Impacts of Radiation and Leaching on Physico-Chemical Properties of Natural Rubber and Its Rheological Studies

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Abstract: Field latex were collected and centrifuged to remove the bark and non-rubber proteineous compounds. The rubber latex was irradiated at variable radiation doses from Co-60 gamma radiation source and rubber films were made by evaporation. The mechanical properties of the films were investigated before and after leaching with different leaching agents such as distilled water, ethanol and methanol. The 12 kGy radiation doses provide the improved properties of the films. It is observed that leaching enhanced the mechanical properties and also found that water acts as a better leaching agent compared to alcohols. The rheology of the natural rubber latex was also studied. The Natural rubber latex (NRL) showed the non-Newtonian Bingham plastic nature and the viscosity decreased with increasing the shear stress. The yield stress was 0.07 dynes/cm^2.

Key words: Co-60 gamma radiation, rheology, Natural rubber latex (NRL), non-Newtonian Bingham plastic.

Introduction

The use of synthetic polymers is increasing day by day. But they have many detrimental effects in the form of cytotoxicity. Natural polymeric materials e.g. natural rubber which is non-toxic and biodegradable has been used. Natural rubber latex is obtained from the tree *Hevea Brasíliansis* of the *Euphorblaceace familly*. Generally, on average the field latex contains about 70% water, which required to be removed to concentrate the field latex for wide range of applications. Concentrated NRL has found applications in manufacture of dipped goods, adhesive/binders, thread, carpet/rug, molded foams etc. Of these, the dipped goods which include hand gloves, balloons, condoms, bladders, catheters/tubes etc. account for about 60% of NRL uses [1].

Vulcanization is a process where the formation of a molecular network is constructed by a chemical bond among independent chain molecules of elastomeric materials. Thus the vulcanization is intermolecular reactions which increase the retractive force and reduce the amount of permanent deformation remaining after removal of the deformation force. Many studies [2] have been carried out on vulcanization of NRL as well as synthetic polymers and many reactions are assumed. German and Auerbach [3] stated that the essential feature of all vulcanizing reactions is that they bring about a cross-linking or

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inter connection of the long flexible rubber molecules into a network structure. Jackson and Hole [4] stated that vulcanization primarily is a cross-linking process and introduced a report as the vulcanization of rubber by irradiation with cobalt - 60. Mahfuza *et al.* [5] investigated that the effect of heating and leaching on the properties of radiation vulcanized NRL. Role of leaching on the properties of blend rubber films between irradiated and non-irradiated have been investigated [6]. Properties of radiated and non-radiated NRL with PVA blends by radiation vulcanization have been reported [7,8]. Viscosity of natural rubber solution at very low rates of shear was studied by Morton [9]. Tiu *et al.* [10] reported on the yielding behavior of viscoelastic materials. The impact of radiation and the effects of leaching on the physico-chemical properties of natural rubber films and the rheological behaviour of NRL are investigated in the present study.

Experimental

NRL was collected from Satgaon Rubber Estate, Sylhet, Bangladesh and collected latex was preserved with 20-25 mL/L of 25% aqueous ammonia solution (GPR - BDH England) immediately to prevent coagulation. The centrifuge method using Laboratory scale centrifuge machine SPL-100, Saito, Separator Ltd, Japan was used to concentrate the field latex.

Preparation of irradiated latex

The centrifuged latex containing 60% total solid content (TSC) was diluted to 50 % by adding required amount of 1.5% aqueous ammonia solution. 5 phr n-butylacryl amide (n-BA) from Kanto Chemical Co.Inc., Japan, was used as a radiation vulcanization accelerator (RVA). The RVA was added to the diluted latex dropwise and stirrerd continuously for one hour. Then the latex was irradiated at different radiation doses such as 0, 3, 5, 8, 10, 12, 15 and 20 kGy at the dose rate of 5 kGy per hour at room temperature from cobalt-60 source in the Institute of Food and Radiation Biology, Savar, Dhaka.

Preparation of films

The irradiated latex was cast on raised glass plates for making rubber film. The films were air dried until transparent. They were leached with different solvents such as distilled water, ethanol (BDH England) and methanol (BDH England) for 24 hours at room temperature and then again air dried until transparent. Then the films were heated at $70\ ^{0}C$ for one hour.

Measurement of properties of films

Tensile strength of the films were measured by Instron 1101 testing machine, England, using dumbbell shaped test pieces of the blend films according to the ISO method[11]. The permanent set, swelling ratio, cross-linking density, and elongation were measured according to the ISO methods [11]. Benzene (GPR, BDH England) was used as a solvent in the swelling ratio measurement.

Measurement of stress and viscosity of NRL

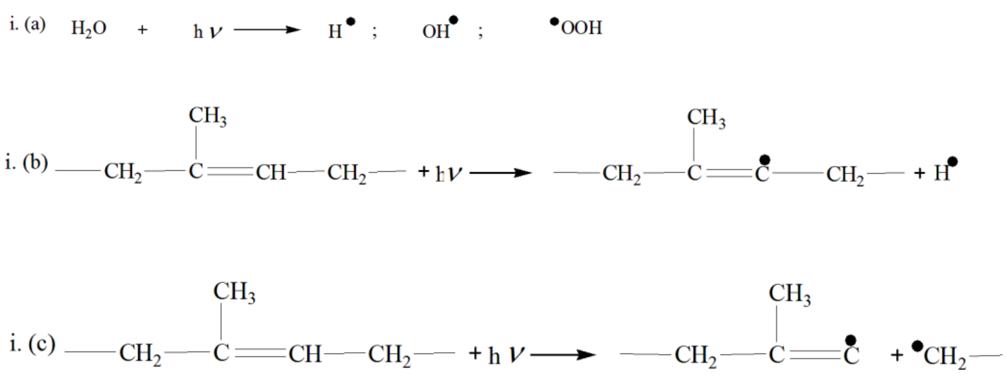
A rotational viscometer with co-axial cylinder system equipped with a stationary outer and a mobile inner cylinder HAAKE Rotovisco RV20 was used to measure the shear stress and viscosity of NRL. MV_1 sensor system combined to Rotovisco basic unit as a torque sensor. The shear stress was measured varying shear rate at 25^0 C and 1% speed. The radius of inner cylinder rotor was 20.04 mm and the radius of outter cylinder was 21.00 mm. The height of the cylinder was 60 mm. The maximum stress 322 Pa and the maximum shear rate 2700 s^{-1} were capable to measure by the instrument. Viscosity of the sample was calculated by the ratio of stress and rate.

Results and Discussion

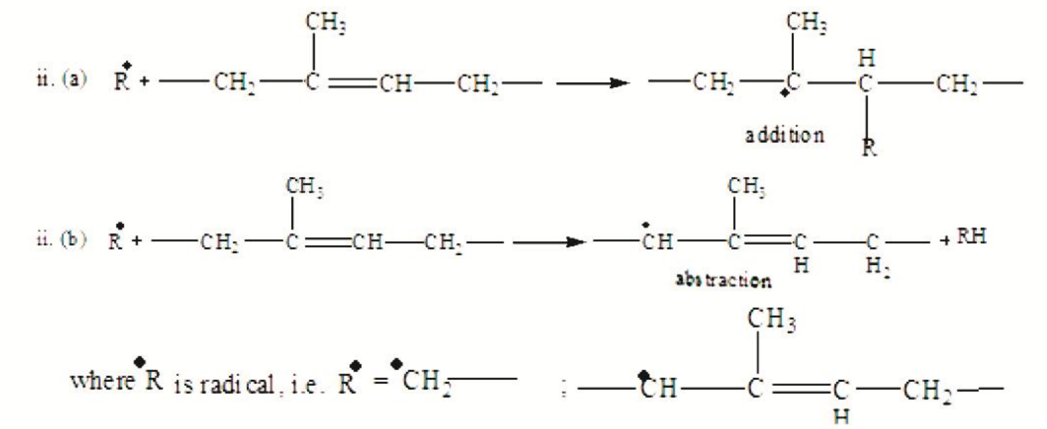
The permanent set values of the leached films and unleached films at different irradiation doses are shown in figure 1. From this figure, it is observed that the permanent set values decreased with increase in the irradiation doses in all types of leached and unleached films. Furthermore, it is also observed that the trends of changes in permanent set at higher doses are small. The decreasing tendencies of permanent set with increasing irradiation dose indicate enhanced cross-linking in the latex during radiation vulcanization. It is also observed that leaching decreased the permanent set and water showed the good effect as a leaching agent compared to alcohols.

The swelling ratios of the rubber latex films prepared under different irradiation doses in the presence of sensitizer and after leaching with different solvents were investigated and the results are shown in figure 2. From this figure, it is observed that the highest value of swelling ratio are found at 3 kGy irradiation and the swelling ratio decreased with increasing radiation doses. After 12 kGy radiations dose the films showed the lowest values of swelling ratio. Furthermore, irradiated films with 10-15 kGy showed almost similar values of swelling ratios. The following reactions in the radiation vulcanization of NRL were proposed [12,13]. The polymer with high cross-link did not swell easily.

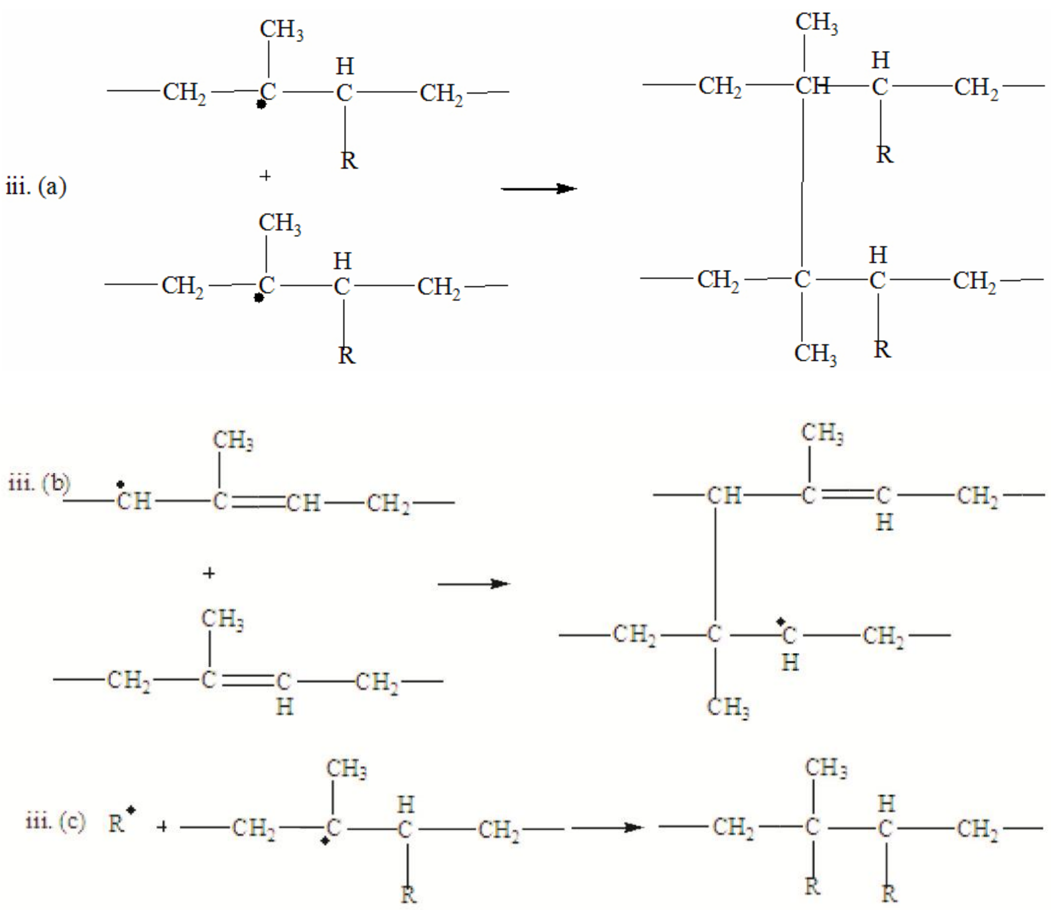
1. Formation of free radicals:



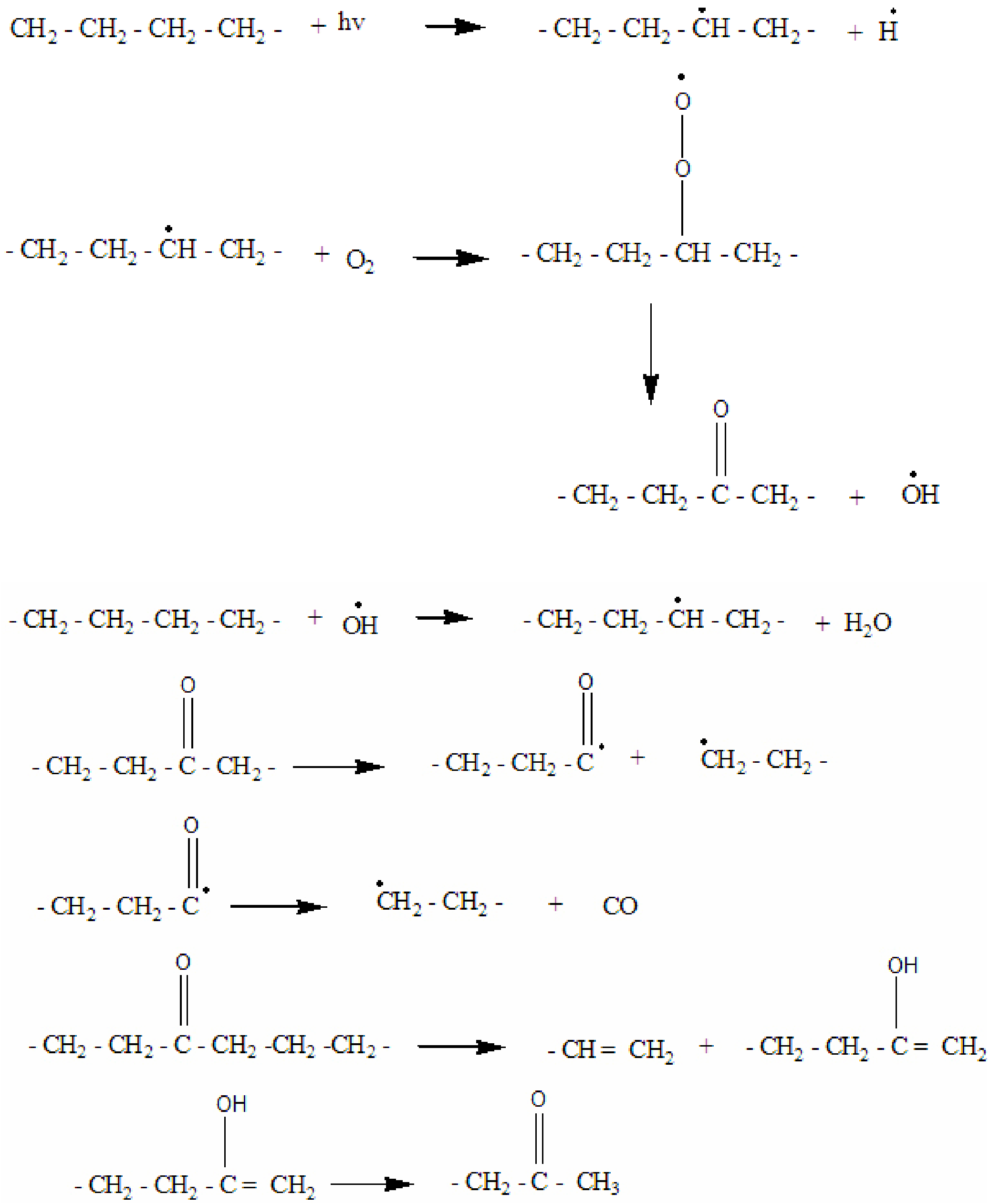
2. Attack on polyisoprene chain by various radicals R^*



3. The polymer radiacls may recombine or attack a double bond of another polymer molecule to produce cross-links.



The cross-linking density of the rubber latex films of different irradiation doses are shown in figure 3. From this figure, it is observed that the cross-linking density increased with increasing the radiation doses. The highest cross-linking density is found at 12 kGy radiation dose. After that radiation doses, the cross-linking density decreased which indicates depolymerization or chain scissors of the polymers. The following reactions of degradation in the presence of irradiation were proposed [14].



The results of gel contents of the rubber latex films are shown in figure 4. It is observed that the gel content increased with the increase of radiation doses. The increase of gel content indicates the formation of three dimensional networks during radiation vulcanization. The films leached with water showed higher gel content compared to those leached with alcohols. It may be concluded that the proteinous materials are removed during leaching. More polar and high di-electric solvent exhibited good behavior in the removal process.

The tensile strength of the rubber latex films at different irradiation doses are shown in figure 5. The tensile strength increased with the increase of radiation doses and at 12 kGy radiation dose the highest tensile strength is found. The rate of increase of tensile strength is higher at lower doses. It may be concluded that the fast vulcanization reactions occurred at lower doses and then the rate decreased.

The large or bulky groups or radicals are present in the reaction media at the moment of higher radiation doses and the presence of large groups increase the steric hindrance in the reaction. Thus the reaction rate decreased. The leached films showed the higher value of tensile strength compared to unleached ones and water leached films showed the highest value of tensile strength as compared to others. It may be concluded that the proteinous materials free films are capable to prevent breaking during applying the stress.

The shear stress and shear rate of NRL at 25^0 C for MV_1 system and 1% speed are measured at different shear rate. The shear stresses are plotted against the shear rate which is shown in figure 7. From this figure, it is observed that the shear stress vs shear rate curve does not pass through the origin but rather intersects the shear stress axis at a particular point referred to as the yield value. The yield value is a critical stress below which no flow occurred. It is also observed that the shear stress increased with increased shear rate. Thus the solution behaves as the non-Newtonian Bingham plastic nature [15].

The equation describing plastic is $U = (t - f)/D$, where f is the yield stress or intersect on the shear stress axis in dynes/cm^2. A Bingham body does not begin to flow until the shear stress corresponding to the yield value is exceeded. At stress below the yield value, the substance acts as an elastic material and above the yield stress material resembles a Newtonian system.

The viscosity vs shear rate plot of the NRL at 25^0 C for MV_1 system and 1% speed is shown in figure 8. The viscosity decreased with the increase of shear rate. Viscosity decreased drastically at a very small shear rate and with further increase of shear rate it reached a limiting value. Substances which show such property is called shear thinning behavior. Observing the flow curve, having definite yield value and the viscosity curve showing shear thinning property it may be concluded that NRL possess non-Newtonian plastic types of flow behavior. The flow curve can be represented by the power law equation $T = KD^n$. The slope of logD vs logT plot gives n. If the value of n is one, the liquid will be corresponding to Newtonian fluid.

NRL is a colloidal suspension of polyisoprene molecules. At rest, the polymer segments in the latex may be entangled and the looping molecular chains have random movement due to Brownian motion. With increasing shear rate, the chain can be oriented parallel to the driving force. Molecular alignments allow particles or molecules to slip past each other more easily and this shows up as reduced viscosity. When the orientation of the molecule reaches an optimum level and then the further shear thinning is not possible.

Conclusion

The permanent set, swell ratios, cross-linking density, gel content, tensile strength and elongation at break of the NRL films were investigated with variable radiation doses. The radiation increased the cross-linking density, gel content and tensile strength and decreased the permanent set, swelling ratios and elongation at break. The results indicated the increase of cross -linking during vulcanization. Cross-linking takes place up to 12 kGy radiation dose and beyond radiation dose, depolymerization occurred. The leaching effect was also studied using different solvents. Water as solvent was the most suitable leaching agent compared to alcohols. The NRL behaves as a non-Newtonian Bingham plastic. The viscosity drastically decreased with shear rate due to the decrease of molecular disorderliness in the dispersion media by applied force. The yield stress for NRL at 25^0 C and 1% speed in MV_1 system was 0.07 dynes/cm^2.

Aknowledgement

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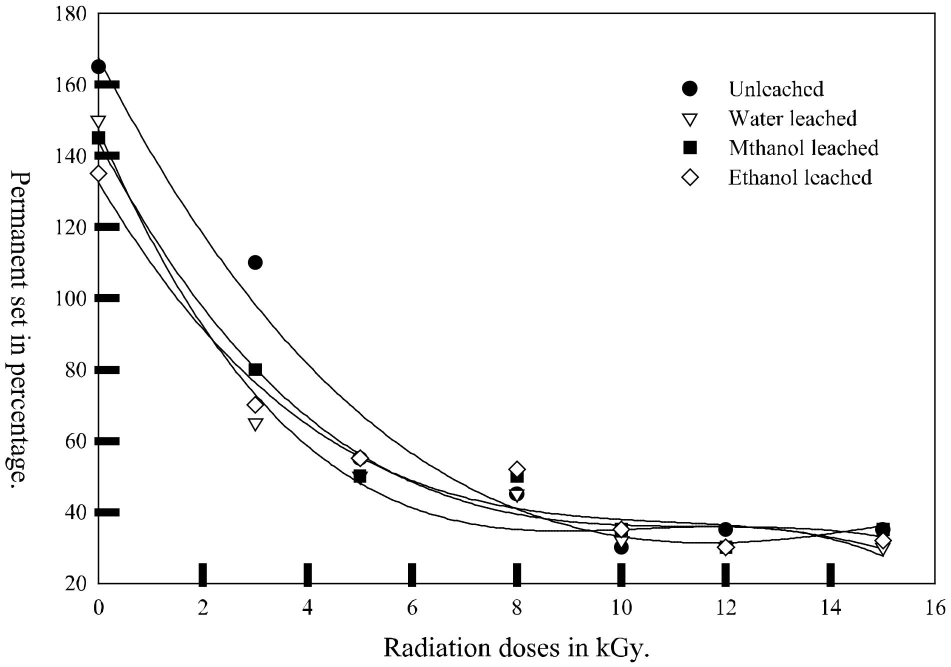

***Fig. 1:** Effect of radiation doses and leaching on permanent set of NRL films*

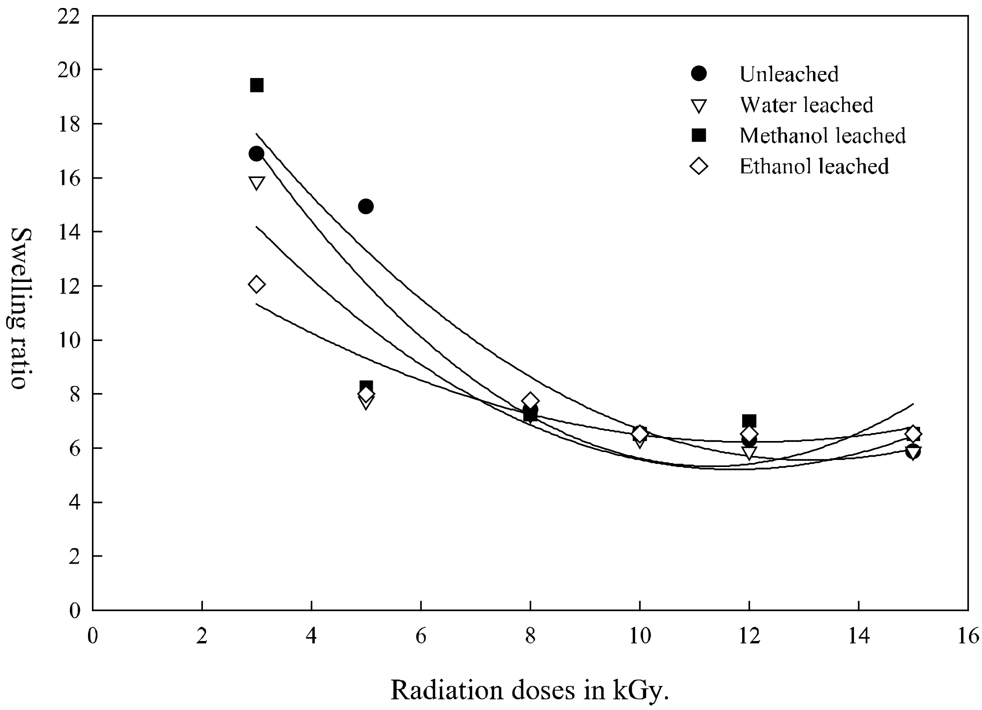

***Fig. 2:** Effect of radiation doses and leaching on swelling ratio of nrl films.*

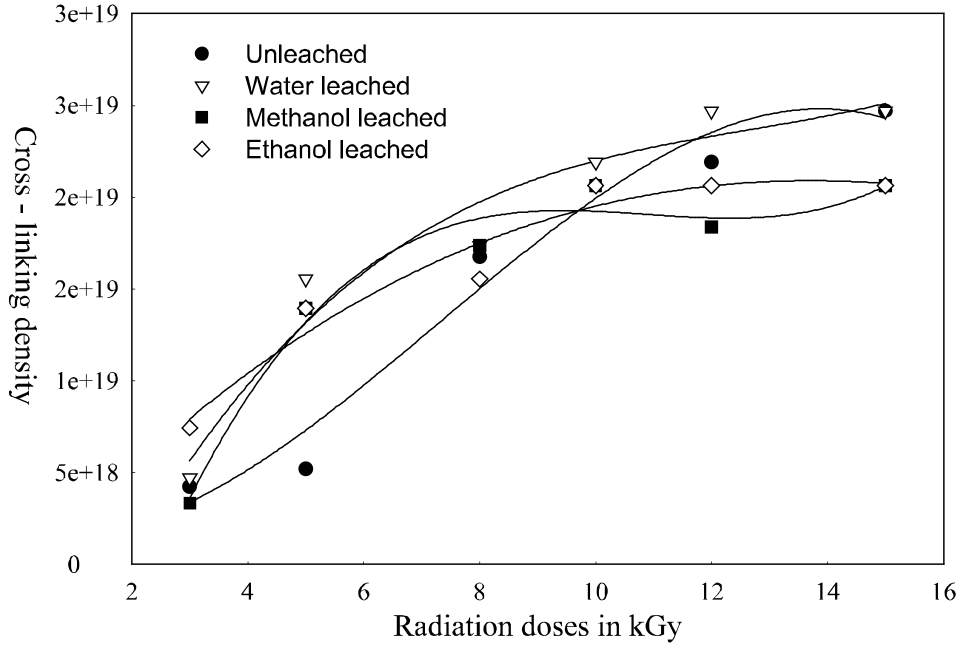

Fig. 3: *Effect of radiation doses and leaching on cross - linking density of nrl films.*

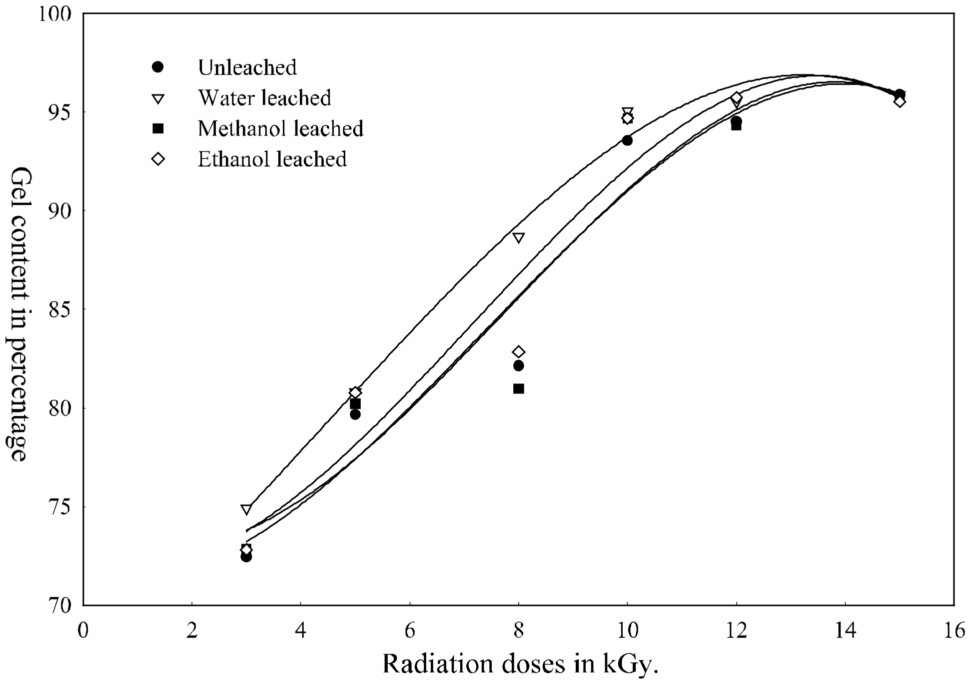

Fig. 4: *Effect of radiation doses and leaching on the gel contents of NRL films.*

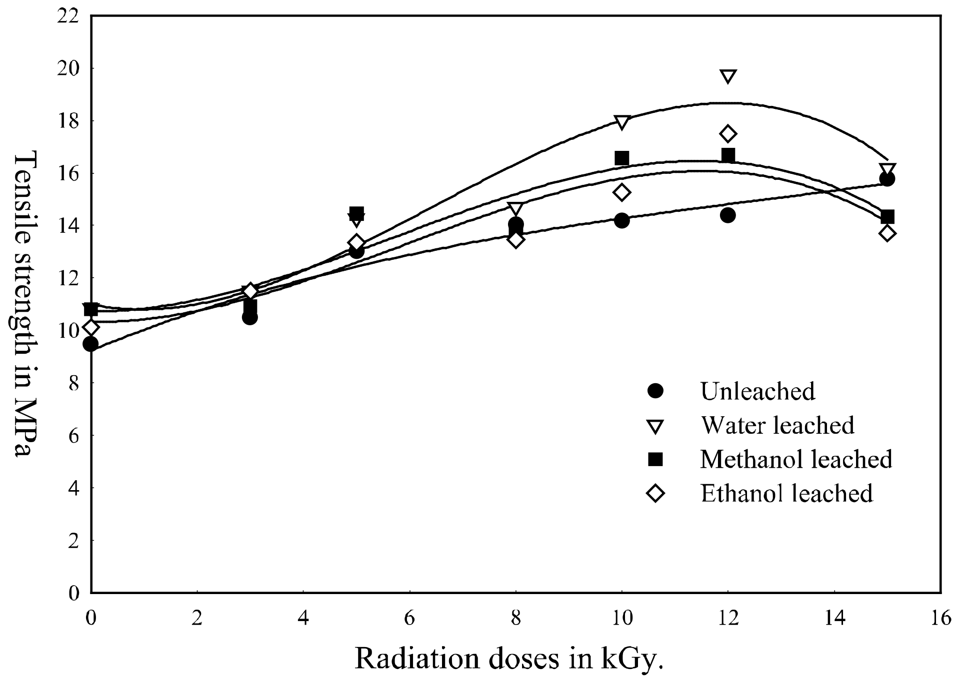

Fig. 5: *Effect of radiation doses and leaching on tensile strength of NRL films.*

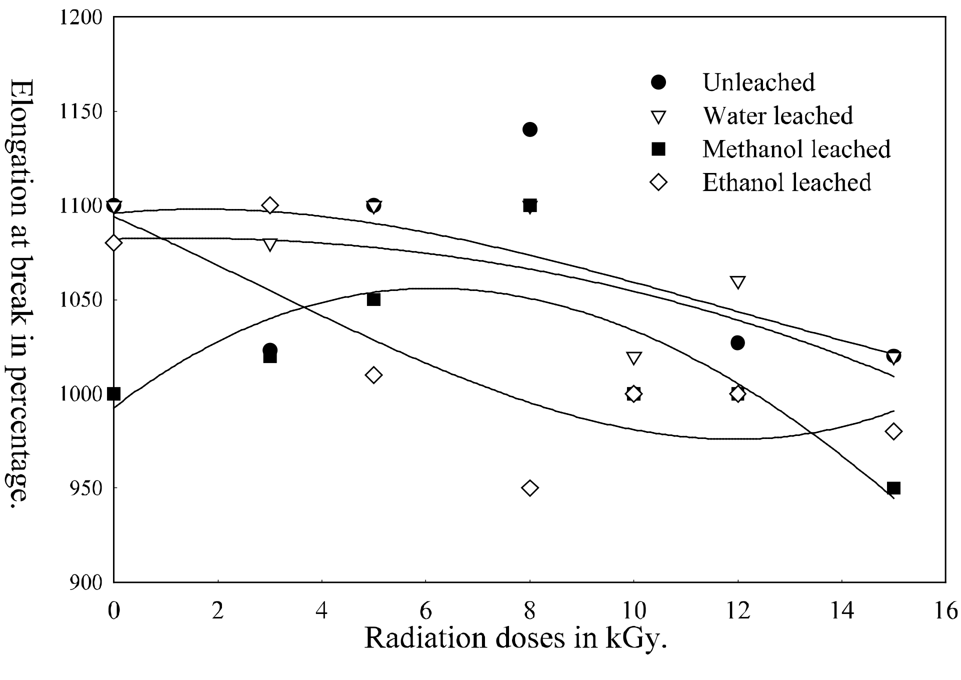

Fig. 6: *Effect of radiation doses and leaching on elongation at break of NRL films.*

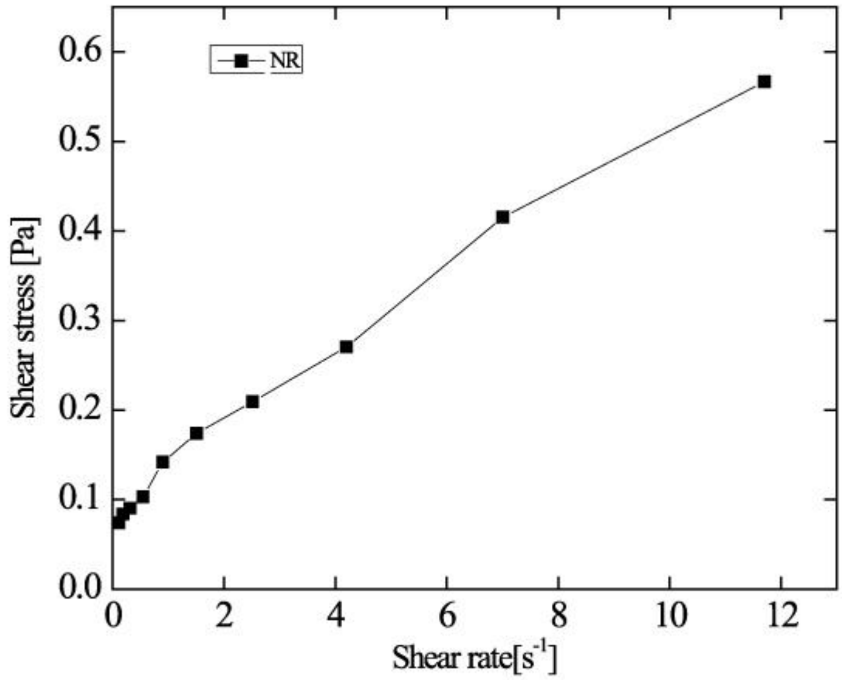

Fig. 7: *Shear stress vs shear rate plot for NRL at 1% speed, 25^0C and MV_1 system.*

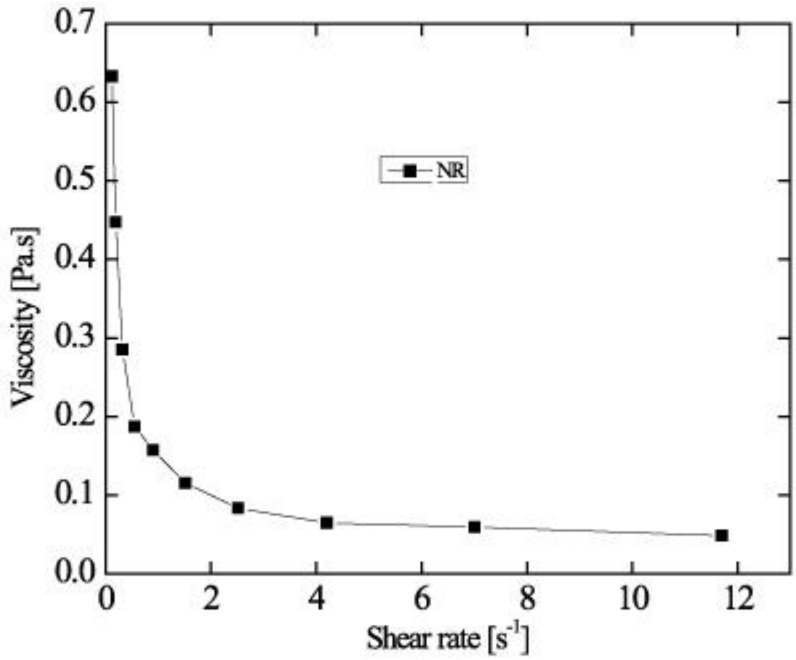

Fig. 8: *Viscosity vs shear rate plot for NRL at 1% speed, 25^0C and MV_1 system.*