Chapter – 8

Summary, Conclusions and Scope for further works
Summary:

The present thesis focuses on the structure-property relationship of four major types of polyester industrial yarns viz. High modulus low shrinkage (HMLS), High tenacity (HT), Low shrinkage (LS) and Super low shrinkage (SLS), which are used for specific applications. All these yarns have been produced in spin draw machines from polyester chips having the same molecular weight (intrinsic viscosity of around 0.90).

These yarns have been characterized in detail for their structural, morphological, chemical, thermal, physical and mechanical properties. An attempt has been made to explain the structure-property relationship of these polyester industrial yarns. Furthermore, yarn structure developed during different stages of spinning process was also characterized to study the role of undrawn yarn structure on the final drawn yarn structure.

These yarns have been processed through their respective processes to produce the final products. Yarn structure and their characteristics have been studied on intermediate and final products to study the changes in yarn structure, which occurs in the course of the downstream processes. An effort has been made to explain the influences of these changes in yarn structure on properties of the yarns, taken out from the intermediate and final products.

Structure-property relationship of polyester industrial yarns:

Structural and morphological studies have revealed the following major differences amongst four different types of polyester industrial yarns:

- Crystallinity of all the four yarns varies within a narrow range (41 - 45%). However, crystal size of HMLS polyester yarn has been found to be larger than the other yarns investigated in this thesis. Crystal size and crystallinity are relatively low for HT polyester yarn.

- Long period of HT polyester yarn is the highest (~160 Å), whereas other three polyester yarns have comparable long period (~ 142 Å).
- Birefringence and amorphous orientation factor exhibit a linear relationship amongst these yarns. HT polyester yarn has the highest birefringence and amorphous orientation, whereas SLS polyester yarn has the lowest birefringence and amorphous orientation.

- Even though amorphous orientation of HMLS yarn is relatively low (compared to HT yarn), it has high amorphous modulus. This may be attributed to higher fraction of tie molecules present in the structure of HMLS yarn.

A relative comparison of the key structural parameters amongst the four different types of polyester industrial yarns have been depicted in section 4.2.6 (chapter 4), which is one of the important outcomes of the present study.

Morphological studies of undrawn yarns revealed that the structure of the HMLS undrawn yarn is significantly different from that of the other three yarns. Birefringence of HMLS undrawn yarn is notably higher, resulting higher crystallinity and crystal size than other undrawn yarns. This arises due to the major differences in spinning conditions e.g., (a) quench air temperature viz. hot quench (against cold quench for other yarns) (b) higher speed of the 1st godet roll and (c) higher number of filaments (means lower denier per filament). All these changes in process parameters for HMLS polyester yarn lead to a different undrawn yarn structure which is crystalline and oriented.

Structural differences on the fully drawn yarns are created through individual set of drawing and heat setting process conditions which are specific for each of these polyester industrial yarns. Stress-strain curves of the yarns have been divided into two groups. LS and SLS yarns have significantly lower “initial modulus” and higher “breaking elongation” compared to HT and HMLS yarns. This is primarily attributed to the lower amorphous orientation of LS and SLS yarns. Molecules in the amorphous region of LS and SLS yarns are coiled to a higher extent than the other two yarns. These molecules get straightened at the initial stages of application of load during tensile test. The differences in tensile properties are further magnified through “modulus vs strain” curves of these yarns. The first peak is recorded at a lower level of strain (< 2%) for all the yarns. This is associated with the early response of the structure / molecules (due to their inertia)
when a tensile force is applied on the yarn. However, the second peak is associated with the response of the yarn structure when the molecules in the amorphous regions get straightened. The second peak of the modulus vs strain curve of LS and SLS yarns occurs at higher strain level (than HT and HMLS polyester yarns) primarily because of their lower amorphous orientation.

The plot of shrinkage vs amorphous orientation of these yarns show a linear relationship. Maximum shrinkage of HT polyester yarns and minimum shrinkage of SLS polyester yarns can be explained by their highest and lowest amorphous orientation respectively.

Detailed studies on hysteresis indicate that “work loss” increases exponentially with increase in “extent of stress relief”. Absolute values of “work loss” are lower for HMLS and HT polyester yarns than LS and SLS yarns. This is explained through their structural characteristics. Higher overall orientation of HT and HMLS polyester yarns as reflected by their birefringence values (and thus higher initial modulus) have resulted lower work loss than LS and SLS polyester yarns. Higher crystallinity of HMLS yarn leads to better hysteresis performance (lower work loss) than HT polyester yarn especially at elevated temperature. Hysteresis is an important performance test for HT and HMLS polyester yarns since these two yarns are used for products like conveyor belt and tyre respectively which are subjected to cyclic loading during service.

A good correlation has been found between peak temperature of “tanδ” (in high speed dynamic test) and the peak temperature of “work loss” (in slow speed hysteresis test). HMLS yarn has the lowest tanδ value followed by HT and LS / SLS yarns. Specific yarn structure, viz. higher tie molecule fraction of HMLS yarn resulted lower tanδ than HT polyester yarn. HMLS yarn has lower tanδ, lower loss modulus and higher storage modulus. These properties make the HMLS polyester yarn suitable for high speed passenger radial tyres.

Creep studies indicate that HT and HMLS yarns have lower creep which is attributed to their higher amorphous orientation and higher fraction of tie molecules than LS and SLS polyester yarns. Lower creep and higher tenacity make the HT polyester yarn suitable for conveyor belt application.
Thermal studies (DSC) of different types of polyester industrial yarns, indicate that structural characteristics and thermal history (drawing and heat setting conditions) influence melting behaviour of the fully drawn yarns. HMLS yarn has higher melting peak temperature (by around 4°C) than other yarns. This may be attributed to its larger crystal size. It is also to be noted that heat setting temperature of HMLS yarn is higher than the other polyester yarns. Melting enthalpy data of different types polyester industrial yarns corroborates the relative difference in crystallinity as determined by WAXS study.

*Structure and properties of HMLS polyester yarns in the downstream processes:*

Key downstream processes of HMLS polyester yarns are twisting, dipping and curing. Pilot facilities have been used to produce greige cord, dipped cord and rubber-cord composites. Rubber-cord composites have been subjected to flex fatigue using compression-tension disc flex fatigue tester. Cords extracted from the rubber-cord composites have been characterized along with greige and dipped cords to study its structure-property relationship.

It is noted that the molecular weight of the polymer (polyester chips) decreases gradually during downstream processes. The drop in intrinsic viscosity / molecular weight is due to the breakage of the ester bonds which is caused by different factors at various stages. The drop in intrinsic viscosity between chips and yarn is attributed primarily to the thermal degradation of polymer melt during spinning (polymer melt temperature is maintained around 295°C). The drop in intrinsic viscosity between greige cord to dipped cord is attributed to the hydrolytic degradation during heat setting process in dipping (at a temperature of around 230°C). Further decrease in intrinsic viscosity / molecular weight on cured cord and fatigued cord may be attributed to the chemical degradation viz. hydrolysis and aminolysis. There is no significant difference in intrinsic viscosity between dipped cord and “heat set” cord. The experiment of producing “heat set” cord by using water instead of standard dip solution helps to draw inference that there is no significant adverse impact of resorcinol formaldehyde latex resin (RFL) on degradation of polyester during dipping.
WAXS experiments on rubber and polyester yarn mixed samples, indicate a linear relationship between crystallinity as determined through WAXS and the proportion of polyester fibre in the mixture. The derived linear equation was found to be useful to study the effect of curing / fatigue on crystallinity of the parent yarn by comparing the crystallinity values as determined through WAXS and the estimated values using the derived linear equation as mentioned above.

During dipping process, crystallinity and crystal size of HMLS polyester yarn have been found to be increased slightly which may be attributed to the heat setting effect during dipping. There is no significant change in long period of the dipped cord with reference to that of the parent yarn. During curing and flex fatigue, crystallinity of the parent yarn does not undergo significant changes.

Retention of tensile strength of the parent HMLS polyester yarn at the downstream processes has been studied. Strength loss from yarn to cord is around 8-10% (yarn to greige cord conversion efficiency is around 90 to 92%). Considering greige cord strength as the reference, there is no further loss of strength up to the cured cord. However, around 32% loss of strength (with reference to cured cord strength) has been recorded which is only due to flex fatigue. There is gradual decrease in molecular weight of the parent yarn during each of the downstream processes. However, the major cause for higher drop in strength during fatigue is attributed primarily to the rupture of the filaments at the cord surface and the bias failure due to shear yielding caused by repeated compression and tension cycles. Initiation of the adhesion failure at the cord-rubber interface leads to open structure and finally fatigue failure. Dynamic adhesion at the cord-rubber interface, plays a very important role on strength retention of the cord post fatigue.

An elaborate experiment of dynamic mechanical properties, conducted on HMLS polyester dipped cord (1000/2 denier) indicates that at 100°C, tanδ values remain relatively low for a wide range of frequencies (up to 25 Hz). This property makes the HMLS polyester yarn suitable for usage in high speed passenger radial tyres. It may be noted that the dynamic loading frequency of 25 Hz translates to a speed of around 175 km/hr for a high speed passenger radial tyre.
Warp cords have been taken out from the dipped belting fabric for characterization. Dipped belting fabric was produced in a plant dip unit. Rubber-cord composite samples were taken directly from a conveyor belt (4 ply construction) for fatigue test using Scott flex tester.

Like HMLS polyester yarn, in case of HT polyester yarn also, the original molecular weight of the polyester chips is decreased gradually upto fatigued cord. However, it is interesting to note that during fatigue test, higher degradation occurs on the cords pertaining to the bottom ply. Higher drop in intrinsic viscosity / molecular weight of the cords corresponding to the bottom ply (post fatigue) has been observed. Bottom ply of the rubber-cord composite is subjected to a higher extent of compression fatigue during scott flex fatigue test, which causes higher degradation. The drop in intrinsic viscosity / molecular weight is attributed to the breakage of the ester bonds. Increase in carboxyl group number corroborates the degradation of polyester.

WAXS study on dipped cords made out of HT polyester yarns indicates that there is no significant change in crystallinity after dipping. However, it is interesting to note that the “long period” decreases significantly from greige cord (160 Å) to dipped cord (143 Å). Relaxation during dipping appears to be the primary reason for decrease in long period of the dipped cord. It is to be noted that for tyre cord fabric, (HMLS polyester yarn), a net stretch of around 1.5% is applied during dipping, whereas a net relaxation (around 4%) is applied during dipping of belting fabric. Extended chains in the amorphous phase can get coiled due to heat setting under relaxation during dipping, leading to decrease in long period.

Removal of rubber from the cord surfaces of the 4-ply conveyor belt sample was difficult. Due to the presence of rubber, no proper data could be obtained from the WAXS / SAXS studies conducted on the cords taken out from the conveyor belt. However, it can be safely assumed that crystallinity does not undergo any significant change after curing and fatigue. This conclusion is arrived on the basis of the detailed study conducted on HMLS yarn.
A relative comparison on the yarn structure between HMLS and HT polyester yarns at different stages of processing has been depicted in section 3.3.5, which is one of the important outcomes of the present study.

Studies conducted on the cords extracted from the conveyor belt samples reveal the differences between top ply and bottom ply with special reference to the strength retention post fatigue. It is noted that up to cured cord stage, strength retention of the HT polyester cord is around 79% of the parent yarn strength. During scott fatigue test, no further drop in strength has been observed for the cords pertaining to the top fabric ply. However, significant drop in strength has been recorded (further by around 28% with respect to the yarn strength) for the cords pertaining to the bottom fabric ply. The major cause for drop in strength in flex fatigue is attributed to the rupture of the filaments at the cord surface and the bias failure due to shear yielding caused by repeated compression and tension cycles. The substantial drop in strength of the cords pertaining to the bottom ply is due to severe compression fatigue. It is known that drop in strength of the cord in a rubber-cord composite during fatigue is higher during compression cycle. This is attributed to the failure of the cord rubber interface which is under severe stress during compression. This finding bears significance because in actual service conditions of the conveyor belt, bottom ply is subjected to the compression fatigue when it passes through the end pulleys.

Findings of the creep and hysteresis studies bear significance considering the service conditions of the conveyor belt. During service of a conveyor belt, hysteresis occurs during running condition of the conveyor belt; whereas creep occurs while the belt is stopped under loaded condition. Actual growth of the conveyor belt is influenced by the combined effect of hysteresis and creep characteristics of the warp cords. It has been noted that “creep” and “work loss” of the cords both increase after fatigue and at elevated test temperature. This is associated with “lengthening” of the conveyor belt and higher energy absorption on prolonged service.
Structure and properties of LS/SLS polyester yarns in the downstream processes:

The downstream processes of LS and SLS polyester yarns are similar and is simpler compared to that of HMLS and HT polyester yarn. The final product i.e., coated fabric goes for mostly static applications. Findings of the studies conducted on LS polyester yarns taken out from the greige and coated fabric indicate that there is no significant change in microstructure of the yarns except the long period of the weft yarns. Post coating, there is decrease in long period of the weft yarns, which is because of the widthwise shrinkage, occurred during coating and heat setting process.

There is slight drop in molecular weight of the warp and weft yarns after coating. Increase in carboxyl group number of the yarns taken out from the coated fabric corroborates the degradation of polyester. This is due to thermal degradation of polyester in presence of coating chemicals. However, its impact on mechanical properties of the coated fabric is not significant.

There is loss of strength of the parent yarn by around 8-10 % during yarn to fabric conversion process. This is attributed to the abrasion between yarn and guides, which happens during warping and weaving process. However, it may be noted that there is no further drop in strength of warp and weft yarns during coating process.

Creep is an important property of the LS PET yarns used in coated fabric, since some of the products like tensile structure & tents are subjected to tension during service. Creep of the warp and weft yarns pertaining to the greige fabric is comparable. However, weft yarns, taken out from the coated fabric show higher creep. Higher creep of the weft yarns is attributed to the decreased “long period”. This is because of width wise contraction of the fabric, occurred during coating process.
Conclusions:

The present study leads to the following conclusions:

1. Each of the four types of major polyester industrial yarns studied in this project has unique structure and morphology. This has resulted unique set of mechanical, thermal and dynamic properties of the individual type of polyester industrial yarns, which are used for different end use applications.

2. “Amorphous orientation” has been found to be one of the key structural parameters which influence most of the important yarn properties.

3. The unique combination of higher crystallinity, crystal size, tie molecule fraction and moderately high amorphous orientation make the HMLS yarn as the most dimensionally stable yarn amongst the four types of polyester industrial yarns studied in the present work.

4. The molecular weight of the polymer (polyester chips) decreases gradually during the downstream processes upto fatigued cord (HMLS and HT polyester yarn). Highest drop in molecular weight occurs during spinning process.

5. There is no significant adverse impact of resorcinol formaldehyde latex resin (RFL) on degradation of polyester during dipping.

6. There is slight increase in crystallinity and crystal size during dipping of cords made out of HMLS polyester yarn.

7. Long period of HT polyester yarn is decreased significantly during dipping of belting fabric.

8. During curing and flex fatigue (HMLS and HT polyester yarns) crystallinity of the parent yarn does not undergo significant changes.

9. There is no significant change in microstructure of the LS polyester yarns except long period of the weft yarns in the final product (coated fabric).


11. A good correlation exists between the peak temperature of “work loss” (hysteresis test) and peak temperature of “tanδ” (dynamic test).
12. At 100°C, tanδ of HMLS polyester dipped cord has been found to be relatively low and its magnitude remains at the same level for a wide range of frequencies (up to 25 Hz).

13. Significant loss of strength occurs during compression-tension flex fatigue of HMLS polyester cord. This is primarily due to failure of dynamic adhesion at the cord-rubber interface because of “axial compression”, causing rupture of filaments at the cord surface.

14. There is significant drop in strength of the cords pertaining to the bottom ply of the conveyor belt (HT polyester cord) as compared to that of the other plies.

15. Loss of strength of the cord (yarn to dipped fabric) is significantly higher in case of belting fabric (HT polyester yarn) as compared to that of tyre cord fabric (HMLS polyester yarn).

**Scope for further works:**

The outcome of the present work provides inputs for further works in the field of both academic research and industry.

- Significant efforts have been made in the present work to study the microstructure of the yarns / cords extracted from the intermediate and final products. Further works with respect to macro structural analysis on intermediate and final products may be explored which may further unfurl the scope of improving the strength retention in the final product.

- Loss of strength of the cord made out of HT polyester yarn during curing (cured conveyor belt) is found to be higher than HMLS polyester yarn. Hence, improvement in strength realization of HT polyester yarn from dipped fabric to cured belt may be an area for further research which is directly related to the service performance of the conveyor belt.

- Post fatigue strength loss of the cords pertaining to the bottom ply is found to be significantly higher than the other plies of the conveyor belt. Therefore, improvement of dynamic adhesion especially between bottom ply and the bottom cover compound is of paramount importance to enhance the fatigue
performance of the bottom ply. Hence, it is an area for further work to enhance the durability of the conveyor belt.

- HMLS type of polyester yarn may be explored for making conveyor belt (instead of HT type polyester yarn) towards improvement in dimensional stability, strength realization post cure and fatigue of the serviced conveyor belt.

Substantial efforts have been made in the present work towards laboratory simulation of the tests with respect to the final products viz. passenger radial tyre and conveyor belt. Further works in this area may be explored. Cords may be extracted from the serviced tyre / conveyor belt for studying structure-property relationship.