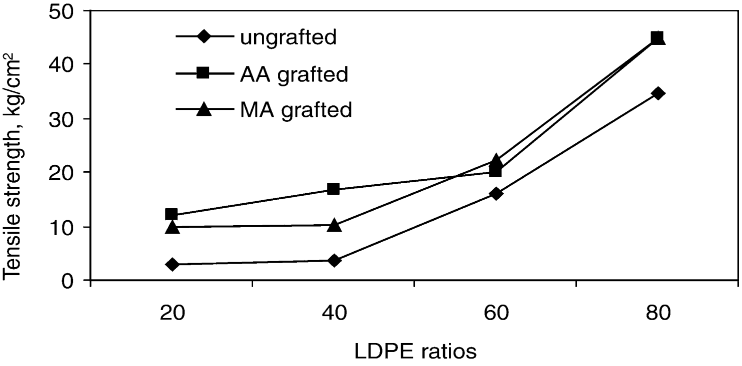


FIGURE 2 Tensile strength of LDPE/NBR blends.

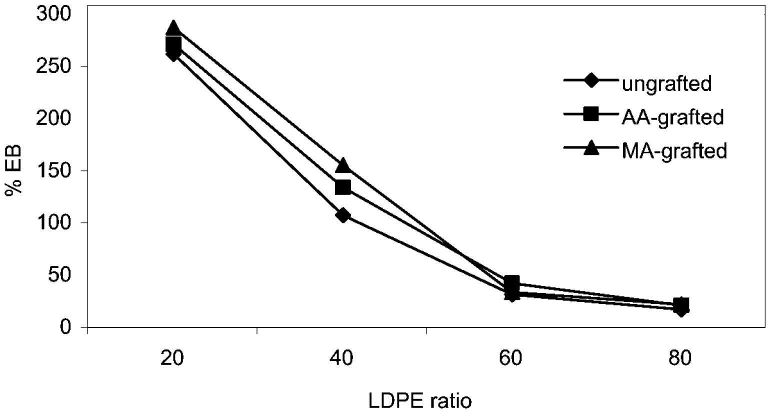


FIGURE 3 Elongation at break of LDPE/NR blends.

tensile strength of pure LDPE is much higher than elastomers like NR and NBR. So, as LDPE ratios increase tensile strength increases due to the increase of total stiffness of the compounds. In ungrafted compounds the tensile strength is found to be lower, which again confirms that due to grafting strength of the compounds increase.

Figure 3 shows percentage elongation of grafted compounds with respect to LDPE ratios. In all cases of ungrafted, AA grafted, and MA grafted compounds the percentage elongation of the compounds are found to be decreasing as LDPE increases. This is due to the flexibility of elastomers in the grafted compounds. The phenomenon was found to be similar in NBR grafted compounds shown in Figure 4. The ungrafted compounds shows lower percentage elongation

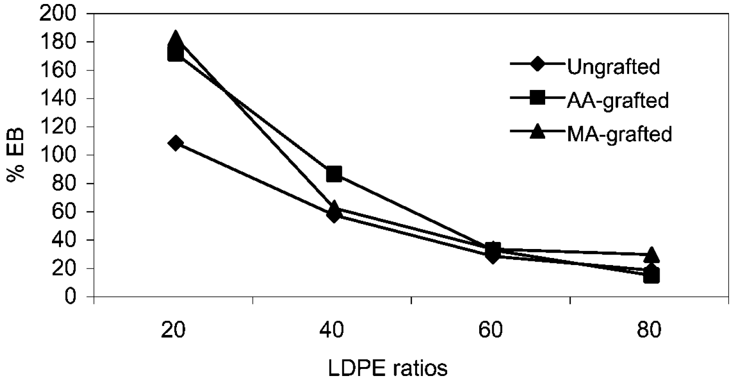


FIGURE 4 Elongation at break of LDPE/NBR blends.

compared to grafted compounds. Grafted compounds posses better flexibility due to the bulky side chains, which impart higher elongation compared to ungrafted compounds.

Figure 5 shows tensile strength of LDPE/NR compounds after aging. The strength of compounds was found to be decreasing after aging, due to the higher amount of degradation in elastomer phase of the compounds. Ungrafted compounds show around 20% reduction in strength after aging. In grafted compounds the reduction is less, in between 1–5%. This shows that as grafting is given to the compounds the stability of the compounds improves.

Figure 6 shows tensile strength of LDPE/NBR compounds after aging. The strength of compounds was found to be decreasing after aging. It is due to the higher amount of degradation in elastomer phase of the compounds. Ungrafted compounds show around 50% reduction in strength after aging. In both types of grafted compounds the reduction is less, in between 1–5%, similar to the previous case.

Figure 7 shows the effect of aging on percent elongation of ungrafted and AA and MA grafted NR compounds. As LDPE ratio increases elongation decreases due to lower elongation properties of LDPE. Due to aging a small amount of degradation has occurred and results are less than the original values.

Figure 8 shows the effect of aging on percent elongation of ungrafted and AA and MA grafted NBR compounds. As LDPE ratio increases elongation decreases due to lower elongation properties of LDPE as similar to the previous blends. Due to aging a small amount of degradation occurred and results are less than the original values.

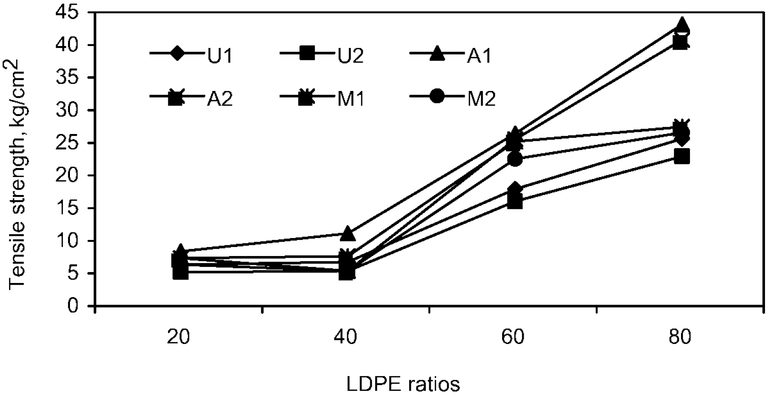


FIGURE 5 Aged tensile strength of LDPE/NR blends. U—ungrafted, A—acrylic, and M—maleic grafted; 1 indicates before and 2 indicates after aging.

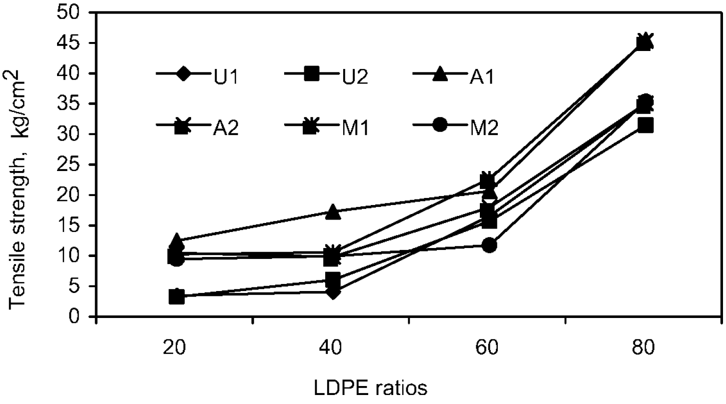


FIGURE 6 Aged tensile strength of LDPE/NBR blends. U—ungrafted, A—acrylic, and M—maleic grafted; 1 indicates before and 2 indicates after aging.

Table 2 shows the result obtained from durometer hardness tests. Hardness of ungrafted compounds is comparatively less. Due to grafting the stiffness of the compounds are increased. Similar effect is observed in both NR and NBR compounds.

Surface Resistivity and Volume Resistivity Tests

Surface resistivity (Rs) and volume resistivity (Rv) of the compounds are nearly equal. Surface resistivity, $Rs = 1.4 \times 10^{11}\ \Omega$ and volume

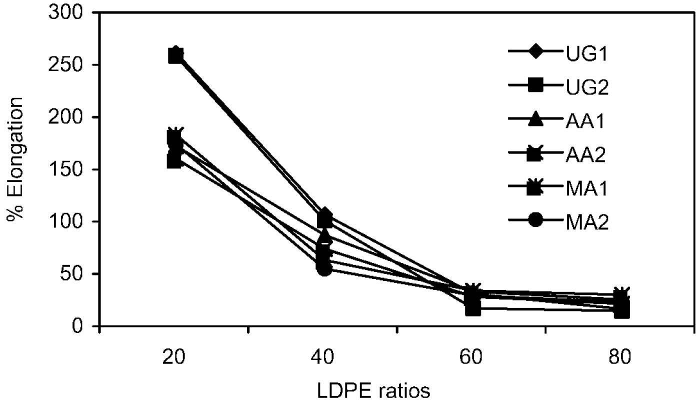


FIGURE 7 Aged elongation at break of LDPE/NR blends. U—ungrafted, AA—acrylic, and MA—maleic grafted; 1 indicates before and 2 indicates after aging.

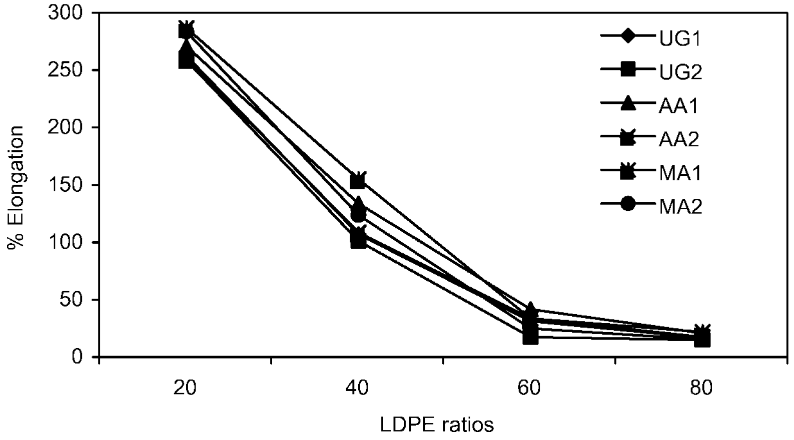


FIGURE 8 Aged elongation at break of LDPE/NBR blends. U—ungrafted, AA—acrylic, and MA—maleic grafted; 1 indicates before and 2 indicates after aging.

resistivity, Rv = 1.6×10^{12} Ω. These compounds are very good electrical insulators.

Abrasion Resistance

The abrasion loss was found to be too negligible for all compounds.

Flammability Test

Time taken by ungrafted blends of LDPE/NR and LDPE/NBR was between 15 to 25 s. At the same time grafted blends of LDPE/NR and LDPE/NBR were taken 35 to 40 s.

TABLE 2 Durometer Hardness of the Compounds (Shore A)

LDPE/NBR	LDPE/NR	Ungrafted	AA grafted	MA grafted
	80/20	90	97	95
	60/40	82	90	85
	40/60	65	70	69
	20/80	55	57	58
80/20		95	97	98
60/40		85	86	87
40/60		65	70	72
20/80		55	58	56

Chemical Resistance/Immersion Tests

Grafted compounds are much more resistant to the medium (like toluene, HCl, NaOH, and caster oil) and only a slight amount of swelling was observed. Ungrafted compounds show color change and crazing by the chemicals. Due to grafting the compounds became stiffer and solvents were unable to penetrate to the structure. In oil immersion no change was observed to the compounds.

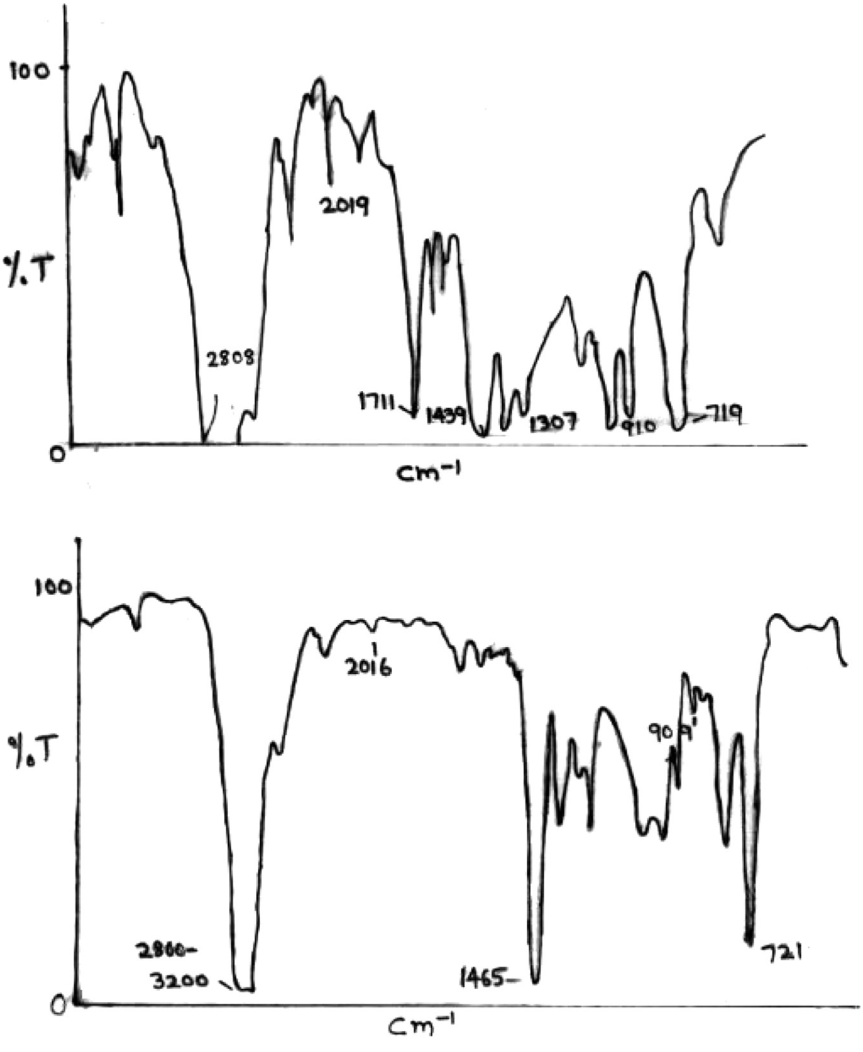


FIGURE 9 The FTIR spectrum of ungrafted LDPE/NBR blends.

Solubility Tests

All grafted compounds were insoluble in organic solvents and also in water. Ungrafted compounds softened due to swelling in organic solvents. This is due to the increased stability of the bonds after grafting.

FTIR Spectrum Analysis

Figure 9 shows the FTIR spectrum of the ungrafted LDPE/NBR compound. Figure 10 shows FTIR spectrum of maleic anhydride grafted LDPE/NBR compound. On comparing the 2 diagrams it is clear that the peaks at 2016 cm^{-1} is wider in ungrafted than grafted. This peak is for cyanide functional group in NBR. In the grafted compound this peak is smaller, which indicates that those sites are used for grafting. Similarly, in a grafted compound a peak observed at 1303 cm^{-1} of $-C{=}N$ or $-NO_2$ stretching frequency, confirmed the reaction had taken place through the cyanide group. A peak at 1077 cm^{-1}, which is attributed to the $-C-O$ stretching frequency. Maleic anhydride on radical formation gives carbonyl functional groups. As all the sites may not be used for grafting unreacted carbonyl groups are present in the spectrum. The peak between 2800–3200 cm^{-1}, 1430–1470 cm^{-1}, 910–920 cm^{-1}, and 719–720 cm^{-1} are peaks for C–H bending and

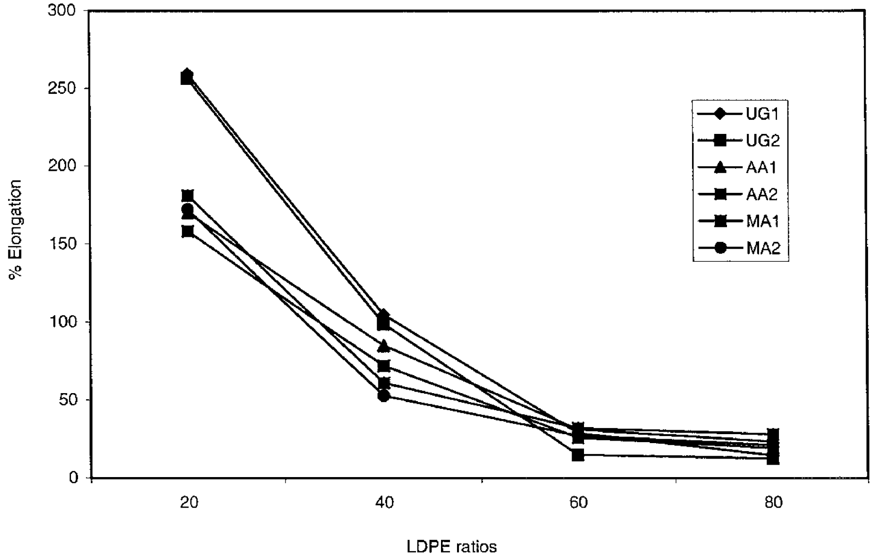


FIGURE 10 The maleic anhydride grafted LDPE/NBR blends.

stretching. All these peaks became narrow in grafted compounds, confirming that those sites are occupied for grafting.

CONCLUSIONS

Grafting of natural rubber and nitrile rubber on low density polyethylene was performed successfully using acrylic acid and maleic anhydride. FTIR spectral analysis gives confirmation to grafting reactions. The grafted compounds were found to be superior compared to ungrafted compounds in mechanical properties, chemical resistance aging, and so on. In case of natural rubber–grafted compounds the strengths were better than nitrile rubber, but in aging nitrile rubber is superior. Natural rubber possesses low thermal resistance compared to all synthetic rubbers. Results conclude that for blending of LDPE with natural rubber/nitrile rubber grafting is the proper rout that gives promising results.

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