Chapter IV

SUMMARY AND CONCLUSION.

Natural rubber (NR) is one of the cheapest and easily available raw materials for the industrialist. Consequently more than 50,000 rubber products are being manufactured and used currently. This number, of course, includes the synthetic rubber products also. Many more products are being added to the list day by day. Those based on natural rubber, because of their eco-friendly nature, are being preferred over the synthetic rubber products. Further the usefulness of natural rubber has been expanded in recent times by chemical modifications. One such process is block copolymerisation. This has yielded a new category of materials with unique combination of properties provided there is different blocks in the macromolecular structure. For example, combination of soft elastomeric blocks of natural rubber and hard thermoplastic blocks of polyurethane leads to a macromolecule with unique set of properties. The present work aims at the characterisation of these block copolymers with a view to study specifically the effect of NR block length on their properties.
The block copolymers were prepared by following the methods reported earlier in which short chain of NCO–terminated natural rubber (HTNR) were coupled with polyurethane blocks. NR segments of varying size \[ \bar{M}_v = 8500, 14200 \text{ and } 22400 \] were used in the copolymerisation. Each of these NR samples was made to combine separately with polyurethane blocks derived from five different diols and toluene diisocyanate giving rise to a number of series of block copolymers. Each series thus consists of specific NR segments and a given diol with the hard to soft segment ratio varied over a wide range to get individual block copolymers within the series. The chain extender diols used were ethylene glycol (EG), propylene glycol (PG), 1,3–butane diol (1,3–BDO), 1,4–butane diol (1,4–BDO) and bisphenol A (BPA). All the block copolymers were subjected to testing and analysis with a view to assess the effect of soft segment molecular weight on the polymer properties.

### 4.1 Preparation and characterisation of liquid NR (HTNR).

As mentioned above three grades of liquid natural rubber were used in the present synthesis. They were prepared by the photochemical depolymerisation of NR in the presence of hydrogen peroxide. Samples with molecular weight \( (\bar{M}_v) \) 22400, 14200, and 8500 could be made by varying the exposure time to 20, 30, and 40 hours respectively.

Chemical analysis of the above samples gave a hydroxyl functionality, which is slightly less than two, viz., 1.98. Structure of the liquid rubber molecules samples has been ascertained by IR spectroscopy. The characteristic absorption frequencies of cis–1,4–polyisoprene are retained in the IR spectra showing that the photochemical process has not affected the basic polymer structure. The presence of primary hydroxyl groups is confirmed by the broad band at 3600–3400 cm\(^{-1}\).
4.2 Block copolymerisation.

The block copolymers were synthesised by the two-shot process in which the HTNR was endcapped with toluene diisocyanate and then chain extended with the respective low molecular weight diol. On the basis of experimental observations it seems that an excessive increase in the molecular weight of HTNR is affecting the efficiency of the chain extension process. The product in such cases is formed only after prolonged reaction time. This could be due to the lower reactivity of the long HTNR chains, which coil up and thus partially masking the end hydroxyl groups restricting their reaction with the isocyanate groups. The IR spectra of the block copolymers showed absorption peaks characteristic of NR soft segments and the polyurethane hard segments indicating block copolymerisation. Moreover, the spectra taken at the intermediate stages during the polymerisation also indicate the occurrence of the chain extension reactions in the system. Since the nature of chain extender diol or molecular weight of HTNR does not alter the basic chemical structure of the samples, the IR spectra were found almost identical in all cases. Based on the IR analysis of the reaction system a probable set of chemical reactions has been proposed for the block copolymerisation process (Scheme I).

The samples were made in sheet form by casting the reaction mixture. They were then characterised by various analytical methods such as thermal analysis, tensile testing, tear testing and microscopy studies.

4.3 Thermal analysis.

4.3.1 Differential scanning calorimetric analysis.

All the DSC thermograms in general, showed two glass transitions at temperatures below ambient and above ambient respectively. The former was assigned to the NR soft segment and the
latter to the hard segments. Soft segment glass transition was found independent of its segment length, the type of chain extender diol and the composition of the block copolymer (i.e., the hard segment to soft segment ratio). The former observation points to the fact that the NR chains are devoid of any sort of interaction among themselves and are distributed as loose chains. Similarly the other two findings suggest that there is complete phase separation existing in the samples due to lack of interaction between the polar hard segments and the non polar soft segments. Thus it is found that the soft segment molecular weight does not have any notable effect on the thermal transitions of the block copolymers.

The hard segment transition, however, undergoes a change with the nature of the diol used and the respective segment length. Highest hard segment Tg is observed for NR/EG block copolymers and it varies in the order NR/EG > NR/BPA > NR/PG > NR/1,3-BDO ≥ NR/1,4-BDO. The Tg values seem to increase with decrease in the size of the carbon chain of the extender diol. The presence of bulky side groups which inhibits free rotation of the carbon chain and for the same reason aromatic ring systems in the diol cause an increase in the Tg values. All these observations are suggestive of the high intermolecular interaction existing among the polyurethane blocks. The shorter the size of the extender diol the more frequent would be the presence of polar urethane groups offering higher extent of interaction.

4.3.2 Thermogravimetric analysis.

The thermal stability of the block copolymers prepared from HTNR of different molecular weights and different chain extender diols were studied by thermogravimetric analysis. The following observations were made from an assessment of the thermal data. The thermograms show a two-stage decomposition pattern indicating the presence of two separate phases in the
block copolymers. Variation in the segment size of soft NR blocks brings about only negligible change in onset temperature of mass loss, peak temperature etc. However, the hard segment degradation temperature is found varying with the increasing segment length and also with the type of extender diol. This could be attributed to the intermolecular interactions existing in them.

Change in onset temperature of mass loss for the first stage decomposition was observed with a change in the extender diol. Thermal stability is maximum when 1,4-butane diol is used as the chain extender. This is because of the straight chain nature of this diol, which permits better ordering of the hard segments. Moreover, the primary hydroxyl groups present in the chain extender form stable urethane groups. Ethylene glycol also qualifies this and gives better thermal stability for the corresponding samples. The stability is minimum when an aromatic diol such as bisphenol A is present in the sample. This may be because of the electron withdrawing nature of the aromatic ring, which makes the urethane linkage less stable. PG-, and 1,3-butane diol–based block copolymers show greater stability than the aromatic one probably due to the presence of a methyl side group in them which stabilises the urethane linkage by +1 effect.

The second stage decomposition is attributed to the degradation of NR soft segment. Due to the absence of any intersegmental interaction and crystallinity within this phase, the thermal degradation is independent of the soft segment content. Also this stage of degradation is independent of the type of hard segments. This again indicates the absence of any interaction between the respective phases present in the block copolymers. The degradation temperature for the NR segments remain almost unchanged irrespective of its molecular weight. This is expected of a highly phase separated block copolymer in which the soft segment are present as loose chains.
4.4 Tensile Testing.

4.4.1 Tensile strength.

All the samples were subjected to tensile testing and the results are analysed with a view to correlate the tensile properties with the soft segment molecular weight, the hard segment content and the type of diol present in the hard segment. It is found that the samples exhibit higher tensile strength with increasing hard segment content. Such a variation in tensile strength is a natural consequence of the rigidity of the respective samples. Successive increase in the hard segment content makes the sample progressively rigid with high tensile strength, modulus of elasticity and low elongation at break. Thus the nature of the sample changes from a soft elastomer to a rigid elastomer and then to a rigid and toughened plastics as the hard segment content increases from 30% to 70%.

The tensile strength is found to vary with the chain extender diol present in the block copolymer. A comparison of tensile strength of all the products with 70/30 composition (Figure 3.55) shows that BPA–based samples possess the highest tensile strength among all (Figure 3.55 to 3.58). This is attributed to the right quality of product in terms of block copolymer structure, formed through efficient and systematic chain extension of the HTNR with the hard segment. It is to be noted in this context that the aromatic phenol is more reactive towards the isocyanate yielding the product readily. Moreover, the BPA–based polyurethane is highly rigid due to the presence of aromatic ring structure causing higher tensile strength. Next higher values for tensile strength are shown by the EG– and 1,4–BDO–based samples. However, they differ by the fact that EG–based copolymer shows high value with low molecular weight HTNR (NR₁) whereas 1,4–BDO–based samples show high values with high molecular weight HTNR (NR₃). The high value for EG–based sample with NR₁ is attributed to the higher rigidity of the material offered by
the polyurethane hard segments. The shorter ethylene glycol chains in these hard segments ensure frequent appearance of urethane groups along the segments chain so that there would be high extent of intermolecular interaction causing high rigidity. As the NR segment becomes longer as in NR$_2$ and NR$_3$ the tensile strength is found to decrease which is attributed to the lowering of rigidity due to the longer soft segment chains.

In the case of 1,4--BDO--based copolymers the hard segments are not as rigid as in the above samples because the diol in the case possesses a longer and flexible carbon chain. However, they show better tensile strength at NR$_3$ (Figure 3.49). This could be explained by the increased reinforcing effect of the hard domains in these products as in the BPA--based samples and the subsequent strain--induced crystallisation of the longer soft segments in the block copolymers. At this juncture it is to be noted that the hydroxyl groups present in EG and 1,4--BDO are more reactive towards isocyanate. The other two diols viz., PG and 1,3--BDO, on the other hand possess a secondary hydroxyl group which has lower reactivity towards the isocyanate. This is reflected in the tensile properties of the corresponding block copolymers, which show lower tensile strength at almost all compositions compared to the product from the former group of diols.

A notable feature regarding the NR/BPA samples is that at NR--8500 the tensile strength varies over a wide range as the hard segment is increased from 30% to 70% (Figure 3.52). The corresponding values tend to converge at NR--14200 and the convergence is found to be higher at NR--22400. Convergence at NR--14200 occurs when the values for 50%, 60% and 70% hard segment samples decrease and 30% and 40% samples increase as NR segment length is increased from 8500 to 14200. However, convergence at NR--22400 occurs as all the values increase when the NR molecular weight varied from 14200 to 22400. The 50%, 60% and 70% hard segment samples show smaller increase in tensile strength whereas the 30% and 40% hard
segment samples show larger increase. All these mean that as the soft segment molecular weight is increased from 8500 to 22400, the higher hard segment samples show a two way change, i.e., an initial decrease followed by a subsequent increase. The net effect is a flat trend in tensile strength values for these samples at both lower and higher NR molecular weight value. On the other hand the lower hard segment samples, viz., those with 30% and 40% hard segment, show continuous increase, i.e., initial slow increase and subsequent sharp increase to reach very nearly the convergent level. This kind of variation finally yields very close values of tensile strength for all compositions, i.e., almost similar values of tensile strength are obtained for samples based on NR-22400 as the hard segment content is varied from 30 to 70%. This is a favourable situation for the 30% and 40% hard segment samples which show highest tensile strength.

The decrease in tensile strength registered for the higher hard segment samples as the molecular weight of NR is changed from 8500 to 14200 is caused by the higher flexibility of NR-14200. This factor is also valid when NR molecular weight is increased to 22400. Inspite of this the tensile strength of these samples increases and this is attributed to the strain-induced crystallisation which is an inherent property of natural rubber. This effect is very prominent in the 30% and 40% hard segment samples with NR-22400. The continuous increase in tensile strength at all stages for these samples shows that they possess the optimum number of hard domains which act as physical crosslinks of the soft segment and reinforce them. Thus 30 to 40% of hard segments based on BPA along with NR molecular weight of 22400 are the optimum factors which give better quality block copolymers.

The variation of tensile strength of 1,4-BDO-based samples with respect to soft segment molecular weight is not well pronounced as in the NR/BPA samples (Figure 3.49). Samples with 70, 60 and 50% hard segment do not exhibit much variation in tensile strength. When the hard
segment is increased to 60 and 70%, the strength decreases slightly in going from NR–8500 to NR–14200 and then increases at NR–22400. The trend is similar to NR/BPA samples. An interesting feature here is that the tensile strength shows an increase when the NR molecular weight is increased to 22400. As before this is also explained on the basis of the strain–induced crystallisation of the longer NR chains. However, this trend is reversed in 1,3–BDO–based samples. Here the tensile strength shows a continuous decrease with NR molecular weight. Almost a similar trend is shown by the propylene glycol–based samples too. Pronounced decrease in tensile strength is observed in the case of EG based samples. This is so because of the abnormally high value at NR–8500 for the samples with 40 to 70% hard segment content. This high value of tensile strength for these compositions is attributed partly to the high rigidity of the EG–based polyurethanes and partly to the gelation of these samples at higher hard segment content.

4.4.2 Modulus of elasticity

Modulus of elasticity of the block copolymers follows the same course as that of the tensile strength. All the series of samples show increase in Young’s modulus with increase in hard segment content. The values are found to be very low at 30% and 40% hard segment content. Above this level of hard segment, sharp increase in modulus values is observed. This is very prominent in the case of BPA–based samples (Figure 3.53). Such behaviour is consistent with the high rigidity of the hard segments involving BPA. Samples based on 1,4–BDO also show similar variation in Young’s modulus.

Among all the chain extender diols used, BPA–based samples show the highest modulus values. At high hard segment content 1,4–BDO also gives similar values. Samples based on the other diols exhibit only low or moderate values of Young’s modulus (Figure 3.59 to 3.62).
Effect of molecular weight of soft segment on the Young's modulus is assessed by close comparison of the curves in Figure 3.41, 3.44, 3.47, 3.50 and 3.53. In most cases low hard segment samples (30% or 40%) show a flat trend in modulus as the soft segment molecular weight is increased. The 50% hard segment samples also follow similar course. Above this, the 60% and 70% hard segment samples show sharp decrease in the values with increase in soft segment molecular weight. For example, EG–based samples show a drastic decrease in the Young’s modulus values (Figure 3.41) for almost all compositions ranging from 70/30 to 30/70. NR/PD samples with 30/70 and 40/60 compositions show decrease in modulus of elasticity with increase in NR molecular weight whereas other compositions with lower hard segment content give almost steady values. In the case of NR/1,3–BDO samples except for 40/60 sample, all others show decrease in the Young’s modulus as before. The Young’s modulus of NR/1,4–BDO samples show flat trend with respect to NR molecular weight at 70/30, 60/40 and 50/50 compositions (Figure 3.50). The highest value is shown by 30/70 sample, i.e., with the highest hard segment content. This is natural consequence of the high intermolecular interactions present in such samples. The values spread over a wide range for the different compositions containing NR–8500 with highest value for 30/70 composition and they converge to lower values for samples containing NR–14200 and NR–22400

However, a different trend is observed for the BPA–based samples. Although the modulus decreases in going from NR–14200, it increases, as the soft segment molecular weight becomes 22400. This is the trend with the 70%, 60%, 50% and 40% hard segment samples. The 30% sample, however, shows a continuous increase in Young’s modulus with increase in the NR molecular weight from 8500 to 22400 (Figure 3.59). This is a
unique behaviour associated with BPA-based samples. This phenomenon is explained by the strain-induced crystallisation of the NR segments of higher molecular weight in the corresponding polymer.

4.4.3 Elongation at break.

As is expected, the elongation at break decreases with hard segment content in all the series of block copolymers. Among all the chain extender diols BPA-based samples show the least elongation at break and the PG-based samples are showing high elongation and the values are increasing with increasing NR molecular weight. The highest elongation of 275.6% was observed for NR3/PG(70/30) and the lowest value of 75% was observed for NR3/BPA(70/30). The elongation at break of all other samples lie in the above range. A notable feature observed is that the BPA-based samples are also showing appreciable extent of elongation comparable to other samples. Considering the high level of tensile strength and modulus properties of these samples, this kind of elongation property is unexpected. But it could be an indication to the reinforcing factor which is present in these samples. The NR3/BPA (70/30) sample in particular is showing higher tensile properties, viz., high strength and elongation at break, which is characteristic of a reinforced material. The reinforcing effect which exists in BPA-based samples and to a lesser extent in the 1,4-BDO-based samples is considered as contribution from the respective hard domains. Systematic and efficient chain extention in these samples leads to the formation of hard domains which are capable of reinforcing the soft segments together when the domain content is at optimum levels. Such reinforced soft segments of optimum length can exhibit strain-induced crystallisation, which in turn improves the tensile properties.
4.5 Fracture Studies.

One representative sample from each series was subjected to fracture studies. Except one or two series, samples selected for this purpose were having 50/50 proportion of hard and soft segments. It helped in assessing the effect of soft segment molecular weight on the fracture mechanism of these samples. The fracture surface of samples which are prepared from HTNR of lower molecular weight, i.e., 8500 generally has an undeformed appearance. Ridges and striations are absent on the surface. This is an indication that the failure of the sample takes place by rigid fracture. As the molecular weight of the rubber increases to 14200, the fracture surface is found to be in a deformed state with torn fragments and ridges present all over the surface. This is indicative of tearing of the sample, characteristic of a ductile fracture. Samples with NR of still higher molecular weight, viz., 22400 also gave fracture surface with ridges and wavy nature. This is consistent with a highly deformed surface showing ductile fracture. The shift from a rigid fracture to ductile fracture with an increase in NR molecular weight is discernible since the flexibility of the sample goes up with increasing soft segment length. Irrespective of the type of chain extender diol all the samples follow the same trend suggesting that the fracture mechanism of the sample is governed by the soft segment molecular weight at the composition studied. It is only natural that the fracture mechanism would show variation with hard segment content.

4.6 Morphology.

Morphology of the block copolymers was studied with the help of SEM micrographs of the fracture surface. TEM analysis would have been more useful in this respect, but lack of such facilities prompted the use of SEM data for the purpose.
All the SEM photographs show the presence of two phases in the samples. This kind of a two-phase morphology is quite expected since the block copolymer involves segments which are incompatible with each other. In most cases, the natural rubber is present as a continuous phase and the polyurethane component is kept dispersed as a discrete phase in it. Cocontinuous phase distribution is also observed in certain cases like the NR1/PG (50/50) samples.

This discrete phase distribution becomes prominent as the molecular weight of NR increases. Now the polyurethane is seen in the form of beads, which are distributed randomly in the sample. These are obviously the polyurethane homopolymer, which remain unreacted with the NR segments during the chain extension process. Voids are also present on the fracture surface which are formed by the pull out of beads during the tensile fracture of the test samples.

As stated above the fraction of polyurethane remaining as homopolymer increases with an increase in the molecular weight of NR segments. This tendency has already been attributed to the lower reactivity of the terminal hydroxyl group of the high molecular weight NR because of the masking of these groups by the large polymer coils. However, in the case of the BPA–based sample the polyurethane bead size and density seem to remain lower at higher NR molecular weights. Also these samples exhibit better tensile properties compared to similar samples with the other chain extender diols. These observations suggest that BPA polyurethanes undergo better chain extension with NR segments of higher molecular weight so that the amount of polyurethane homopolymers is present in smaller quantities in these block copolymers. The higher reactivity of BPA towards isocyanate has already been discussed.

The two–phase morphology observed in the samples appears as dispersion of hard phase in the natural rubber matrix. This phase seems to be in the form of discrete particles with a bead shape. The dispersion of beads suggest that they consists of homopolymers of polyurethane which
remain unattached to the natural rubber segments. The SEM studies provide only this much information regarding the morphology of the samples. Further investigation in this regard is needed especially with TEM under high resolution to identify the hard domains formed by the union of hard segment present in the block copolymeric structures. The consumption of \(-\text{NCO}\) groups in the NCO-\text{endcapped} natural rubber shows the introduction of polyurethane segments to the block copolymer structure.

### 4.7 Tear strength.

The tear strength increases with an increase in the hard segment content of the samples. This effect is quite natural since the tear propagation would be disrupted by the hard domains situating along the tear paths. As the hard segment content increases the domain density also increases and there would be effective hindrance of the tear propagation. Also the soft segments are held firmly with the sort of physical crosslinks offered by the hard domains.

It was noted from figures 3.68, 3.69 and 3.70 that the NR-8500 based samples show steady increase in tear strength at all compositions whereas the other two categories based on NR-14200 and NR-22400 show high values at 50–60% hard segment content and then remains almost steady. In the case of the former category of samples, viz., those based on NR-8500., the steady increase in the tear strength at all compositions is the outcome of an effective chain extension process. As a result the soft segments are firmly linked to the hard domains enhancing the tear strength. This may not be the case with samples based on NR-14200 and NR-22400. Because of their high segment length, chain extension process does not occur as effectively as in the previous one. Moreover, at high hard segment content there is more chance for the homopolymerisation of polyurethane. This is evidenced by the presence of large number of dispersed beads of unattached
polyurethane homopolymers in the fractograph. Since the hard segments are separated as homopolymers, the physical crosslinking density would decrease drastically and hence the tear strength also tends to decrease.

Regarding the effect of chain extender diols on tear strength, it has been observed that the block copolymers prepared from BPA–have the highest tear strength values compared to those prepared from aliphatic diols. This is expected since the BPA–based polymers have the most rigid hard segments, which are efficiently connected to the NR segments. Next highest values are shown by NR/1,4-BDO samples. These are also better quality samples evidenced by their tensile properties. Samples based on the other chain extender diols are showing better properties as their usual behaviour.

For the series of sample with NR-8500, the tear strength is found to increase steadily with the hard segment content. Such behaviour is consistent with the view that the hard domain density would increase with hard segment content and the hard domain which are densely distributed in the rubber matrix, can effectively prevent the tear propagation in the sample. As the molecular weight of the NR is increased to 14200 there is generally a decrease in the tear strength values. Moreover, the values do not exhibit a steady change although they increase with hard segment content. Beyond 60% hard segment content the values either decrease or remain almost steady. A similar behaviour is shown by the samples prepared using NR-22400 soft segments. A steady increase in tear strength values observed in general for the samples from 30% hard segment to 60% hard segments. Thereafter the values show a flat trend.

It has been observed that the tear strength decreases as the molecular weight of NR soft segments increases from 8500 to 14200. This must be due to the increase in flexibility of the block
copolymers caused by the increase in the size of the soft segments. But as the molecular weight of
the soft segments increases further to 22400, the tear strength of some sample is found increasing.
This increase is more pronounced in samples prepared from bisphenol A. This must be due to the
reinforcing factor as described in the case of tensile behaviour.

The fluctuation from regular behaviour in some high hard segment content samples is due
to the structural irregularities of products. This can be explained as follows. As the size of the
natural rubber soft segment increases, the mobility of the chains as well as their
reactivity decreases. Given this situation when the isocyanate and diol are present in excess,
they may preferentially react together to form homopolymers causing structural irregularities in
the main product.

To sum up the thermal properties of the block copolymer samples are influenced only by
the chain extender diols and are generally independent of the soft segment size. However, the
mechanical properties are greatly influenced by the type of chain extenders as well as the soft
segment size. With regard to the soft segment size, tensile strength and modulus of elasticity are
found to be the highest for samples with lower molecular weight, viz., NR-8500. As the molecular
weight increases to 14200, there is a drop in these values, which is nullified on further rise in the
NR molecular weight to 22400. The latter effect is attributed to strain-induced crystallisation of
the NR segments of sufficiently higher length. This is reflected in the tear properties also.

However, in practical terms, the improvement in the properties at NR molecular weight of 22400
is outdone by the inefficient chain extension reaction involving these longer soft segments which
is evidenced by the higher domain density of the homopolyurethane hard phase present in the
SEM micrographs of the respective samples. These observations suggest that the block copolymer
samples with NR-22400 could outperform those with NR-8500 if efficient chain extension
between the two types of segment is achieved in the former case which would be the subject of further studies in this field.

Fracture mechanism of the samples is also influenced by the soft segment molecular weight. Rigid fracture is transformed into ductile fracture as the NR molecular weight is increased which is a natural outcome of the increased flexibility of the samples containing longer NR segments. Thus, the soft segment molecular weight is found to be a critical factor influencing the block copolymer behaviour.

**Scope of further work.**

It is observed that the quality of the block copolymers is affected by the inadequate chain extension occurring under the present reaction conditions. Hence, it is desirable to explore ways to improve the method of synthesis so as to form block copolymers of better quality. Using such improved methods, it is possible to synthesise block copolymers containing different types of hard segments such as polyethers, polyolefin, polyesters etc. This would yield products of diverse characteristics. Further projects for exploring various applications of these block copolymers could be undertaken.
4.11 List of papers.


2. Synthesis and characterisation of segmented block copolymers from HTNR of varying molecular weight and polyurethanes. (in press)

3. Thermal properties of block copolymers prepared from HTNR of varying molecular weight and polyurethanes. (under publication)

4. Morphological studies of segmented block copolymers containing NR and polyurethane. (under publication)

5. Effect of soft segment length on the mechanical properties of NR/ Polyurethane block copolymers. (under publication)