Chapter – 6

Structure and properties of dipped, cured and fatigued cords made out of HT polyester yarns
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6.1 **Introduction:**

It has been mentioned in chapter 3 (section 3.3.6) that dipping of belting fabric was carried out in the standard dip unit at M/s SRF plant. Cords from the warp direction of the belting fabric have been taken out for characterization of the dipped cord made out of HT polyester yarn. Rubber-cord composite samples have been taken directly from a conveyor belt of 4 ply construction (*Figure 6.1*) for fatigue characterization using scott flex tester. This four ply conveyor belt has been produced in a conveyor belt manufacturing plant (refer section 3.3.7). Basic principle of removal of the cords from rubber-cord composite sample is similar for both HMLS and HT polyester cord. However, in case of HT polyester cord, it was required to swell the 4 ply rubber-cord composite samples (conveyor belt) in toluene for longer time (5 days) to remove the cords from the conveyor belt.

*Figure 6.1:* (a) 4 ply conveyor belt sample, showing different layers of belting fabric (b) sample for scott flex fatigue test (c) extracted cord from conveyor belt (d) extracted cord from the fatigued sample
Since conveyor belt samples consist of multiple layers of belting fabric, during scott flex fatigue test, each layer of fabric experiences different extent of stresses. For example, the top ply is subjected to maximum tension and minimum compression, while bottom ply undergoes maximum compression and minimum tension fatigue [1]. Conveyor belt undergoes similar kind of fatigue scenario during service (running over the end pulleys). Cords have been extracted from the individual plies after fatigue for various characterizations. Findings of the various studies conducted on the cords removed from the “top ply” and the “bottom ply” have been discussed in the subsequent sections. Figure 6.1 depicts different layers of fabric inside the conveyor belt and the cords, extracted from the rubber-cord composite samples.

6.2 Degradation of HT polyester yarn during dipping, curing and fatigue:

Basic mechanism of in-rubber degradation of polyester is the same for both HMLS and HT polyester tyre cords viz. hydrolysis and sometimes catalyzed by aminolysis [2,3], which is affected by the ingredients present in the rubber compound. Decrease in intrinsic viscosity and increase in carboxyl group number are the indicators of chemical degradation of polyester yarn / cord. These characterizations were carried out on the regenerated polymer from its rubber composite [4,5] as described in section 3.4.1 to study the extent of degradation of polyester after dipping, curing and fatigue.

Intrinsic viscosity, viscosity average molecular weight and carboxyl group number have been shown in Figure 6.2 and 6.3. Molecular weight of the parent polymer (polyester chips) is reduced during subsequent processing and service (fatigue). The prime mechanism of the degradation of HT polyester cords at different stages is similar to that of HMLS polyester cord.

However, it is interesting to note that the drop in intrinsic viscosity / molecular weight of the cords corresponding to the bottom ply (after fatigue) is higher than that of the top ply. This indicates higher degradation of the cords of the bottom ply, which is subjected to a higher extent of compression fatigue compared to that of the top ply during fatigue test. The drop in intrinsic viscosity /
molecular weight is attributed to the breakage of the ester bonds [5]. Increase in carboxyl group number (Figure 6.3) corroborates the degradation of polyester [5].

Figure 6.2: Intrinsic viscosity and viscosity average molecular wt. of polyester chips, yarns and cords (HT polyester yarn)

Figure 6.3: Carboxyl group number of polyester chips, yarns and cords (HT polyester yarn)
6.3 **Microstructure studies on dipped HT polyester cord:**

WAXS studies have been conducted on the warp cords taken out from the dipped belting fabric. Figure 6.4 depicts the WAXS scans (intensity vs 2θ) of HT polyester yarn and dipped cord. Results of the WAXS study are summarized in Table 6.1. Crystallinity of the dipped cord (39.7%) was recorded lower by around 2% than the yarn (41.2%). However, actual crystallinity of the polymer in the dipped cord is expected to be higher than 39.7%, because the “powdered dipped cord sample” contains around 7% of resorcinol formaldehyde resin (RFL) which is amorphous in nature (refer section 5.3). RFL does not have any crystalline peak, but it increases the area under the amorphous peak, resulting a decrease in crystallinity of polyester in dipped cord as determined by WAXS scan. Hence, it may be inferred that there is no significant change in crystallinity of HT polyester yarn after dipping.

![WAXS scans of HT polyester yarn and dipped cord](image)

**Figure 6.4:** WAXS of HT polyester yarn (1000 denier) and dipped cord (1000/2 denier)

<table>
<thead>
<tr>
<th>HT Polyester yarn / cord</th>
<th>Crystallinity (%)</th>
<th>Crystal size (010): Å</th>
<th>Long period (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yarn</td>
<td>41.2</td>
<td>53.2</td>
<td>160</td>
</tr>
<tr>
<td>Dipped cord</td>
<td>39.7</td>
<td>53.4</td>
<td>143</td>
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**Table 6.1:** Crystallinity, crystal size and long period of HT polyester yarn (1000 denier) and dipped cord (1000/2 denier)
Images of the Small angle x-ray scattering (SAXS) of HT polyester yarn and the dipped cord are shown in Figure 6.5. Sharpness of the image of the dipped cord is decreased due to the presence of RFL. However, from the intensity vs 2θ curves (Figure 6.6), it is evident that the position of the peak (2θ) of the dipped cord is shifted towards higher Bragg angle as compared to the yarn. This means long period is decreased from yarn to dipped cord. Extended chains in the amorphous phase might get coiled due to heat setting under relaxation during dipping, leading to decrease in long period. The half width of the peak of dipped cord is narrower than the half width of the yarn, implying that the length distribution of long period is narrower in the dipped cord.

![SAXS image of HT polyester yarn and dipped cord (1000/2 denier)](image)

**Figure 6.5:** SAXS image of HT polyester yarn and dipped cord (1000/2 denier)

![SAXS analysis: Intensity vs 2θ curve of HT polyester yarn and dipped cord (1000/2 denier)](image)

**Figure 6.6:** SAXS analysis: Intensity vs 2θ curve of HT polyester yarn and dipped cord (1000/2 denier)

It is interesting to note the difference between HT and HMLS polyester yarn with respect to the change in microstructure of the yarn after dipping. In case of HMLS polyester yarn, both crystallinity and crystal size are increased after...
dipping. There is no significant change in long period of HMLS polyester yarn post dipping, however, in case of HT polyester yarn, long period is decreased significantly after dipping. This may be attributed to the difference in dipping process conditions. Cords made out of HMLS polyester yarn are stretched and heat set during dipping. In case of HT polyester yarn, there is no stretch during dipping; fabric is dried, heat set and relaxed during dipping. A net stretch of around 1.5% is applied during dipping of tyre cord (HMLS polyester yarn), whereas a net relaxation (around 4%) is applied during dipping of belting fabric (refer section 3.3.4 and 3.3.6).

6.4 Microstructure studies on cured and fatigued HT polyester cord:

Removal of rubber from the cord surfaces of the 4-ply conveyor belt sample was found to be more difficult than HMLS polyester cord. Rubber content on the cords removed from the composite was higher than 70%. Therefore, it was difficult to measure the crystallinity of the cured and fatigued cords extracted from the conveyor belt. However, it can be safely assumed that crystallinity of cured and fatigued cord does not vary significantly from the crystallinity of the dipped cord. This conclusion is arrived on the basis of the detailed study conducted on HMLS yarn (chapter 5).

An attempt has been also made to measure the long period of the cured and fatigued cord through SAXS. However, the quality of the image obtained in SAXS was not good due to the presence of rubber (Figure 6.7). Hence, the long period of cured and fatigued cord could not be determined. It may be noted that in dipped cord, a significant reduction of long period was recorded as compared to that of the parent yarn.

Figure 6.7: SAXS image of polyester cord (1000/2 denier) made out of HT polyester yarn
6.5 **Microscopic studies on fatigued HT polyester cord:**

Photographs were obtained from the SEM studies conducted on the fractured surface of the tensile tested portion of the fatigued cord (Figure 6.8). Filaments pertaining to the bottom ply show more number of filaments affected due to fatigue than that of the top ply which is evident from the SEM photographs. More number of filaments of the cords pertaining to the bottom ply has shown bias failure when tested for tensile strength after fatigue. It has been mentioned previously in this chapter that bottom ply undergo severe compression fatigue than other plies in the composite. This has resulted higher drop in strength of the cords pertaining to bottom ply which has been discussed in the following section (6.7).

![SEM photographs of tensile tested portion of the fatigued cord](image)

**Figure 6.8:** SEM photographs of tensile tested portion of the fatigued cord (HT polyester cords: 1000/2 denier) pertain to top and bottom ply of the composite
6.6 **Comparison of structural changes between HMLS and HT polyester yarn in the downstream processes:**

Based on the inputs obtained from WAXS and SAXS studies conducted on yarn and dipped cord and the microscopic observation on the fatigued cord, a postulated morphology is shown in **Figure 6.9** to depict the structural changes of HT and HLMS polyester yarns during subsequent stages of processing. Following are the highlights of the structural changes of HT and HMLS polyester yarns which occur during dipping and fatigue.

- There is increase in crystallinity and crystal size of HMLS polyester yarn after dipping. However, there is no significant change in crystallinity of HT polyester yarn during dipping.
- There is significant reduction in long period of HT polyester yarn during dipping, whereas in case of HMLS polyester yarn, no significant change in long period occurs during dipping.

**Figure 6.9:** Postulated morphology of HT and HMLS polyester yarn and its changes during dipping and flex fatigue
- There is no significant change in crystallinity during curing / flex fatigue for both HT and HMLS polyester yarn. It appears that there are some breakage of tie molecules during fatigue of both HT and HMLS polyester yarn which is evident from decrease in intrinsic viscosity and increase in carboxyl group number of polyester after flex fatigue.

6.7 **Strength retention of HT polyester yarn in the downstream processes:**

As mentioned earlier, 4 ply rubber-cord composite samples, were taken out from the conveyor belt and used for scott fatigue test. Sample used for scott fatigue test is depicted in Figure 6.1(b). Rubber-cord composite samples were flexed over a pulley under tension for fixed number of cycles using the test parameters as described in section 3.4.19. Cords were removed from the individual fabric ply of the rubber-cord composite samples after fatigue. Findings of the tensile and other tests conducted on the cords pertaining to the top and bottom ply have been discussed in the subsequent sections.

Tensile strength of the parent HT polyester yarn (1000 denier), greige cord, dipped cords, cured cords and fatigued cords has been shown in Figure 6.10. It is interesting to note that upto 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.

Drop in breaking strength of the cord at different stages of processing can be partly explained by the increased carboxyl group number. Increase in carboxyl group number indicates breakdown of the ester bonds of the main chains, which may be attributed primarily to the thermal and in-rubber degradation. However, the major cause for drop in strength during flex fatigue (bottom ply) is mostly ascribed to the rupture of the filaments at the cord surface and the bias failure of the filaments due to shear yielding caused by the fatigue cycles. Axial compression mechanism explains the important role of the cord-rubber interface.
Initiation of the adhesion failure at the cord-rubber interface leads to open structure and finally fatigue failure (refer section 2.6.2). Dynamic adhesion at the cord-rubber interface plays an important role on strength retention of the cord after fatigue. Also during fatigue, chain scission is likely to occur, mostly in the amorphous phase due to snapping of the tie molecules, since tie molecules bear the maximum load [7,8].

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 [6,9,10].

![Figure 6.10: Strength retention of the cords (1000/2 denier) made out of HT polyester yarn](image)

It may be noted that the results obtained in the present fatigue study, pertains to a specific set of test conditions. Hence, absolute strength of the cords post fatigue does not bear much significance. However, the important aspect to note is the observation on the difference in performance between top and bottom
fabric plies of the conveyor belt samples undergone scott fatigue test. Strength retention of the cords pertaining to the bottom ply is significantly lower than the cords pertaining to top ply. In actual service conditions of the conveyor belt also, bottom ply is subjected to compression fatigue to a higher extent than that of the other plies. Therefore, in a conveyor belt sample after its service, the residual strength of the cords pertaining to the bottom ply is expected to be lower than the cords pertaining to other plies.

**Figure 6.11** depicts the stress-strain curve of cured and fatigued cords (1000/2 denier), made out of HT polyester yarn. Stress-strain curve of the dipped cord has also been included in the graph for comparison.

![Stress-strain curves of dipped, cured & fatigued HT polyester cords (1000/2 denier)](image)

**Figure 6.11**: Stress-strain curves of dipped, cured & fatigued HT polyester cords (1000/2 denier)

Very low stress at the initial part of the stress-strain curves (up to 2.5% strain), may be attributed to straightening of the cords during tensile test. This is due to the crimp (after applying the standard pretension of 0.05 gpd) present in the cords, taken out from the fabric ply [**Figure 6.1 (c), (d)**]. Cords pertaining to the top ply (after fatigue) follow almost a similar stress-strain curve as that of the cured cord. However, cords pertaining to the bottom fabric ply, have significantly lower tensile strength and elongation at break which is evident from the stress-stain curve too.
6.8 **Hysteresis characteristics of dipped, cured and fatigued HT polyester cord:**

Three important features of the conveyor belt carcass are [11]:

- Elastic properties of the carcass when under tension.
- Additional stresses of the carcass due to geometrical conditions of the conveyor belt and the severity of the service conditions.
- Strain of the carcass due to cyclic loading during service. This is associated with “lengthening” of the conveyor belt, resulting movement of the take-up pulleys.

Hysteresis (cyclic loading) studies on conveyor belt were reported considering the above aspects [11]. Some of the key technical aspects considered are as follows.

- Peak load for the cyclic loading study was kept at 40% of the ultimate belt strength.
- Minimum load for the cyclic test was maintained at 15% of the ultimate belt strength.

Considering these basic inputs, an elaborate study on hysteresis characteristic has been conducted on the warp cords taken out from the belting fabric. The study has been conducted at room temperature (22°C) and also at elevated temperature (100°C) using an environmental chamber attached with instron tensile tester.

![Figure 6.12: Typical hysteresis curve of dipped cords (1000/2 denier), made out of HT polyester yarn (1000 denier)](image-url)
**Figure 6.12** describes the basic characteristics of the hysteresis curve generated in Instron tensile tester. Following three characteristics of the hysteresis test have been studied:

- Elongation at peak load.
- Elongation at minimum load.
- Work loss.

Cyclic loading characterization was programmed for 50 cycles and the work loss was determined on the 50th cycle.

**Figure 6.13:** Hysteresis curves of cured cord and fatigued cord (1000/2 denier), made out of HT polyester yarn
Figure 6.13 describes the typical hysteresis curves generated during hysteresis tests of the cured cords and fatigued cords. Figure 6.14, 6.15 and 6.16 depict the results of the hysteresis test of cured cords and fatigued cords. Results of the hysteresis test of the dipped cords have also been included in the figures for comparison.

![Figure 6.14](image1.png)

Figure 6.14: “Work loss” of dipped, cured and fatigued cords (1000/2 denier), made out of HT polyester yarn

![Figure 6.15](image2.png)

Figure 6.15: “Elongation at peak load” during hysteresis test of dipped, cured and fatigued HT polyester cords (1000/2 denier)
It is evident that “work loss” increases from cured cord to fatigued cord. Increasing trend has also been observed in “elongation at peak load” and “elongation at minimum load”. Fatigued cords, extracted from the bottom ply showed relatively higher “elongation at peak load” and “elongation at minimum load” than the cords pertaining to the top ply. As described earlier, cords pertaining to the bottom ply are subjected to severe compression fatigue than other plies. This has resulted not only in maximum loss of strength post fatigue, but also decrease in modulus which is evident from the stress-strain curve (Figure 6.11). At elevated temperature (100°C) tests, “work loss”, “elongation at peak load” and “elongation at minimum load” all were increased compared to those at room temperature tests.

“Elongation at peak load” as well as “elongation at minimum load” are associated with “lengthening” of the conveyor belt, resulting movement of the take-up pulleys. Findings of the hysteresis test (especially elongation at peak load and minimum load) indicate further lengthening of the conveyor belt during service. Increase in “work loss” of the fatigued cords at elevated temperature is associated with higher consumption of energy by the conveyor belt during service.

Figure 6.16: “Elongation at minimum load” during hysteresis test of dipped, cured and fatigued HT polyester cords (1000/2 denier)
6.9 **Creep characteristics of dipped, cured and fatigued HT polyester cord:**

Creep tests were conducted at elevated temperature (100°C) on dipped cord, cured cord and fatigued cord, made out of HT polyester yarn by applying a constant load of 2.0 kg (approx 1 gpd). Results of the creep test are tabulated in Table 6.2. Creep curves of cured and fatigued cords are shown in Figure 6.17. Results of the dipped cords have also been included for comparison.

**Table 6.2:** Creep of the dipped, cured & fatigued cords (1000/2 denier) made out of HT polyester yarn (Test temperature: 100°C)

<table>
<thead>
<tr>
<th>Description</th>
<th>Creep (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Immediate</td>
</tr>
<tr>
<td>Dipped cords</td>
<td>5.3</td>
</tr>
<tr>
<td>Cured cords</td>
<td>6.6</td>
</tr>
<tr>
<td>Fatigued cords - Top ply</td>
<td>7.3</td>
</tr>
<tr>
<td>Fatigued cords - Bottom ply</td>
<td>7.7</td>
</tr>
</tbody>
</table>

It is noted that the creep of the cured cords and the fatigued cords are higher than that of dipped cords. Severity of fatigue of the cords pertaining to the bottom ply is higher than that of other plies. This has resulted not only maximum loss of strength post fatigue, but also reduces modulus and increases creep of the fatigued cord.

**Figure 6.17:** Creep of the dipped, cured and fatigued cords (1000/2 denier) made out of HT polyester yarn (Test temperature: 100°C)
6.10 **Summary:**

There is no significant change in crystallinity of the HT polyester yarn after dipping. However, long period has decreased significantly after dipping, indicating a major change in structure during dipping process. This change in structure leads to decrease in initial modulus, increase in work loss and increase in creep of the dipped cord.

Intrinsic viscosity and viscosity average molecular weight decrease gradually from chip to fatigued cord. This is because of the breakage of the ester bonds which is caused by different factors at various stages of processing. It has been noted that the drop in intrinsic viscosity / viscosity average molecular weight of the cords corresponding to the bottom ply (post fatigue) is higher than that of the top ply. This indicates higher extent of degradation of the cords of the bottom ply, which is subjected to a higher extent of compression fatigue during scott flex fatigue test. Increase in carboxyl group number corroborates the degradation of the polyester.

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 upto cured cord stage, strength retention of HT polyester cords is 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, significance drop in strength has been recorded (further by around 28% with respect to the yarn strength) for the cord pertaining to the bottom fabric ply. Microscopic studies indicate the rupture of filaments at the cord surface and the bias failure of the filaments. This indicates the failure of the cord-rubber interface (mostly the bottom ply) during fatigue. Initiation of the adhesion failure at the cord-rubber interface leads to open structure and finally fatigue failure. Also during fatigue test chain scission is likely to occur in the amorphous region due to snapping of the tie molecules since the tie molecules mostly bear the load. 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.
Observation on the creep test and hysteresis test together 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 happens when the belt is stopped under loaded condition. Actual creep 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 increases after fatigue. This is associated with “lengthening” of the conveyor belt and higher energy absorption on prolonged service.
6.11 References: