CHAPTER 10
CONCLUSIONS

This chapter discusses the main points of all the results contained in this thesis. Also the scope for further studies in the field of polymer recycling has been indicated, focusing the topics still to be explored in this field.
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CONCLUSIONS

Owing to strict regulations in the quality of most of the polymer products, the formation of rejects from polymer industries is considerably high. Since, these materials are stable to most common degrading agencies, their decomposition is a very slow process. The open burning of these rejects creates serious environmental problems due to the release of zinc compounds into the atmosphere. The present work is a study on the recycling of mechanically ground prophylactics rejects as filler in synthetic elastomers and plastics. NR prophylactics filler is prepared by the powdering of waste condom material. Synthetic elastomers involved in the study are an amorphous elastomer, ‘styrene butadiene rubber’ (SBR), a relatively novel strain crystallising elastomer, ‘epoxidised natural rubber’ (ENR-25 and 50) and ethylene propylene rubber (EPDM). Synthetic plastics involved are an amorphous brittle plastic, ‘polystyrene’ (PS) and a semi-crystalline plastic ‘polypropylene’ (PP). The main results in the whole thesis can be concluded as given below.

Prior to the use of natural rubber prophylactics waste as filler in styrene butadiene rubber, it has been ground in a toothed wheel mill to get a rubber powder polydispersed in size. This has been sieved and separated into four different size fractions such as size 1 to 4. A mill-sheeted form of natural rubber prophylactics has also been prepared using a two-roll mill. Different size fractions of prophylactics filler have been characterised by observing their surface morphology using scanning electron microscopy and by analyzing the average particle size, most frequent size range, number and weight average diameters and particle size distribution curves. Scanning electron microscopic photograph of the prophylactics filler reveal that the particles are irregularly shaped with rough surface. From size 1 to 4, the particle size increases and the size distribution widens. Assessment of processing, curing, mechanical, solvent swelling and tensile/tear fractography etc. of styrene butadiene rubber have been done by adding varying loadings (0,10,20,30 and 40 phr) of each fraction to it. In a conventional vulcanisation system, curing characteristics of the styrene butadiene rubber compounds such as optimum cure time, scorch time and induction time have been found to be decreasing with the addition of natural rubber prophylactics filler. This has been identified to be due to the presence of unreacted accelerator in natural rubber prophylactics rejects.
Analysis of rheometric cure curves also shows that the cure reactions follow first order kinetics. The Stress-strain behaviour observed is typical of vulcanised low strength materials, i.e., the stress value is found to be increasing slowly at higher strains. Young's modulus values are found to be unaffected at lower loadings of the prophylactics filler while a slight decrease is observed at higher loadings for most of the cases. The secant modulus M-300 (300 % elongation) decreases up to 30 phr and then increases slightly for 40 phr filler loading. Compared to finer filler particles, better tensile performance has been shown by large prophylactics particles. But tear strength shows superior performance in the case of SBR vulcanisate with smaller filler particles. The comparatively better tensile performance of large sized fillers and mill-sheeted form of the prophylactics filler has been supported by swelling index, cross-link density values, Kraus, Cunneem-Russell equations as well as scanning electron fractography. In these vulcanisates, prophylactics filler particles have been observed as phase separated entities.

The melt rheological behaviour of styrene butadiene rubber compounds filled with natural rubber prophylactics rejects and selected particulate fillers such as carbon black, silica, and marble powder also have been investigated. Irrespective of the composition, prophylactics particle size, mixing conditions and temperature, all the rubber compounds exhibit pseudoplastic behaviour. The increase in the melt viscosity of styrene butadiene rubber compounds with the increasing loading and varying particle size of prophylactics as well as loading of particulate filler has been found to be shear rate dependent. At the highest shear rate, among the particulate fillers used, the order of increasing the viscosity has been found to be marble powder<silica=black. At low and intermediate shear rates and at a temperature of 150°C, the compound mixed for 5 minute showed least viscosity but at highest shear rate the curves converge to a point due to 'spurt' or sudden combined flow. In the case of samples without particulate fillers, the influence of temperature has been found to have a notable effect on viscosity only in the case of gum styrene butadiene rubber compounds. Except at 160°C all the samples filled with particulate fillers have been found to be less pseudoplastic than gum and other prophylactics filled samples. Compared to other equations tried, Eiler van Dyck equation has been found to be giving closely agreeing values of viscosity to that of experimental values while the least agreement is shown by Guth
equation. A decrease in the extrudate distortion also has been observed with the addition of prophylactics and particulate fillers to styrene butadiene rubber compounds.

Use of varying concentrations (0, 10, 20, 30 and 40 phr) of prophylactics filler of varying particle sizes, size 1, 2, 3 and 4 and mill-sheeted form in epoxidised natural rubber (ENR25) has been discussed. Discussions focus on the processing, mechanical and solvent swelling behaviour of gum and prophylactics filled epoxidised natural rubber compounds. The increase in the fastness of cure reaction with the loading of prophylactics has been found to be due to the presence of unreacted accelerator in the prophylactics rejects. In the case of ENR-25, better tensile and tear properties have been exhibited by smaller size prophylactics fillers, especially size 1 at most of the loadings. Among the theoretical models used for the prediction of Young's modulus, Mooney and Guth equations have been found to be giving close values to that of experimentally observed values, mainly at higher loadings of 30 and 40 phr of prophylactics filler. Swelling studies, Kraus, Cunneen-Russell and Lorenz-Park equations and the scanning electron fractography of the samples have supported the comparatively better performance of size 1 prophylactics filler in epoxidised natural rubber vulcanisates. As prophylactics filler particles remain as phase separated entities in ENR-25, these are considered as filled composite systems than as blend systems.

The processing aspects, mechanical and dynamic mechanical analysis of epoxidised natural rubber, ENR 50 containing prophylactics (size 2 fraction) and particulate fillers (carbon black (HAF), silica and marble powder) also have been studied. All the rheographs obtained are typical 'S' shaped curves. The variation of minimum rheometric torque with the loading of prophylactics and particulate fillers is dependent on the composition of the system. Among the particulate fillers, only black has been found to be increasing the minimum torque in ENR/40 phr prophylactics system. Only carbon black and silica have been found to be increasing the maximum rheometric torque. The decrease in optimum cure time and increase in the speed of the vulcanisation reaction also has been observed with prophylactics and particulate fillers in most of the cases. The stress-strain curves of the gum and prophylactics filled ENR vulcanisates are different from typical vulcanised low strength materials due to the strain crystallising nature of ENR. With the addition of prophylactics filler, the young's modulus values show a slight increase. The addition of carbon black, silica and marble powder also increases the young's modulus. The addition of prophylactics in
particulate containing systems increases the young's modulus except in the case of silica. Improvement in the overall mechanical properties of ENR-50 composites with the loading of prophylactics and particulate fillers has been evidenced by the increase in tensile and tear strengths. As the concentration of prophylactics increases, storage modulus values also increase. This is normal to be expected from the presence of crosslinked particles in elastomer matrices. The storage modulus increases with increasing frequency also. Addition of prophylactics filler to epoxidised natural rubber has been found to be increasing the glass transition temperature of epoxidised natural rubber while the presence of carbon black and silica increases it further. An improvement in the hysteresis of the filled ENR-50 samples has been indicated by the reduced damping maximum values of ENR-50 at 100 Hz. Increased concentration of particulate filler in the prophylactics phase has been noted from the analysis of filler distribution by damping maximum values. Good agreement between the tensile strength values and crosslink densities obtained from dynamic mechanical data and swelling studies at room temperature have been observed. Addition of particulate fillers decrease the energy of activation for glass transition of the ENR-50 samples while the loading of prophylactics filler in the presence of particulate filler increase the values.

The development and characterisation of novel ethylene propylene diene rubber (EPDM) compounds have been discussed. Studies in this section makes a comparison between EPDM samples containing NR prophylactics as well as ISNR-5. The cure curves of EPDM compounds have been found to be the resultant of slow curing or marching cure curve of EPDM and that of fast curing 'S' shaped curing curve of natural rubber. Minimum torque in rheographs shows a slight increase with prophylactics loading. Substitution of natural rubber in the place of prophylactics filler results in a low value of minimum torque. This is true at both 10 and 40 phr loadings of the inclusions in EPDM. This is due to the lightly crosslinked nature of the prophylactics. The maximum torque ($M_t$) of the samples is found to be decreasing with prophylactics loading. The curing properties such as optimum cure time, scorch time and induction time have been found to be decreasing with the loading of prophylactics filler. But for most of the cases the value obtained for compositions with virgin natural rubber (ISNR-5) has been found to be lower than that with prophylactics filler. This behaviour is due to the difference in the curing behaviour of EPDM and ISNR-5. Increased cure rate index and cure rate constant values with the addition of prophylactics and increased
temperature clearly indicates the presence of unreacted accelerator in the prophylactics rejects and the cure activation at high temperature. These observations have been supported by the higher value of energy of activation for the gum EPDM compound. The cure kinetic plots are found to be almost linear which proves that the cure reactions proceed according to first order kinetics. Thermal ageing produces mixed results showing the improvement/deterioration in properties. Unaged tensile strength has been increased with the loading of prophylactics up to 30 phr. Samples with virgin natural rubber give better tensile strength compared to those with prophylactics. Physical cross-links determined from Mooney-Rivlin equation agree with the tensile strength values for most of the cases. Tear strength increases sharply with the loading of prophylactics and levels off at higher loadings. Better values are shown by the substitution of prophylactics filler with ISNR-5 only at 10phr. At 40 phr, the tear strength for EPDM / ISNR-5 system is lower than EPDM / prophylactics. The diffusion process in EPDM vulcanisate is found to be anomalous. The observed variation in the equilibrium swelling has been supported by the intrinsic diffusion coefficient and molar equilibrium sorption constant while at 40°C sorption and permeation coefficients also has been found to be in agreement. The perfect linearity of the sorption kinetic plots at room temperature reveals the first order kinetic process.

It has been observed that pure polystyrene exhibits linear or near linear stress-strain behaviour while that of its composites with prophylactics show deviations from linearity. A drop in the Young’s modulus and tensile strength values has been observed with the loading of prophylactics. The better performance of size 1 prophylactics filler in the case of Young’s modulus and impact strength has not been observed in the case of tensile strength. The strain induced crystallisation of prophylactics particles in filled polystyrene composites has been proved by Martin-Roth-Stiehler plots. Scanning electron microscopic observations has been proved to be useful to understand the operating mechanism of impact toughening in polystyrene composites. In loss modulus-temperature plots pure polystyrene exhibits only one transition around 85°C while all composite samples exhibit two transitions, one around -58 to -36°C range due to prophylactics and the other around 100°C which is due to polystyrene. The phase-separated nature of the composite samples has been supported by both loss modulus-temperature and tanδ - temperature plots presenting two well-defined transitions. The glass transition values of polystyrene determined from the loss modulus-
temperature plots have been found to be increasing with the frequency of measurement except in the case of pure polystyrene. An irregular increase in the Tg value of polystyrene has been observed with the loading of prophylactics. Particle size of the prophylactics filler is not found to exhibit any clear trend in the variation of Tg values.

The use of reclaimed and chemically modified prophylactics rejects in unmodified and chemically modified prophylactics rejects also has been investigated. Epoxidation of prophylactics rejects at room temperature has been carried out by in-situ formed performic acid using a mixture of formic acid and hydrogen peroxide. A mixture of chloroform and alkali in the presence of a phase transfer catalyst has been used for the dichlorocarbene modification of prophylactics at room temperature. De Link process has been employed for the reclamation of prophylactics rejects in a two roll mixing mill. The preparation of maleic anhydride modified and phenolic modified polypropylene in hot two-roll mill is done using maleic anhydride/dicumyl peroxide mixture and dimethylol phenol/stannous chloride mixture respectively. The characterisation of chemically modified prophylactics and polypropylene has been characterised by infrared spectroscopy, chemical analysis, variation of glass transition temperatures and contact angle determinations. Epoxy group in the epoxidised sample is confirmed by the presence of FTIR peaks around 870 cm\(^{-1}\) and 1300 cm\(^{-1}\) while dichlorocarbene modification is confirmed by peaks at 1070 cm\(^{-1}\) (cyclopropane ring) and 746 cm\(^{-1}\) (C-Cl stretch). Up to a reaction time of 144 h, increase in epoxy values has been observed. The magnitude of epoxy value has been found to be highest for the sample treated with 20 % epoxidation reagent. Similarly, up to 4 h an increase in the chlorine content of dichlorocarbene modified samples has been found with a leveling off behaviour afterwards. Stiffened of polymer chains after chemical modifications show increase in the glass transition values. Increased polarity resulting from the chemical modifications has been found to be reducing the contact angle of a sessile drop of water on the surface of chemically modified materials. The thermal stability has been found to be reduced with epoxidation due to the formation of acidic compounds during thermal degradation. Similar results have been noted with dichlorocarbene modified samples also. A reduction in tensile strength has been observed with the addition of reclaimed prophylactics rejects while an increasing trend has been observed in the case of epoxidised prophylactics with both maleic anhydride and phenolic modified polypropylene and dichlorocarbene modified prophylactics with phenolic
modified polypropylene. Impact modification of polypropylene has been found to be more effective with reclaimed prophylactics than chemically modified forms. α-Monoclinic structure of polypropylene has been proved by the results of X-ray diffraction.

Scope for further studies

Further studies in this area may focus on the following aspects.

1. Development of compatibilised blends based on ENR/PVC, NR/PVC and Nylon/EPDM blends involving NR prophylactics rejects.
2. Development of NR prophylactics vulcanisates filled with particulate fillers and reinforced with natural fibres for non-critical applications.
3. Development of toughened polystyrene materials by soaking NR prophylactics rejects in styrene (compounded with polymerising and crosslinking agents) and thermal treatment.