University of Alberta

Design of Crack Resistant Thermoplastic Roadway Markings

by

Laura-lee Brown ©

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Abstract

Thermoplastic roadway markings provide a high quality, longer lasting, solvent free alternative to paints. Typically, these materials are more abrasion resistant, more retro-reflective and exhibit increased adhesion properties. Two different modes of failure have been observed. The first is the transverse cracking of the lines, which is occurring consistently in intervals of 10 – 15 cm. The second mode of failure is chipping or raveling along the outside and crack edges of the marking. This is noted to progress more rapidly as the marking ages.

The focus of this study was to understand the mechanisms of failure, which would provide an indication of possible improvements for the current systems. The development of a set of criteria for optimal performance properties would allow for the formulation of new roadway marking materials. Numerous experimental formulations were developed exhibiting limited success.

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Table of Contents

Chapter 1 Introduction

Chapter 2 Material Characterization

Chapter 3 Cracking Studies

Chapter 4 Experimental Formulations

Chapter 5 Conclusions and Future Work

List of Tables

List of Figures

Nomenclature

MMA	Methyl Methacrylate
AADT	Annual Average Daily Traffic
AAWT	Annual Average Weekly Traffic
TP	Thermoplastic
DSC	Differential Scanning Calorimetry
AC	Asphalt Concrete
ASTM	American Standard Testing Method
ACO	Asphalt Concrete Overlay
PDI	Polydispersity Index
GPC	Gel Permeation Chromatography
L/D	Critical Aspect Ratio
L	Low resin content
M	Mid resin content
H	High resin content
X_i	New component I
α	Thermal expansion coefficient
L_o	Initial length of the sample
ΔL	Change in length of the sample
ΔT	Change in temperature experienced by the sample
σ	Thermal stress
F	Force

E	Modulus of elasticity
$\Delta\sigma$	Thermal stress difference between substrate and marking
δ	Solubility parameter
ρ	Density of the amorphous polymer at room temperature
M_o	Molecular weight of the repeating unit
F_i	Molar attraction constant for component I
δ_i	Solubility parameter of the homopolymer corresponding to monomer i
w_i	Weight fraction of repeating unit i
$\overline{M_w}$	Weight average molecular weight
$\overline{M_n}$	Number average molecular weight
M_i	Molecular weight of polymer molecule i
N_i	Number of polymer molecules with molecular weight M_i

Chapter 1

Introduction

1.1 Industry Overview

Roadway markings save lives. (Miller, 1993) The benefit-cost analysis performed by Dr. T.R. Miller in 1993 suggests that longitudinal pavement markings reduce crashes by 21%. They can also result in the improvement of traffic flow during peak hours by increasing average speeds by 3.2 km/hr. The 1993 analysis indicates that every $1 spent results in $60 in cost benefits.

With benefits like these, the importance of good quality, long lasting roadway markings becomes clear. Manufacturers must ensure that their product can withstand the conditions to which it will be subjected. Harsh climates, traffic volume and snowploughing are all factors that will reduce the lifetime of roadway markings. Products should be formulated with consideration for the specific environmental conditions they will face.

The most important factor is marking visibility. If the roadway marking is not visible to the driver, it can be considered non-existent as there will be no benefit to the driver. In areas with ambient light, the marking will be visible if it is not obscured by dirt or debris and not worn or chipped away. In the absence of ambient light, retroreflection is a measure of the marking's visibility. Retroreflectivity is defined as the phenomenon which occurs when "light rays strike a surface and are redirected directly back to the source of light." (Migletz et al, 2001)

Retroreflection is achieved in roadway markings with the addition of glass beads, which act to reflect the light back to the source. Beads can be added to the formulation and/or applied to uniformly cover the marking immediately after application, prior to drying. The application of beads on the surface also helps to initially keep the marking clean, to reduce wear on the marking and to increase visibility in both ambient and non-ambient light conditions.

Once the surface layer of beads has been worn away, the properties of the roadway marking continue to be important as it is necessary that the markings continue to be visible throughout their lifetime. The marking must maintain adequate retroreflectivity, withstand traffic, environmental conditions, and not retain dirt. Once the marking is no longer visible, it is considered to be non-functional, and will then require replacement. Depending on the type and formulation of the marking, service life can vary from 6 months to 7 years. (Miller, 1993)

Traffic paints are the most widely used roadway marking materials. They are inexpensive, fast drying, and relatively easy to install. Drying times can be easily regulated by the amount and type of solvent used. However, solvent use decreases the appeal of paints for environmental reasons. The alternatives are water-borne paints, the drawback is the increased drying time required. Traffic paints have the shortest service life, from 6 – 12 months. They also have poor visibility at night and when wet. (Miller, 1993, Lu et al, 1998, Dale, 1988)

Preformed tapes are also simple to install, and typically have initial appearance and reflectivity 5 – 6 times greater than traffic paints. However, their performance is largely dependent on the pavement conditions and number of pieces used. The service life is 2 – 6 years. Preformed tapes show extremely poor durability on concrete or old asphalt concrete pavements. (Lu et al, 1998)

Methyl methacrylate (MMA) roadway markings can be both sprayed as paints or extruded. This is a developing technology and as such, there is limited information available on their performance. The estimated service life is 2 – 7 years. To date, they have shown good wet and night visibility, good retroreflectivity, as well as good durability. MMA roadway markings can be applied at temperatures much lower than those required for other markings with a minimum application temperature of –3°C. They are expected to perform extremely well in colder climates. Further long-term study is required to provide an adequate comparison with other roadway marking materials currently in use. (Lu et al, 1998)

Thermoplastic roadway markings are also very popular. These formulations typically include a resin binder, pigment, fillers, aggregates, and glass beads. They are more expensive to purchase and apply than traffic paints; however, the service life of 4 – 10 years results in a comparable service life cost. The climate in which these markings are applied is the determining factor in their service life. In more temperate climates, a thermoplastic marking may last in excess of 10 years. However, in a colder climate, the marking may show failure after only one winter cycle. This is due to a number of factors including: (1) low temperature sensitivity of the resin binder, (2) high abrasion due to anti-icing sands, snowploughing and increased tire wear, and (3) failure due to inappropriate application i.e., temperatures too low, freezing or thawing conditions.

Thermoplastic roadway markings are typically applied at a greater thickness than traffic paints, which results in improved wear resistance. The addition of glass beads to the formulation ensures that as it wears, retroreflectivity is maintained. (Dale, 1988) Thermoplastic markings have dry visibility comparable to traffic paints, and exhibit superior visibility in wet conditions. (Lu et al, 1998, Miller, 1993)

Table 1.1 is a comparison summary of these four types of roadway marking materials. (Lu et al, 1998)

Table 1.1: Comparison of Roadway Marking Materials

Traffic Marking Material	Expected Service Life (years)	Typical Marking Thickness (mm)	Lowest Air Temperature for Installation (°C)	Initial Cost of 10.2 cm line ($/m)
Traffic Paint	4 mos – < 1	0.2	7	0.10 – 0.20
Preformed Tape	2 – 6	1.5	13	4.85 – 5.41
MMA	2 – 7	1.0	-3	0.82 – 4.10
Thermoplastic	1 – 7	3 – 7	11	0.98 – 1.31

Figure 1.1 had been adapted to show the comparison of traffic paint, preformed tape and thermoplastic on asphalt concrete when subjected to 6-36" snowfall. (Dale, 1988) The graph shows the expected lifetime of the markings when subjected to various traffic flows, recorded as annual average daily traffic (AADT). Thermoplastic roadway markings have the longest expected lifetime and are thus the choice marking for use in areas with significant snowfall at any rate of traffic flow.

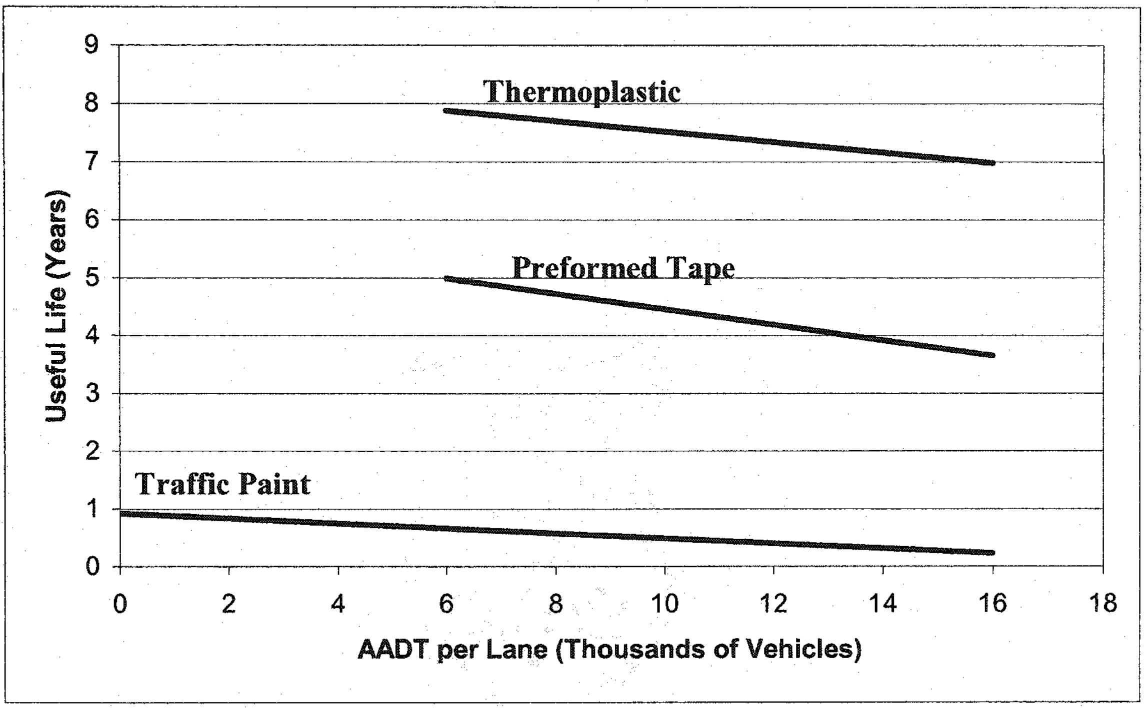

Figure 1.1: Life Expectancy on Asphalt Concrete for 6-36" Snowfall

As the focus of this project is thermoplastic roadway markings, the following discussion will focus on such materials. Thermoplastics are a group of polymers exhibiting the characteristic of being able to melt reversibly on being heated. They are visco-elastic and their properties vary greatly with temperature. The thermoplastic will be hard and brittle below the glass transition temperature (T_g), and soft and rubbery above it. (Ogorkiewicz, 1969)

Typically, thermoplastics are solids at room temperature, become liquid as temperatures are increased, and solidify again on cooling. This is the characteristic that makes them useful as roadway marking materials. There are no solvents used in thermoplastic formulations. Therefore, thermoplastic formulations are preferred over traffic paints for environmental reasons.

A sample formulation is as follows: (Dale, 1988)

Table 1.2: Sample Thermoplastic Roadway Marking Formulation

Material	% by Weight
Resin	18
Pigments and fillers	57
Glass beads	25

Thermoplastic roadway markings are typically manufactured and applied by different groups of individuals. The product is generally available in two different forms from the manufacturer. The majority of thermoplastic material is dry mixed and packaged in thermoplastic bags, which are also part of the formulation. The entire bag can be melted and mixed for application. This leads to some concern that adequate mixing may not be achieved. The alternative is for the manufacturer to melt and mix all of the components during production. The mixture can then be extruded into blocks, which can simply be re-heated prior to application. (Dale, 1988)

Thermoplastic formulations are heated to application temperature, 200°C ± 20°C, in large holding tanks. The tanks are flame heated and therefore must be mixed constantly to eliminate the formation of hot spots. Upon application to the asphalt concrete, the marking is cooled to ambient temperature. The rate of cooling is dependent on the environmental conditions and asphalt concrete temperature at the time of application. Due to the extended periods of time that these formulations are held at elevated temperatures, it is important that they remain stable. The following two graphs show viscosity as a function of temperature and viscosity at approximately 218°C as a function of heating times for two different thermoplastic (TP) formulations. (Dale, 1988)

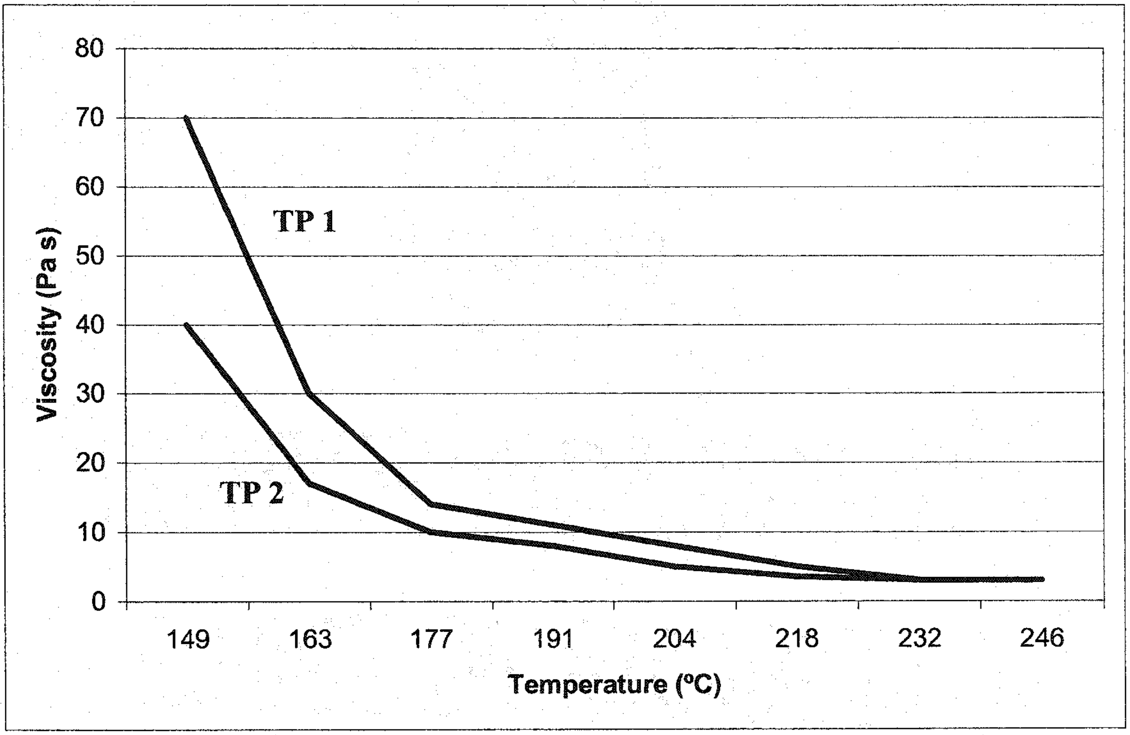

Figure 1.2: Brookfield Viscosity versus Temperature

From Figure 1.2, the viscosity at application temperature of 200°C ± 20°C is below 10 Pa·s. This allows the mixture to flow from the heating tank to the roadway surface. However, it is not too low that the marking will not hold its shape after extrusion onto the roadway.

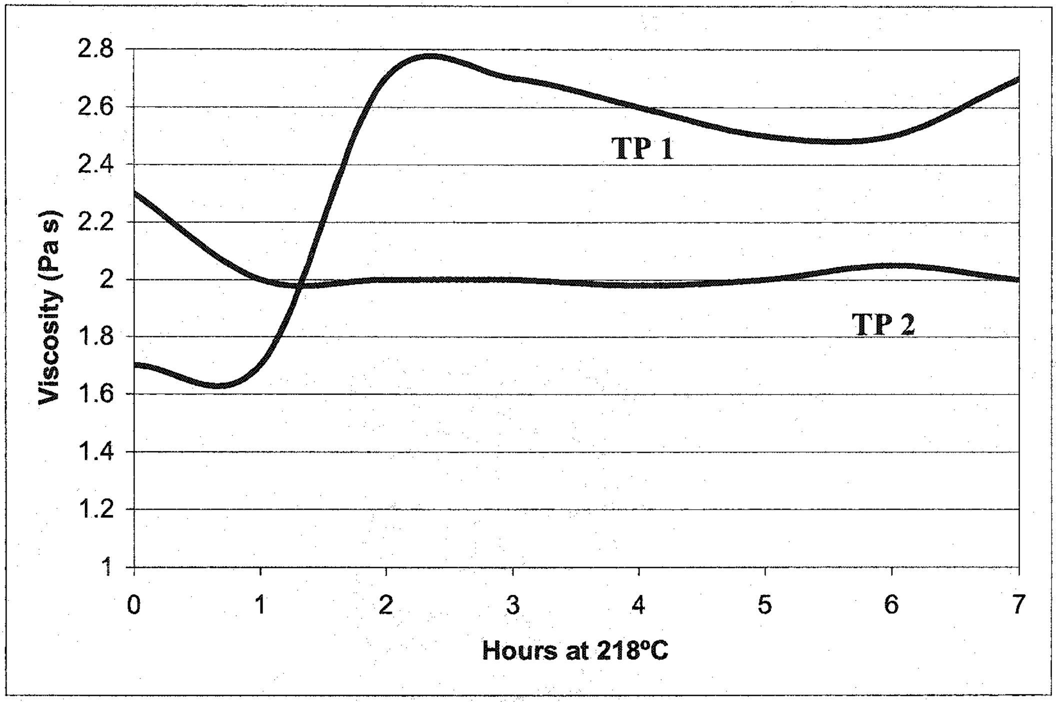

Figure 1.3: Viscosity at 218°C versus Time

Differences in performance will be observed depending on the specific amount and type of polymer used in the formulation. Figure 1.3 indicates that there is some variation in viscosity over time. TP 1 shows an initial increase in viscosity, possibly due to the cross-linking of the polymer molecules, followed by a maximum after approximately 2 hours, and continuing fluctuations at higher viscosities with increasing time. TP 2 shows an initial decrease, possibly due to the degradation of the polymer molecules, followed by a leveling trend after approximately 1 hour. Any trend observed is highly dependent on the formulation tested.

Scorching of the thermoplastic is highly possible during the manufacturing, re-heating and application phases. All of these processes must be done at moderate temperatures to ensure that the formulation is not adversely affected when exposed to extreme temperatures. However, for optimal adhesion of the marking to the asphalt concrete, it is important that the mixture be heated to application temperatures. Figure 1.4 is a representation of the bond strength as a function of application temperature. (Dale, 1988) Optimal temperatures range from 190°C to 200°C, depending on the formulation.

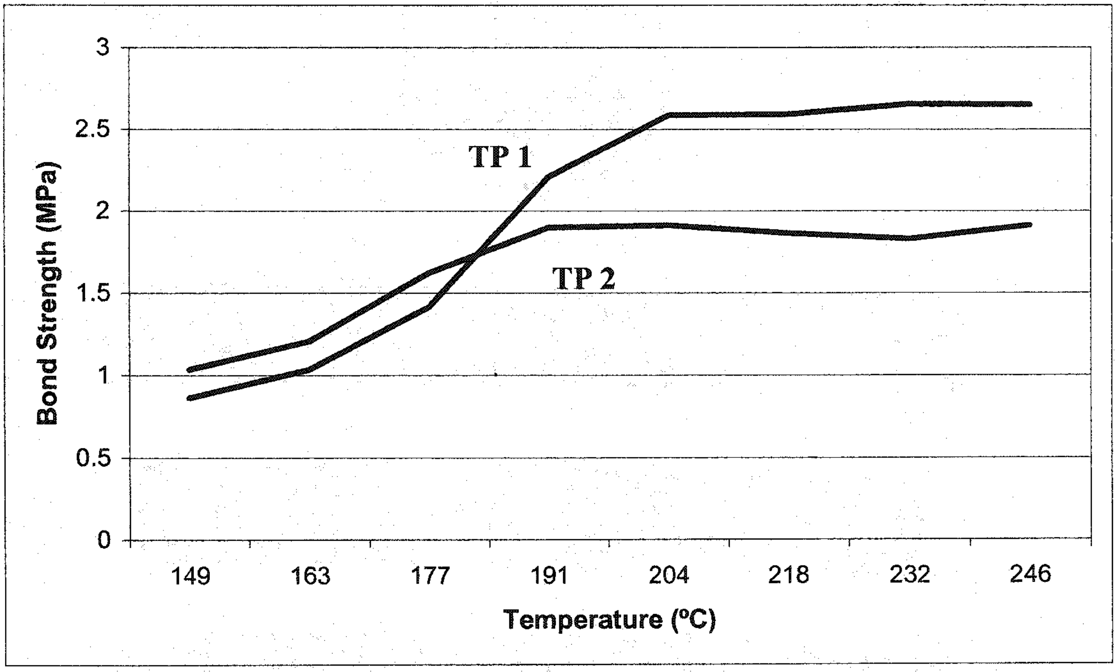

Figure 1.4: Bond Strength versus Application Temperature

There are two methods utilized in the application of thermoplastics. Spraying is used when a thinner marking is required. Extrusion is preferred over sprayed thermoplastics since the resultant markings are thicker and more defined. Extrusion systems were studied in this project. Typical thickness ranges from 2-3 mm for surface laid and 7-9 mm for inlaid roadway markings.

The two methods used in the extrusion of the thermoplastic material are the "dragging die" or shoe method, and the "ribbon extrusion" method. (Dale, 1988) The "dragging die" or shoe method was used in this study. The hot material is released from a holding tank into the die or shoe. The shoe is heated to ensure that the material is not allowed to cool prior to application, and is equipped with a gate, which is controlled by the applicator. It is set to the width and thickness that is required for the specific application. The gate is opened and the shoe dragged forward, resulting in the formation of the marking. The speed at which the application equipment is moving forward is critical to ensuring that the markings are of uniform thickness through the entire length and over the complete job. (Dale, 1988)

The condition of the asphalt concrete is also paramount in the application process. The thermoplastic will have weakened bonding to a wet or dirty surface; therefore, it is critical that the surfaces, depressions, and crevices be clean and dry. However, if the asphalt concrete is sufficiently worn or cleaned too vigorously, resulting in the polishing of the large aggregates, adhesion will also be weakened. The polishing results in a decrease in the roughness of the substrate surface resulting in a decrease in the mechanical adhesion of the marking to the asphalt. Therefore, the asphalt concrete surface should be sufficiently clean to allow the high viscosity material to adequately wet and penetrate into the aggregate and asphalt cement. This will result in the formation of the optimal mechanical and chemical bond between the thermoplastic material and the asphalt cement and aggregate. (Dale, 1988)

Due to the large number of variables in the application process, the marking's performance is highly dependent on the applicator's technique. It is critical that the application crews be well trained and that the markings be frequently inspected to ensure quality is maintained. (Dale, 1988)

1.2 Project Overview

Lafrentz Road Services is the principle formulator and applicator of thermoplastic road markings in the Edmonton area. The bulk of the white thermoplastic material is based on two different formulations. 0320 has shown remarkable resilience in the Edmonton area; however, cracking still occurs significantly earlier than expected. 0333 is the alternate formulation, but it does not exhibit adequate performance, with premature cracking often noted within the first year.

Two different modes of failure have been observed. The first is the transverse cracking of the marking as seen in Figure 1.5. This occurrs across the smallest cross section of the line and occurs consistently in intervals of 10-15 cm. In markings with a greater cross section, cracking is noticed in both the transverse and the longitudinal directions resulting in the formation of rectangles or squares that measure 10-15 cm.

Figure 1.5: Transverse Cracking of Thermoplastic Roadway Marking

The second mode of failure is raveling and chipping along the edges of the markings as seen in Figure 1.6. This is noted to progress more rapidly as the marking ages and is also noted along the cracked edges over time.

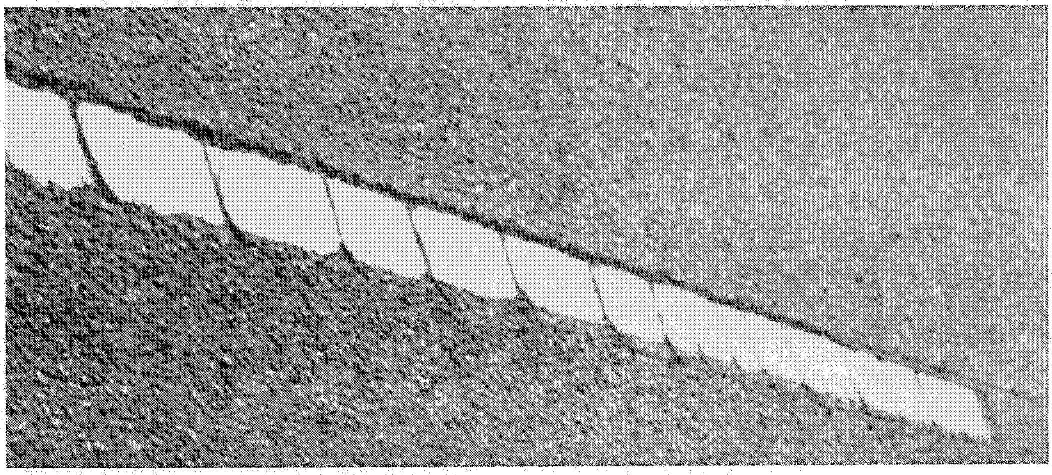

Figure 1.6: Raveling and Chipping Along the Edges

The goals of this study were twofold with the primary objective to determine and explain the mechanisms of failure. This was accomplished with the analysis of the current formulations. Secondly, a modification of the current formulations, based on the information gathered in the determination of the mechanisms of failure, was desired to reduce the incidence of failure. From the understanding of the mechanisms of failure will come an indication of the properties that a superior formulation will exhibit.

Due to the complications associated with the recreation of the cracking, in addition to the fact that any insight into the cause of failure would be highly dependent on the conditions of the experiment and would give limited information about the mechanism of failure and physical properties of the formulations, an alternative direction was required. Comparison of solubility parameters and thermal expansion coefficients of the component polymers indicated that failure was not occurring completely as a result of the incompatibility of the components with each other or with the asphalt. Therefore, it became probable that failure was also affected by a phenomenon being experienced by the component polymers.

If the polymers within the marking crystallize and melt, they introduce stress into the system. As the crystals are formed, there is a larger build up of stresses in the longitudinal direction due to the increased length in that direction. These stresses are not isotropic. The increase in stress in the longitudinal direction results in the formation of transverse cracks to release these stresses. There exists a critical aspect ratio (L/D) above which only transverse cracks would be observed and below which both transverse and longitudinal cracks would occur. L is the length and D is the width of the sample.

If these polymers were experiencing a phenomenon such as a phase transition within the temperature ranges they were operating, significant reductions in the physical properties would be noted. For example, if the polymer were passing through its glass transition temperature, it would change from rubbery to brittle and glassy. Or, if it were to pass through its crystalline temperature, it would result in the formation of brittle crystals. To further enhance the effect of these transitions on the marking system, stresses are built up within the marking as the polymer repeatedly passes through the various transition temperatures. Due to the temperature cycling occurring over the operating lifetime of these markings, significant stresses would have the opportunity to accumulate. As the stresses accumulate, the release of these stresses will become necessary resulting in the fracturing of the marking. For the best performance of the coating system, there should be no transitions occurring within the operating range of the marking. (Schoff et al, 2001)

In-lab testing of the formulations was used to determine which formulation performed best and to ensure that promising formulations met the required standards.

Chapter 2

Material Characterization

In order to characterize and analyze the polymers used in various thermoplastic roadway marking materials, various techniques have been used. Each technique gave an indication of the performance characteristics of the individual polymers as well as the formulations being studied. This allowed for the comparison of the original formulations to newly developed systems. Possible mechanisms of failure were evaluated through the analysis of results from different techniques. In the following sections, the basic principles and experimental procedures of the techniques used will be discussed.

2.1 Experimental Procedures

The same procedure was followed for each formulation to ensure that variation in performance could be solely attributed to changes in components and not preparation differences. Complete formulations were prepared for adhesion, water absorption, and tensile testing. These formulations contained all components including pigments, fillers and aggregates. The type of pigments, binders and fillers were not altered: those used in the original formulations were also those used in these trials.

Since all formulations were based on the original formulations, the main polymer components utilized were the same as the original formulations. These components were placed in a mixing pot on a hotplate and allowed to melt as was done with the original formulations. The mixtures were stirred occasionally to ensure adequate mixing and eliminate the formation of hot spots or overheating. Stirring was done by hand with a metal spatula. Once these components were melted and mixed, additional polymer components were added. These components were mixed and heated for approximately one minute. This allowed for the assessment of the component as a viable option without alteration of the original mixing procedures. After one minute, the remainder of the components (pigments, fillers, aggregates, etc) were added, with sufficient time between additions to allow the mixture to return to mixing temperature. This ensured that the mixture was well mixed and reduced the incidence of overheating if the mixture became too thick.

Once the mixture was completely mixed and all components added, it was heated to application temperature. It was then applied to a non-stick surface using a pre-heated hand held extruder and allowed to cool at room temperature. Once completely cooled, the samples were shaped into adequately sized pieces for the type of testing which was to be conducted. Depending on the type of testing required, multiple samples of the same formulation were required.

Samples for differential scanning calorimetry (DSC) testing were also required. However, due to the small sample size utilized for testing, the polymer components were required without the addition of the various other components such as pigments, fillers, aggregates, etc. For this reason, a slightly altered formulation procedure was utilized for the preparation of these samples.

As with the complete formulations, the main polymer components were heated in a pot on the hotplate, stirring occasionally, until mixed and melted. The additional components were then added. Heating and stirring continued for five minutes. The additional time was required to ensure adequate mixing as no further components were added or heating done. The mixture was then poured into a container and allowed to cool at room temperature.

2.2 Component Comparison

In order to explain the characteristics of the complete formulations, independent studies of the polymer components were carried out. This was because once a complete set of data was established for each of the individual components, it could then be used to describe the performance of the complete formulation.

2.2.1 Thermal Expansion Coefficient

Due to the great temperature range encountered by these materials, one possible failure mechanism was thought to be attributed to the difference in the expansion/contraction rates of the marking and the asphalt substrate. As the temperature changes, the asphalt would expand/contract at a different rate than that of the marking thus resulting in increased stresses within the marking/substrate system. This would lead to the formation of cracks as a means of releasing these stresses.

The thermal expansion/contraction coefficient is an important component property. Thermal expansion is defined numerically as: (Osterkamp et al, 1986)

$$\alpha = \left(\frac{1}{L_o}\right)\left(\frac{\Delta L}{\Delta T}\right) \tag{1}$$

where α is the thermal expansion coefficient of the component (/°C), L_o is the initial length of the sample, ΔL is the change in length of the sample, and ΔT is the change in temperature experienced by the sample. For this study, the values for the thermal expansion coefficients were obtained from literature and not calculated experimentally.

As the object is subjected to an increase in temperature, it will expand and conversely, as it experiences a decrease in temperature, it will contract. If the component is capable of absorbing the stresses that occur as a result of this expansion and contraction, no damage to the component will occur. However, if the component is unable to absorb stresses brought on by expansion or contraction, a failure will occur as a result of the necessity to release the accumulated stresses. (Ochi et al, 1991) Individual component thermal expansion coefficients are important when evaluating the performance of a complete formulation as they are an indication not only of how each component will interact with each other within the system, but also how the system will perform as a whole.

If thermal expansion coefficients are significantly different between components that are immiscible, stresses will build up at the interface of the components until such a time as they can be absorbed by the system, or released in the form of microcracking at component interfaces. (Gupta et al, 1994)

To determine the thermal stresses resulting from a change in temperature, the following equation was utilized:

$$\sigma_{restrained} = E\alpha\Delta T \qquad (2)$$

where $\sigma_{restrained}$ is the thermal stress (MPa), E is the modulus of elasticity of the material (MPa), α is the thermal expansion coefficient (/°C), and ΔT is the temperature change experienced by the system (°C).

It is also possible to determine the thermal stress developed between two components or within a marking, which is being restrained by the asphalt concrete substrate.

$$\sigma_{ACrestrained} = E\Delta\alpha\Delta T \tag{3}$$

where $\sigma_{ACrestrained}$ is the thermal stress (MPa) in the marking which is restrained by the asphalt concrete (AC) and $\Delta\alpha$ is the difference between the thermal expansion coefficients of the marking and asphalt concrete (/°C). (Gaughen, 2000)

2.2.2 Solubility Parameter

Determination of the solubility parameters of the components will allow for an estimation of the degree to which the polymers can be expected to interact with each other when mixed together to form the resin. The following equation was used in the determination of the polymer solubility parameter for each component:

$$\delta = {\rho\sum F_i}/{M_o} \tag{4}$$

where ρ is the density of the amorphous polymer at room temperature, M_o is the molecular weight of the repeating unit, and $\sum F_i$ is the sum of the molar attraction constants which were obtained from literature. (Rudin, 1999)

For random copolymers:

$$\delta_c = \sum \delta_i w_i \tag{5}$$

where δ_i is the solubility parameter of the homopolymer, which corresponds to monomer i, and w_i is the weight fraction of the repeating unit of i. (Rudin, 1999)

Two components will be considered to be soluble if:

$$\delta_1 - \delta_2 \leq 2MPa^{1/2} \tag{6}$$

where δ_1 is the solubility parameter of component 1 and δ_2 is the solubility parameter of component 2. (Rudin, 1999)

A comparison can then be made between the solubility of the thermoplastic polymer resin and the substrate. In the case of the system studied here, the asphalt cement solubility and the thermoplastic resin can be compared to determine the extent to which bonding will occur. This will give an indirect indication of the adhesion that is probable within the systems.

2.3 Failure Analysis

It is important that multiple methods be utilized to compare and quantify the performance of the formulations, both original and promising. The formulations will be subjected to a number of tests, which will quantify their performance under various conditions.

In order to understand the cracking mechanism, an attempt was made to re-create the cracking. It was hoped that by changing the experimental conditions and observing how the marking cracked, some indications as to the cause of the cracking would be determined. This would lead to a set of conditions that could be avoided in order to enhance the performance as well as an indication of the type of materials which may be incorporated into the system to decrease cracking.

Testing of formulations on actual asphalt concrete in the environmental conditions experienced by markings on the roads was very difficult. This developed into an increasingly difficult problem as it became apparent that the asphalt upon which the marking was to be applied was not large enough to result in the formation of cracks. The procedure used to form the asphalt substrate into 10 cm rounds was in accordance with ASTM D1559 standard and assured that the samples prepared were of the same compaction and surface as the actual field surface. However, this process could not be altered to incorporate a larger sample. It was determined that a sufficient sample could be formed with the use of a mold and a compaction machine. Due to the size of the compaction machine, the molds would require approximately 350 lbs of premixed asphalt. The asphalt would then have to be cut into workable lengths. The large volume of asphalt combined with the specialized equipment required made it necessary to seek an alternative course of action.

The motivation for the recreation of the cracking was based on the belief that either the thermal expansion/contraction rates of the marking material and the asphalt concrete were significantly different, or that the individual components of the marking formulation were phase separating. If the thermal expansion/contraction rates were significantly different, but adequate adhesion of the marking to the asphalt concrete was present, the result would be a fracture while maintaining the bond between the marking and the asphalt concrete substrate. However, if adhesion were inadequate, visible fracture would likely not occur as the stresses would dissipate without the restraint of the substrate. The marking would be capable of expansion/contraction independent of the asphalt concrete substrate. If the failure occurred as a result of the phase separation of the components, this would result in a failure within the marking itself and would be independent of the substrate upon which it was laid.

Promising formulations could be applied to road surfaces and monitored over a certain period of time. Testing of large numbers of formulations, combined with the large time requirement to complete such testing necessitates an in-lab study method for promising formulations. These tests provided a method for the comparison of new formulations as well as a means of determining if newly altered formulations were superior to the original formulations.

2.3.1 Taber Abrasion

Taber abrasion testing was the most critical test in this project. Requirements have been set by the City of Edmonton for the abrasion resistance of thermoplastic road markings in use in the Edmonton area. It was therefore critical that any new formulations meet these standards.

Taber abrasion testing was used to determine the abrasion resistance of a material when subjected to conditions that mimic the environmental conditions experienced on a daily basis. Figure 2.1 is a photograph of the 5130 Taber Abraser used in these studies.

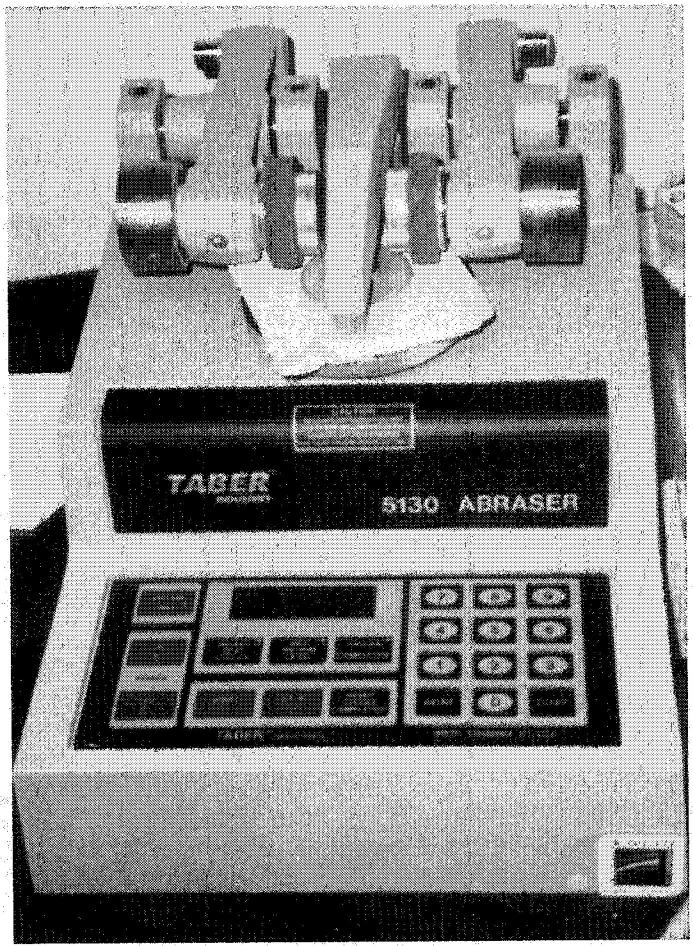

Figure 2.1: Taber Abrasion Tester – 5130 Abraser

The extent of wear observed during testing was dependant on the type of abrading wheels used. Figure 2.2 is a photograph of a set of H-22 Calibrade wheels which were used in this study. The H-22 wheels are among the hardest and most abrasive of the wheels available and were chosen to simulate the conditions experienced on a winter road in the Edmonton area where sand is frequently applied to increase traction in road icing conditions.

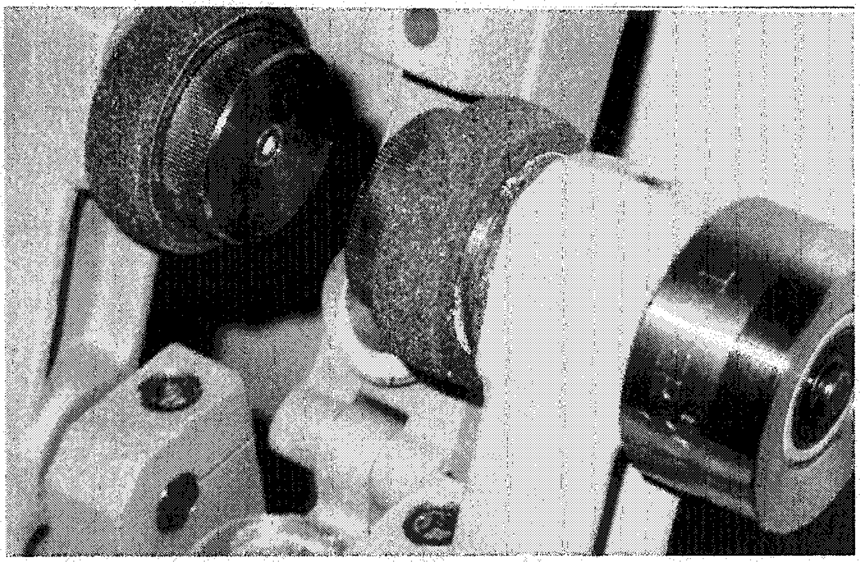

Figure 2.2: H-22 Calibrade Wheels

Abrasion was investigated with the use of a Taber Abrasion Tester in accordance with ASTM D4060. These tests were designed to give an indication as to the wear performance that could be expected from each of the formulations. Tests were completed in accordance with the requirements set out by the City of Edmonton. Samples were run at room temperature with a 500 g weight for 200 revolutions of the H-22 Calibrade wheel kept constantly wet. A loss of material amounting to 0.6 g is the upper limit for the City of Edmonton thermoplastic roadway marking materials.

Samples were weighed dry and allowed to dry overnight prior to re-weighing for weight loss to ensure accurate results. It was determined during water absorption testing that the samples retained water. The revised method resulted in weight losses higher than those expected, as samples tested by the City of Edmonton are weighed wet. This technique was determined to be adequate as the results are comparable to other results and the original formulations were retested using the revised weighing method to ensure consistency.

2.3.2 Adhesion

Adhesion testing was not a requirement for the City of Edmonton; however, it was an important criterion that future formulations exhibit adequate adhesion. The adhesion of the original formulations was felt to be adequate and failure due to loss of adhesion was a not major concern. Adhesion was noted to remain strong with the onset of transverse cracking. The individual pieces resulting from the formation of cracks remained attached to the roadway. Therefore, adhesion testing of the original formulations forms an adequate baseline to which new formulations can be compared.

In-lab studies of adhesion were conducted using the Elcometer 106 Adhesion Tester. Figure 2.3 is a photograph of the testing apparatus.

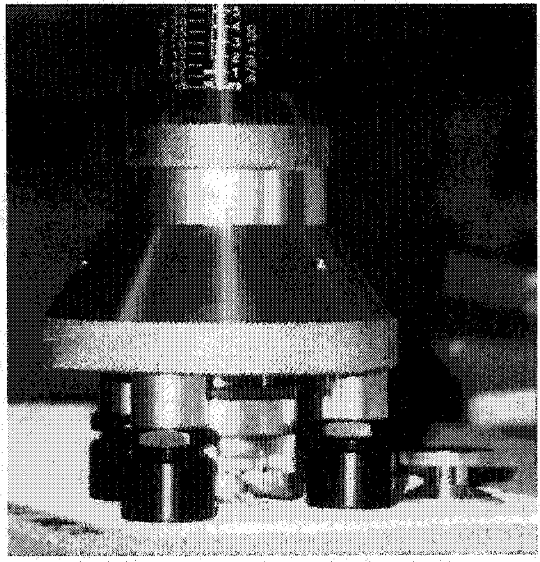

Figure 2.3: Elcometer 106 Adhesion Tester

Asphalt rounds were prepared in accordance with ASTM D1559, which resulted in the formation of samples with the same characteristics as the asphalt, ACO, the main substrate for these systems in the City of Edmonton. The asphalt rounds were wire brushed and then vacuumed to remove any debris that may be present on the surface. This was also done to simulate the cleaning of the surface in the field. All testing was done at room temperature.

A second set of tests was also completed on concrete substrates. Concrete blocks measuring 20cm x 40cm were purchased. The concrete was cleaned with a wire brush and vacuumed prior to application.

The thermoplastic marking material was extruded using the pre-heated handheld extruder directly onto the substrate. The markings were cooled for at least 24 hours prior to the application of the dolly with epoxy. The epoxy was cured for 24 hours prior to the adhesion testing, which was completed in accordance with ASTM D4541.

2.3.3 Molecular Weight Distribution

Degradation of the polymers was a concern as the temperatures used for the processing and application are high and near the upper limits of those suggested by the polymer manufacturers. Degradation of the polymer will result in changes to the polymer properties, which will lead to variations in the performance of the marking. Therefore, it was important to determine the upper limit for heating of the formulations. This would ensure that there was no degradation of the polymer components during the processing or application of the markings.

Molecular weight distribution was a means to determine changes in the molecular weight of polymers after exposure to certain temperatures. It was not considered to be a conclusive method for the determination of polymer degradation; however, it did provide a method for the determination of a critical upper limit for the heating of the components in the processing and application phases. If degradation of the polymer was present, the molecular weight distribution of a unheated component would differ from that of the polymer subjected to heating. The average molecular weight values and polydispersity will show a change.

There are a number of molecular weight averages that can be used to describe a polymer. Two of these were used in this study. Figure 2.4 is a representation of the location of the weight and number average molecular weights in relation to the molecular weight distribution.

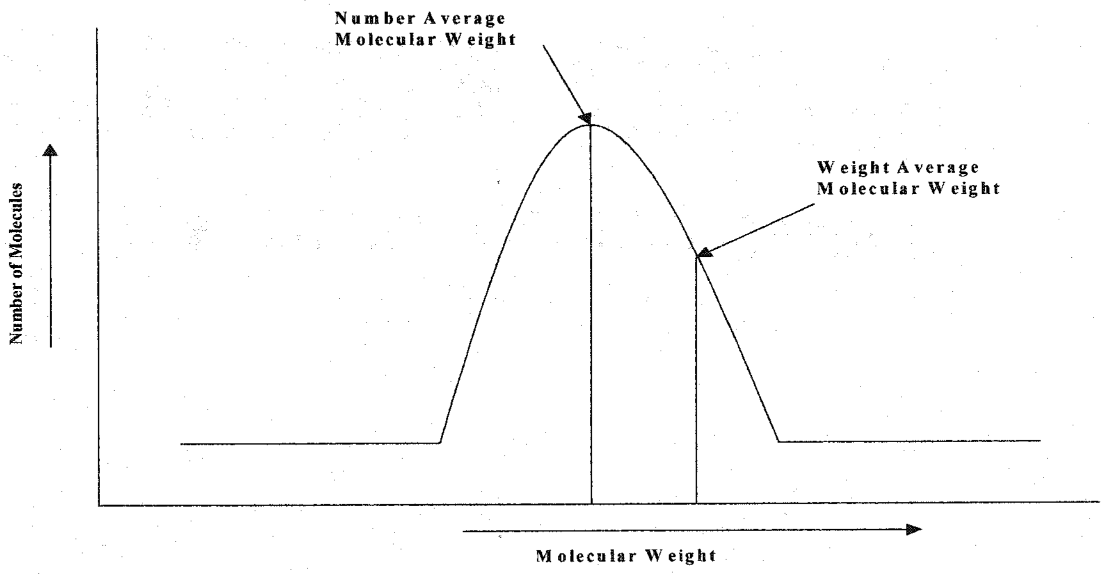

Figure 2.4: Molecular Weight Distribution Curve

The weight average molecular weight is the most meaningful molecular weight when discussing physical properties of polymers. A decrease in the weight average molecular weight is an indication that the average weight of the polymer is decreased, which implies that the polymer chain length is reduced. The reduction in chain length will result in a reduction in properties such as tensile strength due to a reduction in the number of entanglements experienced by the polymer molecules. Similarly, an increase in the weight average molecular weight will indicate an increase in chain length resulting in an increase in the number of entanglements, which will increase tensile strength. Weight average molecular weight is defined by the following expression: (Walker, 1999)

$$\overline{M_w} = \frac{w_1 M_1 + w_2 M_2 + \ldots}{w_1 + w_2 + \ldots} = \sum w_i M_i / \sum w_i \qquad (7)$$

where w_i represents the mass of polymer molecules with molecular weight M_i equal to:

$$w_i = N_i M_i \qquad (8)$$

where N_i is the number of polymer molecules with molecular weight M_i.

Therefore:

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad (9)$$

The number average molecular weight is a representation of the total weight of the material divided by the number of molecules as: (Walker, 1999)

$$\overline{M_n} = \frac{N_1 M_1 + N_2 M_2 + \ldots}{N_1 + N_2 + \ldots} = \frac{\sum N_i M_i}{\sum N_i} \qquad (10)$$

Polydispersity is defined to represent the molecular weight distribution within a polymer sample: (Walker, 1999)

$$PDI = \overline{M_w} / \overline{M_n} \tag{11}$$

The polydispersity of a sample must be greater than or equal to 1 as $\overline{M_w}$ is always greater than or equal to $\overline{M_n}$.

Samples with similar weight average molecular weights can exhibit very different properties based on their polydispersity. They may have a narrow range of molecular weights, low polydispersity, or a very broad range of molecular weights and therefore, high polydispersity. (Walker, 1999)

Samples were prepared at temperatures similar to those experienced in processing and application as well at temperatures 20°C above processing and application temperatures. A final set of samples was heated to extreme temperatures for extended periods of time, in excess of 4 hours. Samples were then tested using Gel Permeation Chromatography (GPC) to determine the average molecular weights and polydispersity.

2.3.4 Water Absorption / Elimination

The degree to which a formulation absorbs, retains and ultimately eliminates water gives an indication of the porosity of the mixture. (Aznar et al, 1997) Water is often absorbed into the microcracks in a system. It is then possible that the water can expand on freezing forcing the opening of the microcrack. The cycle can then be repeated until the microcrack develops into a much larger crack. If the system exhibits minimal retention and quick elimination of the water, less damage should be seen when compared to a system that retains water with limited elimination. It may also be possible for the water to attack the polymer-filler or polymer-aggregate bond resulting in loss of adhesion as is commonly observed in the asphalt cement-aggregate bond. (Young et al, 1998)

A system with minimal absorption and fast elimination is preferred in areas such as Edmonton, which has wet roads combined with near freezing temperatures in the spring and fall.

Samples were formed with hot marking material shaped into small disks weighing 6 –10 grams ensuring that the edges were smooth, which would reduce weight loss due to loss of material. The samples were weighed over a 48 hour period prior to testing to ensure that the samples were adequately cured, thus ensuring that their weight was constant. They were then submerged in distilled water and weighed as the testing continued. After sufficient time had passed, the samples were removed from the water to allow for the elimination of the water. The samples were left at room temperature in the open air and weighed as the testing continued until they maintained a constant weight.

2.3.5 Differential Scanning Calorimetry

Polymers are known to undergo a number of transitions as they pass through certain temperatures. (Walker, 1999) Knowing the temperatures at which these transitions are occurring and the magnitude to which they are occurring becomes very important in the evaluation of each component in the system. The preferred method is differential scanning calorimetry (DSC). The polymer is heated or cooled at a set rate causing it to pass through a phase transition. As the polymer passes through a transition, a difference in the amount of heat required by the polymer to maintain that temperature is noted. This difference in heat flow can be correlated to a specific temperature that is referred to as the transition temperature.

Three transitions are commonly noted in a polymer sample. The glass transition temperature (T_g) occurs when the polymer transitions from a higher heat capacity above the T_g to a lower heat capacity below. Secondly, the crystalline temperature (T_c) occurs when the polymer reaches a high enough temperature above the T_g at which point it has sufficient energy to become ordered, or crystalline. Finally, the melting temperature (T_m) occurs when the polymer is heated above its T_c to a temperature at which there is too much heat in the system causing the crystals to fall apart, or melt. Figure 2.5 is a representation of each of these transitions as they would be seen on a DSC thermograph.

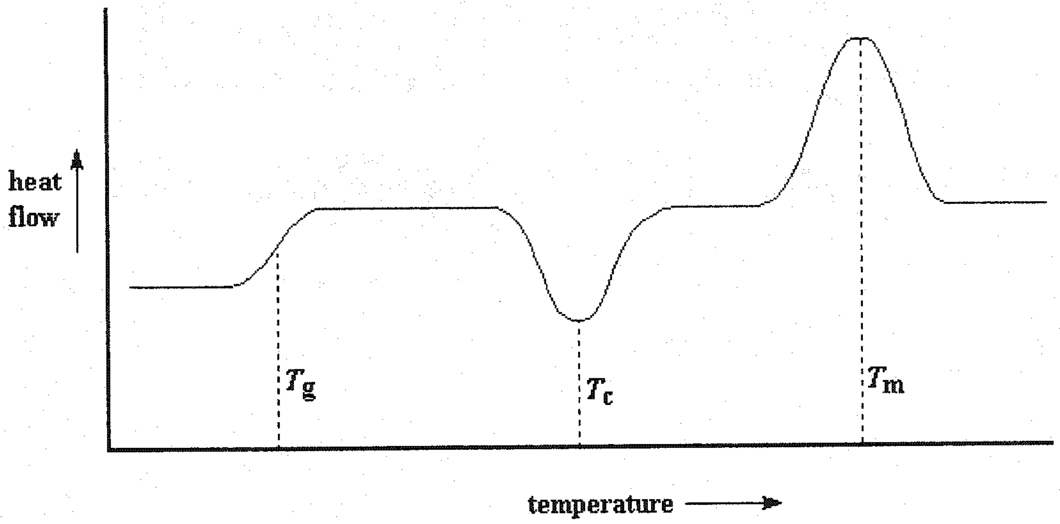

Figure 2.5: Common Features on a Differential Scanning Calorimetry Thermograph

Determination of the transition temperatures for each component as well as the resin mixture is critical. With the knowledge of the transition temperatures for each component it is then possible to determine which component is contributing to transitions that may be occurring within the marking resin systems. Glass transition temperature for the mixture can be determined for miscible components according to the following: (Fried, 1995)

$$m_{mix}T_{gmix} = m_1T_{g\ 1} + m_2T_{g\ 2} + \ldots \qquad (12)$$

This will result in a lower critical temperature for the system. Below this temperature, the mixture will become hard and brittle. The individual components could then be replaced or their percentage within the resin reduced in an attempt to reduce or eliminate the transition within that resin. This will ensure that the stresses built up as a result of transitions occurring within the polymer resins are kept to a minimum.

Samples were prepared as reported earlier with only the polymer components combined. The major components of both formulations as well as the resin of each formulation were run through the DSC over the temperature range of –60°C to 210°C at heating and cooling rate of 20°C/min. These temperatures are approximately 20°C above and below the temperatures normally experienced by the coating from heating for mixing and application to winter road temperatures. Since the environmental conditions to which these formulations are exposed are not constant, an arbitrary heating and cooling rate of 20°C/min was utilized.

2.3.6 Tensile Testing

Tensile testing can be used to determine the mechanical properties of a system, specifically, the magnitude of stress that a system can withstand. (Perera et al, 1981) Once the system has been exposed to various environmental conditions and retested, a determination of the effects of certain conditions on the systems ability to withstand stresses resulting from the thermal expansion and contraction can be made.

Testing was done according to ASTM D 638 with Type V samples cut from a prepared complete formulation. The formulations were prepared as outlined earlier in this chapter. Multiple samples were cut from a single extruded batch with variations in the direction of the cut. Five samples were taken with the direction of testing parallel to the extrusion direction. Five additional samples were taken such that the direction of testing would be perpendicular to the extrusion direction. This was done to determine if a difference in tensile strength could be seen between the samples cut parallel to and those cut perpendicular to the extrusion direction, which would give an indication of a possible alignment of molecules arising from the extrusion of the material.

Chapter 3

Cracking Studies

3.1 Introduction

While trying to determine the mechanism of failure for the transverse cracking of thermoplastic roadway markings, it can be said that, "when failure does occur, generally several mechanisms are going on at that time." (Vallerga, 1981) This leads to a complicated series of events that must be explained if the problem of transverse cracking of roadway markings is going to be understood and new formulations are to be developed.

Due to the uniqueness of both this system and the conditions to which it is subjected, polymer literature was, for the most part, inadequate in providing reference materials. Several coatings sources make reference to cracking of materials upon drying and aging; however, the failure noted is due to the use of solvents. As the solvent evaporates on drying, or other components, such as the plasticizer, leach out over time, the coating becomes brittle and failure is noted. The thermoplastic roadway markings studied did not contain solvents, and the percentage of plasticizer was minimal.

In researching the asphalt concrete substrate, it was found that asphalt concrete has a tendency to transversely crack. The system is similar to the roadway marking systems in that they are both composed of a binder matrix, aggregates, and various other fillers. The asphalt cement matrix is similar in properties and characteristics to a thermoplastic polymer matrix. (Young et al, 1998) A discussion of the transverse cracking of asphalt concrete will provide useful background information for the discussion of the transverse cracking of the thermoplastic roadway markings.

3.2 Transverse Cracking of Asphalt Concrete

The study of the transverse cracking of asphalt cement with the expectation of reducing the incidence and frequency of cracking has been ongoing for a number of years. Transverse cracking of asphalt cement greatly reduces the operational lifetime of the roadway as well as resulting in a great expense for the repair of cracked sections.

Asphalt concrete is a mixture of asphalt cement, aggregate and fillers. The asphalt cement acts as a polymeric binder, and its properties represent the physical and mechanical properties of the entire system. Asphalt cement is essentially a thermoplastic material, which is composed of high molecular weight hydrocarbons. As with a thermoplastic polymer, asphalt concrete exhibits a glass transition temperature (T_g). Above the T_g (~ 140°C), the asphalt cement behaves like a Newtonian fluid, while below the T_g it is hard and brittle and resembles a viscoelastic solid. (Young et al, 1998)

The majority of asphalt cement used worldwide results from the oil or petroleum refining process. This means that the properties such as T_g are highly dependent on the nature of the refining process (additives, processing aids, etc) as well as on the properties of the crude oil or petroleum. (Vallerga, 1981) The structure is typically high molecular weight hydrocarbons ranging in molecular weight from 300 to 2000. They are generally of three different types: (1) aliphatic or paraffinic, (2) napthenic, or (3) aromatic.

The properties associated with viscoelastic asphalt cement are temperature dependent as is expected for a thermoplastic material. This temperature dependence can be linked to changes in viscosity. The greater the rate of change of viscosity with temperature, the greater the asphalt cement's dependency on temperature. Figure 3.1 is a representation of this dependency. The greater the rate of change of viscosity with temperature, the greater the probability of cracking at low temperatures and rutting at high temperatures. (Young et al, 1998)

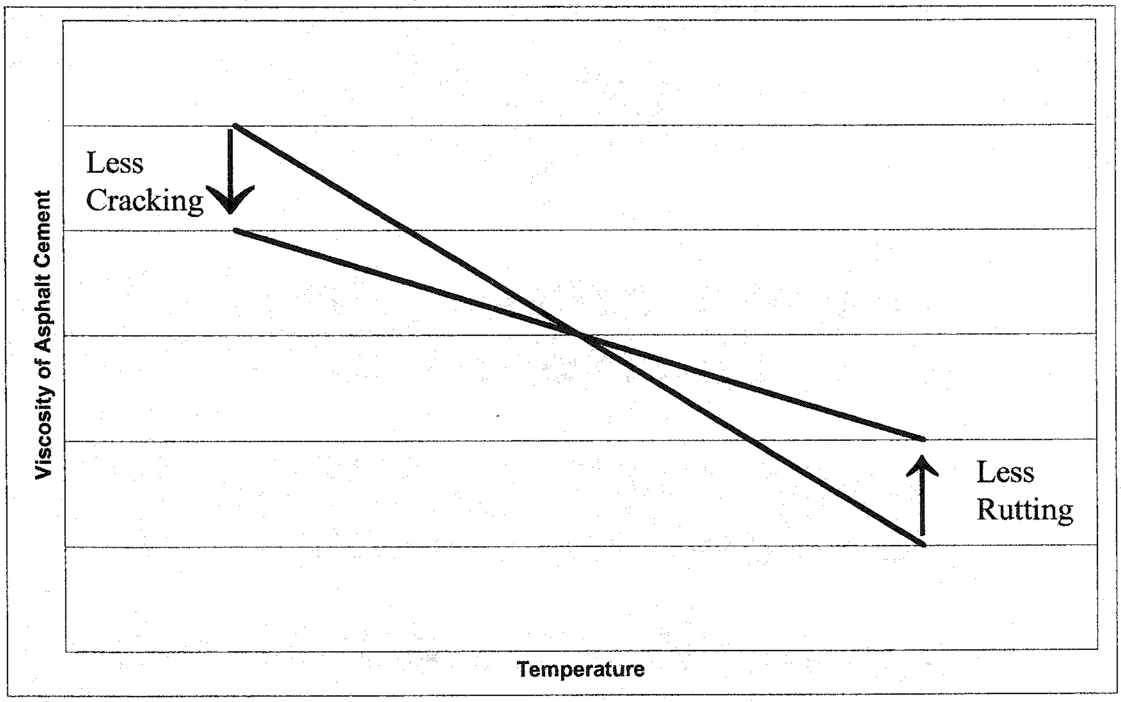

Figure 3.1: Viscosity Dependence on Temperature

The bond between the asphalt cement and aggregate is crucial to the strength and durability of the system. The strength of the bond is dependent on the properties of both the asphalt cement and aggregate. Specifically, the wettability, viscosity, composition, and durability of the asphalt cement, and the surface chemistry, surface texture, porosity, and surface condition of the aggregate are extremely important. (Young et al, 1998)

The most important factor in the determination of the bond strength between asphalt cement and aggregate is wettability. If the asphalt cement is unable to effectively wet the aggregate, a weak bond will result. Factors such as water, which is more polar and therefore exhibits a lower surface energy, will be preferred over the asphalt cement to wet the aggregate surface. This will result in the formation of a water-aggregate bond instead of an asphalt cement-aggregate bond. Bond formation will also be hindered if the asphalt cement is unable to flow into the pores and irregularities on the aggregate surface, due to high viscosity, abnormal loading, or stress concentrations. Water can also cause damage to the asphalt cement-aggregate bond after the bond has been formed. Two possible mechanisms of failure are: (1) the spontaneous formation of an emulsion at the asphalt cement-aggregate interface, or (2) the introduction of surface tension at the air-water-asphalt cement interface causing the asphalt cement film to rupture. (Young et al, 1998)

To further complicate the situation, the asphalt cement is highly processed during the mixing and application of the asphalt concrete. This further alters the properties of the mixture. The most significant changes are due to volatization of light hydrocarbon fractions, and oxidation when reactions occur with environmental oxygen. This leads to the aging of the asphalt cement: it hardens and become less ductile. (Young et al, 1998)

The asphalt cement in the asphalt concrete is in the form of a thick film, therefore, the properties will be different from those obtained in the bulk. This usually results in an increase in the rates of aging and oxidation, (Young et al, 1998) leading to the formation of a more brittle binder and therefore a weaker system earlier than anticipated when calculations were done for the bulk.

The thickness of the film depends on the relative percentage of asphalt cement to the total surface of aggregate. If the system contains a high percentage of asphalt cement, it will result in more viscoelastic mixture. However, if the percentage is low enough so that the asphalt cement is acting as the glue between the aggregates, the system will behave as a solid. The movement of the individual aggregates is restrained resulting in a rigid solid. Sufficient asphalt cement is required to ensure that the aggregate are adequately bound to each other. This higher density, lower percentage asphalt cement system is preferred as the aggregate is more durable than the asphalt cement resulting in a better performance when exposed to operating conditions. However, when these low percentage asphalt cement systems are subjected to repeated vehicle loading, they tend to show a higher rate of failure by fracture or cracking. (Young et al, 1998) The higher percentage asphalt cement systems perform better as they are better able to absorb the stresses associated with vehicle loading.

Another factor affecting the failure, due to repeated vehicle loading, is the tensile strength of the asphalt concrete. The tensile strength is dependent on: (1) the tensile strength of the asphalt cement binder, (2) the percentage of binder used, (3) the adhesion between the binder and aggregate, and (4) the amount of void space remaining after compaction. For rapid loading or low temperatures, the maximum tensile strength of asphalt concrete is 4 – 10 MPa. Tensile strength is extremely important when: (1) the asphalt concrete is subjected to repeated heavy loads at low temperatures, (2) underlying layers are weak, or (3) stresses are built up due to temperature cycling or freeze–thaw. (Young et al, 1998)

Thermal expansion and contraction occur when the system is heated (expansion) or cooled (contraction). This action results in the build up of stresses within the system. The amount of stress built up is dependent on the amount of expansion or contraction occurring. The coefficient of thermal expansion/contraction is approximately 6×10^{-4} /°C for asphalt cement above the T_g and $2 - 4 \times 10^{-4}$ /°C below the T_g. (Young et al, 1998) Stresses can also be introduced into the system via thermal expansion and contraction when different components or layers have different expansion or contraction rates. For example, the thermal coefficient for the aggregates is approximately $5 - 13 \times 10^{-6}$ /°C which is significantly lower than that of the asphalt cement. This leads to the majority of the expansion and contraction of asphalt concrete being as a result of the expansion and contraction of the asphalt cement binder. This also leads to a build up of stress at the asphalt cement-aggregate interface leading to the formation of microcracking.

Thermal coefficients will be affected when components are combined such that certain fillers will restrict the expansion or contraction of the binder. When the fine fillers are added to the asphalt cement, the coefficient of thermal expansion or contraction becomes approximately 6×10^{-5} /°C (Hussein et al, 1998) and the complete asphalt concrete system has a recorded coefficient of approximately 2.5×10^{-5} /°C. (Shen et al, 2001)

Thermal cracking of asphalt concrete occurs via two environmentally induced pathways. Low temperature cracking results from a single drop in temperature below the critical fracture temperature of the asphalt-aggregate mixture. The second is thermal fatigue, which occurs as a result of thermal cycling above the critical fracture temperature. It is a series of repeated temperature fluctuations occurring as a result of daily temperature cycling. This is similar to traffic load induced fatigue cracking, which occurs due to traffic induced loading to the asphalt concrete. (Epps, 2000)

Failure is generally observed in the formation of transverse cracks. The growth of these cracks is nonlinear due to the viscoelastic nature of the asphalt cement. The viscoelastic nature of the asphalt cement results in a decrease in stress at the crack tip. The high percentage of aggregates and fillers results in a tortuous crack growth pathway. The crack must weave through the aggregates and fillers in the asphalt cement stopping and starting as stresses are released and built up. (Hossain et al, 1999)

Cracking may also be induced by decreasing temperatures causing the asphalt cement to contract, but being restrained by underlying layers. (Epps, 2000) The contraction of the asphalt cement matrix may also be restricted by the fillers and aggregates which are present in the system. At temperatures above approximately 0°C, the asphalt cement is viscous enough to absorb the stresses that are introduced. However, below 0°C, the asphalt cement is more brittle and unable to absorb these stresses. The strength of the asphalt cement-aggregate bond is exceeded resulting in the formation of hairline or microcracks. These cracks can then propagate through the asphalt cement matrix releasing stress and resulting in transverse cracking. The formation of microcracks has been hypothesized to lead to the formation of larger cracks via stripping, which is moisture damage to the asphalt cement-aggregate bonds. This is further enhanced with the inclusion of freeze-thaw cycling. (Hussein et al, 1999)

Transverse cracking will occur to release the maximum stress in the longitudinal direction if: (1) the temperature goes below the critical temperature, leading to induced thermal stresses that exceed the tensile strength of the mixture, or (2) the stresses resulting from low temperature cycling exceed the mixture fatigue resistance. For both types of cracking, formation is seen at the top of the layer and propagates down through the layer. (Epps, 2000)

Other factors affecting the cracking are: (1) damage to the asphalt cement during production and over time by age hardening, (2) interactions with the sub-grade, (3) traffic loading, (4) mix aggregate characteristics, (5) layer thickness, and (6) environmental conditions. To ensure optimal performance, a balance between critical temperature and critical stress limits must be found. (Deme et al, 1995) Asphalt concrete mixtures should be selected based on their thermal and mechanical properties, for the environment in which they will be used, to ensure the best performance. (Epps, 2000)

3.3 Transverse Cracking of Thermoplastic Roadway Markings

3.3.1 Introduction

The numerous failure mechanisms noted for asphalt concrete transverse cracking are comparable to those found in this study for the roadway marking materials. The complete system is very similar when comparing the asphalt concrete and roadway marking materials. The matrix in both are composed of long chain, hydrocarbon based materials. The low percentage of matrix binder holds together a very high percentage of fillers, aggregates, and pigments. The function of the total system is highly dependent on the characteristics and amount of binder utilized in both cases.

Through numerous tests, observations, and trial formulations, the marking materials were analysed to determine the causes of failure. The initial investigation into the problem of transverse cracking of roadway markings led to speculation that there may be many different failure mechanisms involved. Comparison with the well documented asphalt concrete systems gave an indication of probable mechanisms of failure. An explanation of how the various mechanisms work together to cause failure was also provided. Tests were then run on the roadway marking materials to determine if similar mechanisms of failure could be defined.

3.3.2 Case Studies

Once markings have been applied to the roadway, there are numerous factors that will affect their performance. The lifetime of the markings will depend on whether they are applied on new or old asphalt concrete, traffic volume, the environmental temperature fluctuations, and numerous other factors. The following photographs illustrate practical examples of roadway marking performance.

Figure 3.2 shows a transversely cracked marking that has adequate adhesion. When examined closely, the cracks are obvious and appear to detract from the markings performance. However, when viewed from a distance, the marking appears intact and completely functional. If the mechanisms of transverse cracking cannot be eliminated, the alternative is to ensure that the adhesion is adequate enough to result in a marking that will remain functional for a long period of time. Ensuring adequate adhesion will also reduce chipping and erosion along the outside and crack edges.

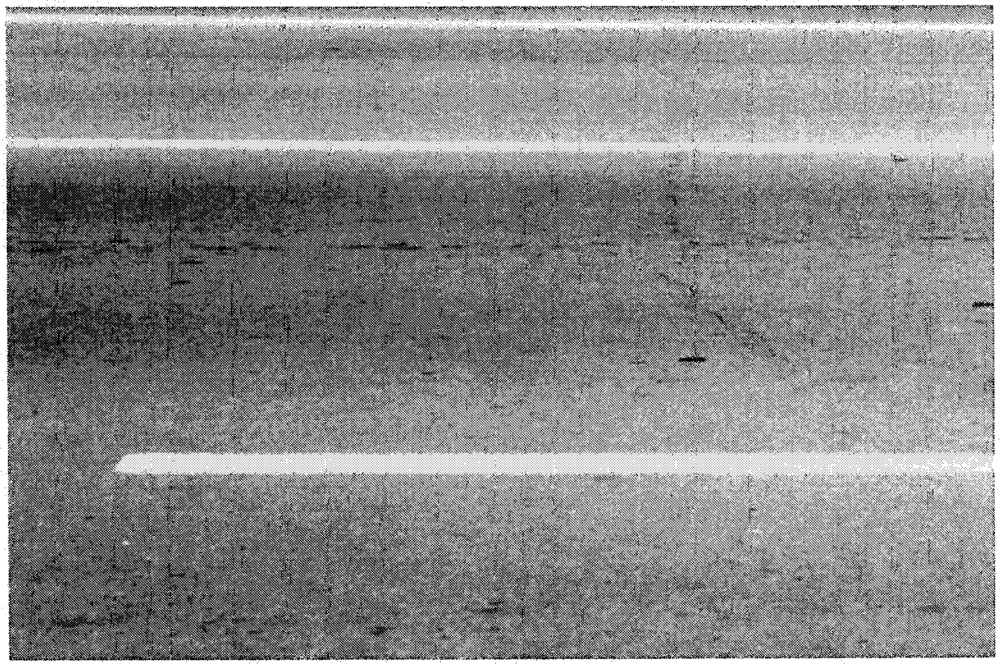

Figure 3.2: Transverse Cracking with Adequate Adhesion

As a marking remains on the roadway, it is subject to numerous conditions that ultimately result in its deterioration. Figure 3.3 represents an aged and severely cracked marking. It is important to note that although this marking is severely cracked, it is still functional, once again, due to adequate adhesion to the asphalt concrete. The outside and crack edges show chipping due to erosion of the asphalt concrete-marking bond, which occurs over time as water and dirt migrate under the marking.

The upper edge of the marking in Figure 3.3 exhibits extreme deterioration at the marking-asphalt concrete interface. Cracking of the asphalt concrete along the edges of the marking occurs since the marking is a white stripe on a black surface. The marking reflects the sun's heat while the asphalt cement absorbs it. This creates an extreme in the thermal expansion properties of the asphalt cement, which is not shared with the marking, causing a crack to develop in the asphalt cement. (Dale, 1988)

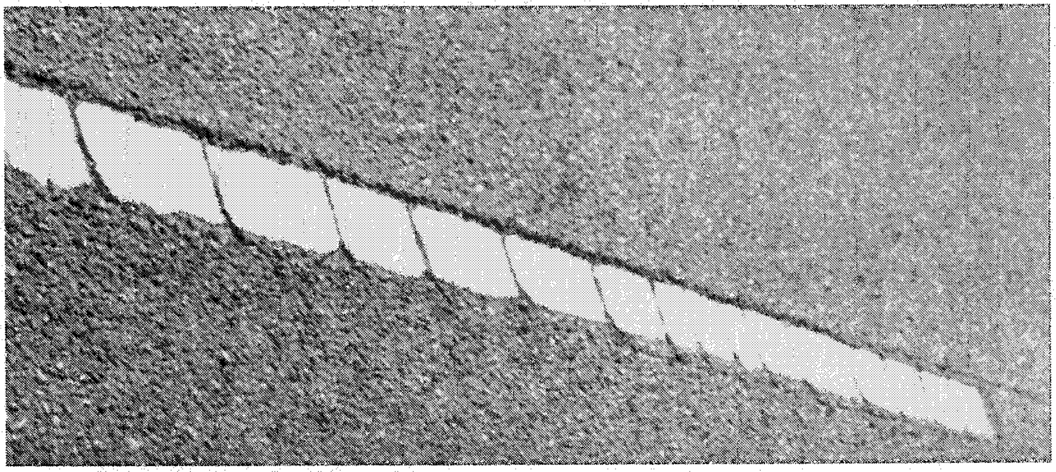

Figure 3.3: Aged and Chipped Marking

Inlaid markings also show transverse cracking as can be seen in Figure 3.4. Once cracking occurs, the marking is more susceptible to erosion of the adhesive bond since the water and dirt can accumulate and settle in the groove. Once loss of adhesion occurs, the pieces will be shattered or pulled out by passing traffic resulting in missing pieces as seen in Figure 3.4. This example represents a still functional marking; however, as adhesion failure continues, the marking will be removed section by section. This photograph also illustrates advanced stages of cracking and chipping along the outside and crack edges. This also contributes to the erosion of the adhesive bond by increasing the area for dirt and water to settle.

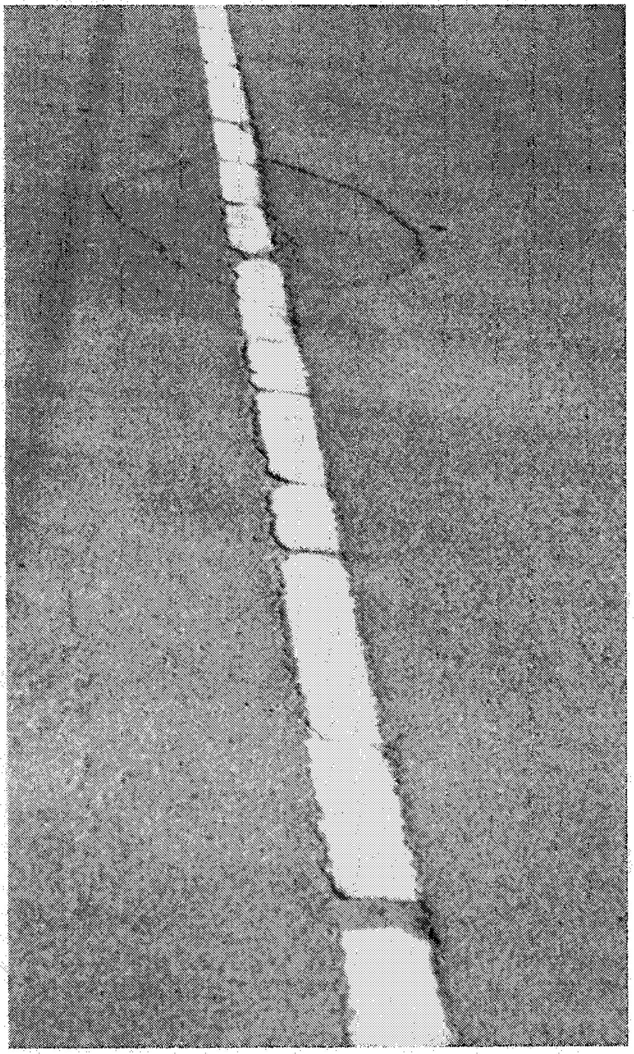

Figure 3.4: Inlaid Marking

Other mechanisms of failure include abrasion. Figure 3.5 illustrates a marking, which suffered severe abrasion due to snowploughing causing the unique striping pattern. This photograph shows that even with severe abrasion damage, the marking continues to function to separate lanes, and was not completely removed. However, the marking is now much more susceptible to chipping and lesser abrasive forces.

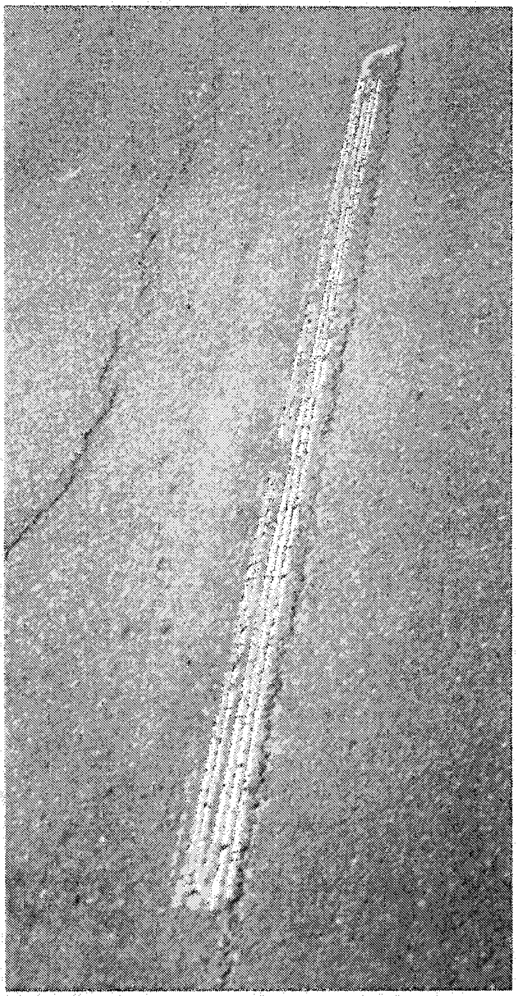

Figure 3.5: Severe Abrasive Damage

A marking, which is not properly applied, will result in a reduction of the bond strength between the marking and the asphalt concrete. This will result in a slight air void between the marking and asphalt concrete, which when driven over by traffic, will be compressed causing the marking to fracture. Figure 3.6 illustrates this phenomenon, showing cracking along the leading edge.

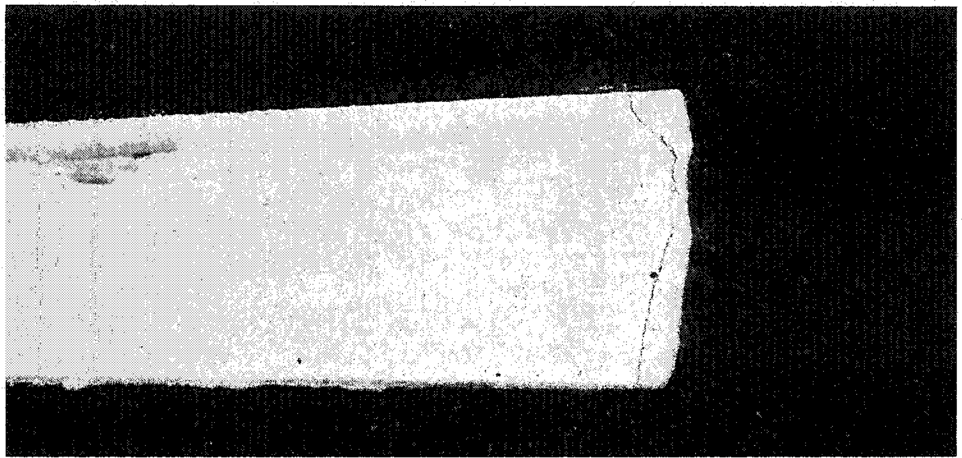

Figure 3.6: Air Void Cracking at the Leading Edge

Markings applied correctly in low traffic areas show extreme resistance to transverse cracking. Figure 3.7 is a photograph of a marking applied in a residential neighbourhood with an average annual weekday traffic (AAWT) rate of approximately 5000 vehicles per weekday. The photograph was taken one year after the markings application in Edmonton.

This marking has been through one complete winter cycle where temperatures were extremely low (-35°C) for extended periods of time. However, due to the location of the marking, traffic volume was minimal. This is an indication that transverse cracking occurs via multiple mechanisms and that cold temperatures alone are not sufficient to cause cracking. Traffic volume above a threshold limit must also be present.

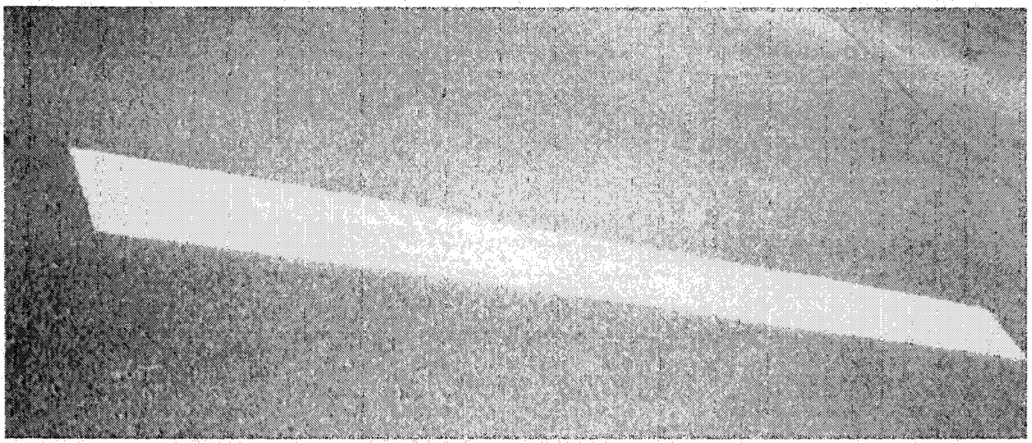

Figure 3.7: Marking After One Year Exhibiting No Transverse Cracking

Since thermoplastic roadway markings are typically applied to areas of high traffic volume, the loading component is generally present to an amount sufficient to induce cracking once temperatures fall below a certain threshold. However, as seen in Figure 3.7, when markings are applied in residential or other areas with low AAWT rates of approximately 5000 vehicles per week, cracking is not automatic once temperatures fall. In comparison, high traffic volume would be in the range of 90,000 to 100,000 vehicles per week.

Asphalt concrete itself is susceptible to transverse cracking, if cracking occurs across a marking, the marking will also transverse crack. Figure 3.8 is a photograph of a marking similar to the one in Figure 3.7, which does not exhibit transverse cracking itself, but due to the cracking of the asphalt has developed a crack following that in the asphalt. This is due to the marking's low strength, which inhibits the marking's ability to remain intack without support below it.

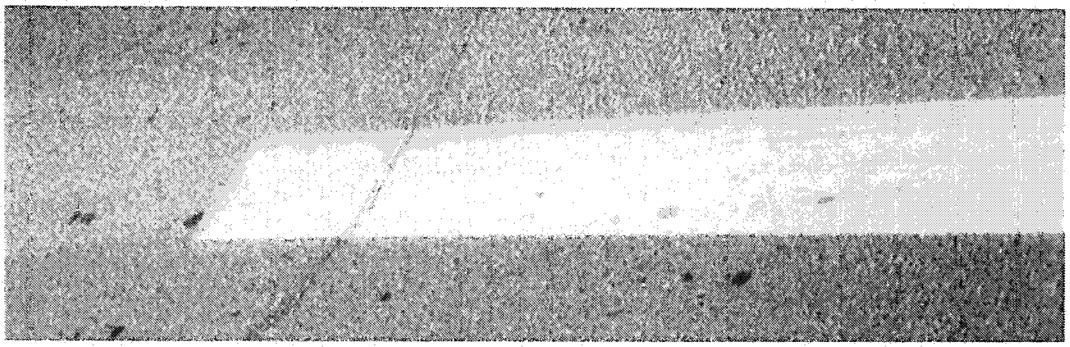

Figure 3.8: Transverse Cracking of the Asphalt Concrete

Abrasive wear of transverse markings in low traffic areas can be seen in Figure 3.9. Wear patterns in the areas of highest traffic concentration are distinct with complete abrasion of the markings in some instances.

Figure 3.9: Abrasive Wear of Transverse Lines at Low AAWT rates

In order to describe the various failures shown in Figures 3.2 to 3.9, an investigation into the properties of the individual components and polymer resins utilized in these formulations is required. With a knowledge of the environmental and loading factors which contribute to these failures, the properties of the components will further explain the mechanisms of failure.

3.3.3 Solubility Parameters

A comparison of the various components for their compatibility within the system and their ability to deal with the various conditions they are subjected to was conducted. Solubility parameters show that the main polymer components are soluble as seen in Table 3.1.

Table 3.1: Solubility Parameters for the Major Components

Component	Solubility Parameter ($MPa^{1/2}$)	
A	16.9 – 17.45	(Small's Method – Appendix A)
B	15.9	(Small's Method – Appendix A)
C	18.0	(Brandrup, 1989)
E	16.46 – 16.64	(Small's Method – Appendix A)
Asphalt cement	18.3	(Toluene solubility)

As can be seen from Table 3.1, the solubility parameters of the components are of similar magnitudes. Components with solubility parameters that are within 2 $MPa^{1/2}$ are considered to be soluble. (Rudin, 1999) Therefore, these components are considered to be miscible and it is unlikely that the phase separation at the polymer-polymer interface can be considered as one of the mechanisms of failure. This is further supported by results obtained from DSC testing as discussed in Section 3.3.7. The solubility parameters are also similar between the polymers and the asphalt. This indicates that there is some intermingling at the interface of the asphalt and the lines. This will increase the adhesion strength.

3.3.4. Thermal Expansion Coefficient

Thermal expansion coefficients were also compared as seen in Table 3.2. Some variation exists between different sources for the values for thermal expansion. The thermal expansion coefficient is dependent on the fillers, aggregates, pigments, etc within the system. Thermal expansion coefficients for the polymer components and asphalt concrete show some difference, however, due to the low magnitude, appear to be a small contributor to the cracking.

Table 3.2: Thermal Expansion Coefficients

Component	Thermal Expansion Coefficient (/°C)
Polymer (B)	$7.3\text{-}8.0 \times 10^{-5}$ (Hall, 1981)
Polymer (C)	$16.0\text{-}20.0 \times 10^{-5}$ (Hall, 1981)
Resin (approximation)	14×10^{-5}
Marking material (approximation)	1.9×10^{-5}
Asphalt cement	18×10^{-5} (Hussein et al, 1998)
Asphalt cement with fillers	6.2×10^{-5} (Hussein et al, 1998)
Asphalt concrete	2.5×10^{-5} (Shen et al, 2001)

The thermal expansion coefficients as seen in Table 3.2 for asphalt cement and component B when looked at in the context of a typical temperature fluctuation in the Edmonton area, can be seen to show a significant difference. For a temperature change of 40°C, which is a typical seasonal change, there is a .0032m/m to .008 m/m change for the polymer components and a .001 m/m change for the asphalt. This is approximately a three to eight fold difference with the asphalt restricting the shrinkage of the polymer. This will result in the development of a stress in the polymer system.

3.3.5 Thermal Stress

Table 3.3 is a summary of the thermal stresses resulting from a 40°C temperature change. (see Appendix A for calculations) These values give an indication of the magnitude of the stresses that will be present when a temperature change of 40°C is observed. These values can be compared to the cohesive strength of the asphalt substrate to determine if the marking will fracture. If the cohesive strength of the asphalt concrete is higher than the thermal stress, the marking will fracture. Alternately, if the cohesive strength is lower, the asphalt will fracture.

Table 3.3: Thermal Stress Resulting from a 40°C Temperature Increase

Thermal Stress (MPa)	Component B	Component C	Resin	Marking
Restrained	3.08	7.2	5.6	0.76
Asphalt Concrete (AC) Restrained	2.08	6.2	4.6	0.24
Average	2.58	6.7	5.1	0.5

After calculation of some measurements for expansion and contraction over certain temperature ranges, the slight differences in the thermal expansion coefficients translate into large differences in contraction and expansion. The difference between the asphalt and marking's thermal expansion coefficients results in approximately a 1% restriction of the marking material's contraction by the asphalt concrete.

These slight differences can translate into large stress accumulations within the marking material. Even daily temperature fluctuations are significant to induce cracking. Thermal stresses can be compared to the cohesive strength of the marking and the asphalt concrete. Thermal stresses are relieved with the cracking of the weaker material. (Gaughen, 2000) When the calculated data for thermal stress is compared to the asphalt concrete cohesive strength (4-10 MPa (Young et al, 1998)), the higher cohesive strength of the asphalt concrete will result in the cracking of the marking to relieve the stresses. However, if the cohesive strength of the asphalt concrete is lower than that of the marking, the result will be the fracture of the asphalt. The marking will also show cracking due to loss of support from the asphalt concrete substrate.

The force exerted by thermal expansion/contraction as seen in Table 3.4 varies depending on the thickness of the line. Sample calculations are available in Appendix A. Inlaid lines are typically 7-8 mm in thickness with surface lines only 2-3 mm. As the winter approaches or if the line is applied on a cool day, stresses are increased due to the increased cross sectional area. Initial cooling in the fall may result in a large enough stress for the line to crack immediately. As the degree of microcracking is increased, the stress required for fracture is reduced, thus aged lines will require forces like those seen in the summer temperature fluctuations. Comparably, a new line may not see cracking even on a cold winter night, if it remains intact for its initial cooling.

Table 3.4: Force Exerted by Thermal Expansion and Contraction

	Initial Cooling		Daily Cycle	
	Summer	Fall	Summer	Winter
Contraction force (N) of the marking–surface laid	5.76	6.3	0.36	1.44
Contraction force (N) of the marking–inlaid	15.36	16.8	0.96	3.84

Thermal expansion and contraction also builds up stresses within the marking material regardless of the substrate upon which it is applied. On cooling, a stress of approximately 5 N can be accumulated for a surface laid material and approximately 15 N for an inlaid marking due to its increased thickness. This is a significant stress for the system to absorb. If the system is unable to absorb these stresses, the stress will continue to increase as cycling continues until such a time as they release leading to the cracking of the marking. Stresses can also build up via traffic cycling over the line. Once again, if the marking is unable to absorb them, the stresses will build up until cracking occurs.

If the thermal stresses are not large enough to result in complete cracking of the marking material, or conversely the asphalt cement, which leads to the marking cracking, microcracks will develop. Once the microcracks are present, the system is more susceptible to failure by lesser stresses.

It is optimal if the marking can absorb the stresses as they are applied eliminating the accumulation of stresses within the system, and therefore eliminating cracking. There are many factors that will limit the marking's ability to absorb stresses. Markings may show reduced ability to absorb stresses as they age due to hardening of the resins causing them to loose elasticity. Markings may also show limited stress absorption if they are below their glass transition temperature (T_g), causing them to be brittle and glassy.

3.3.6 Glass Transition Temperature

Glass transition temperatures (T_g) for the individual components as well as formulations are shown in Table 3.5

Table 3.5: Glass Transition Temperature

Polymer	Glass Transition Temperature (T_g) °C	Method of Determination
A	63	Component Specification
B	-17	Component Specification
C	50	Component Specification
E	-66.9	Component Specification
0320	22	Calculations (Appendix A)
0333	25	Calculations (Appendix A)

Glass transition temperatures (T_g) are an important characteristic in the evaluation of individual components as well as in the formulation as a whole. In immiscible systems, a low T_g component can be combined with a high T_g component such that the low T_g component will be effective in the reduction of brittleness at low temperatures while the high T_g component will increase elasticity at higher temperatures. (Kraton, 2002) However, with a miscible system, which is the type of system studied, the T_g is additive and will result in a single T_g for the complete system. The T_g of the systems studied is between 20°C and 25°C as seen in Table 3.5. This is not an optimal temperature as it is far too high to adequately reduce brittleness at low temperatures and too low to effectively increase elasticity at higher temperatures.

With a T_g of 20°C to 25°C, the components experience thermal transitions a daily basis and become brittle for most of the night cycles. The opportunity for transition into the amorphous region, where stresses can dissipate, will be increasing low. This results in the build up of stresses, and likely the introduction of a great deal of microcracking due to temperature and vehicle loading. The difference in thermal expansion coefficients then becomes a very important contributor to the transverse cracking. With a weakened system from the transitioning, a smaller amount of stress imparted by thermal expansion/contraction is all that is required to fracture the line.

As the marking is brittle below the T_g, it is more susceptible to traffic loading. This leads to an increase in transverse cracking as the tire rolls over the marking imparting a downward force progressively over the length of the line.

The T_g should be well below the environmental temperature lows, or utilize an immiscible system in which one component has a low T_g and the other a high T_g. This would make for a system that exhibits good temperature stability at both temperature extremes.

Along with T_g, there are other transitions that the thermoplastic polymer matrix will undergo as it passes through various temperature. Crystalline polymers will crystallize at certain temperatures so called the crystallization temperature (T_c). This causes a contraction of the system as the molecules arrange into an ordered crystal system. Crystalline systems are rigid and brittle. Alternately, if the temperature continues to rise, resulting in a further increase to the system's energy, the crystals will melt or fall apart (T_m). This results in an expansion within the system as the molecules become random coils. The random nature of the system at this time implies that it is expanded and the molecules have more mobility. This expansion and contraction occurs as the thermoplastic polymer matrix melts and crystallizes, which causes an increase in the stresses within the system.

A semi-crystalline polymer would show promising results within these systems as it would provide the abrasion resistance as well as the ability to absorb stresses. However, it would be imperative that any thermal transitions occur outside of the temperature range encountered by the markings. (Schoff et al, 2001) It would also be important to ensure that the polymer components were compatible to reduce the incidence of phase separation or microcracking between the components.

3.3.7 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to determine values for T_g, T_c, and T_m for the various polymer components and the thermoplastic polymer resins. Figures 3.10 to 3.13 illustrate these transitions for the major polymer components as well as the resin of formulations 0320 and 0333.

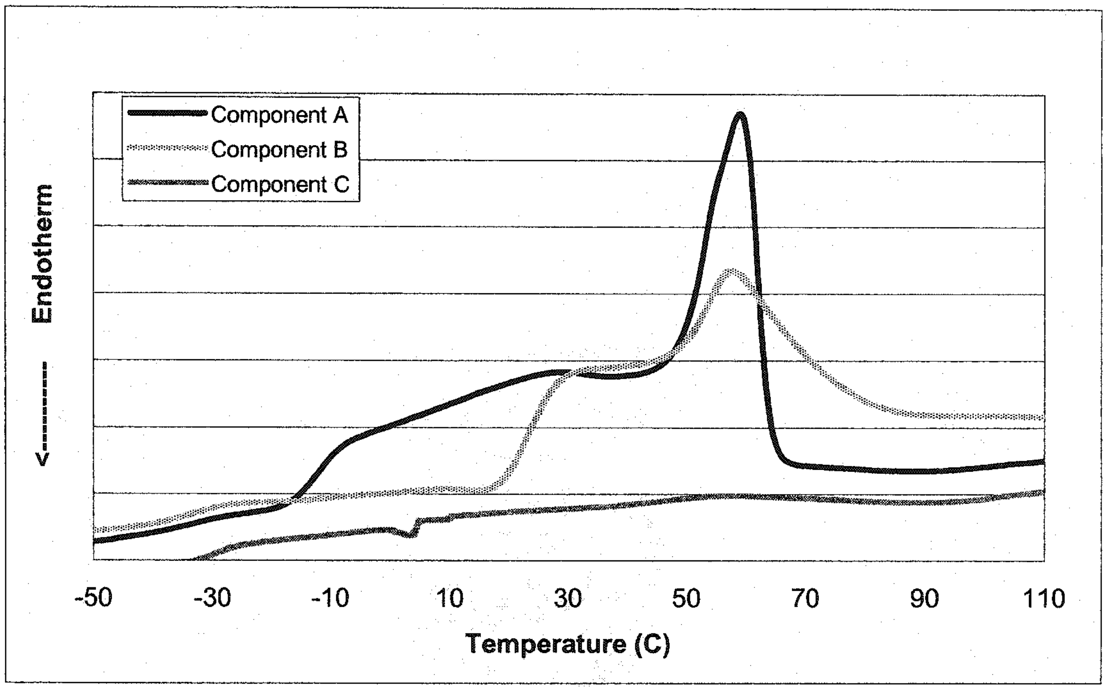

Figure 3.10: DSC Cooling Curve for Components A, B, and C

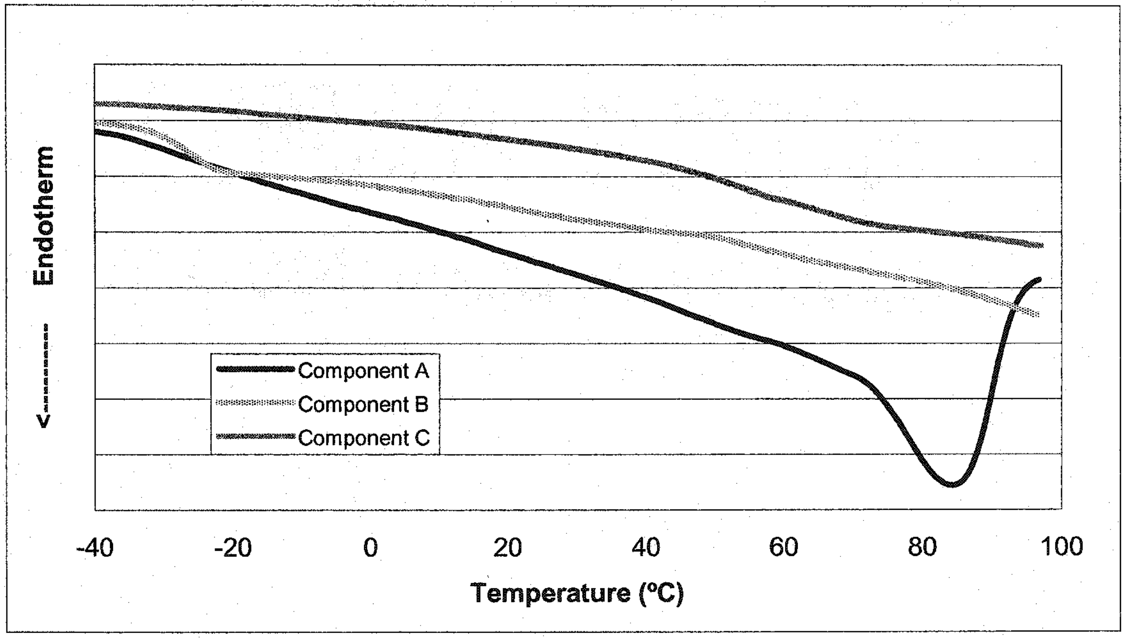

Figure 3.11: DSC Heating Curve for Components A, B, and C

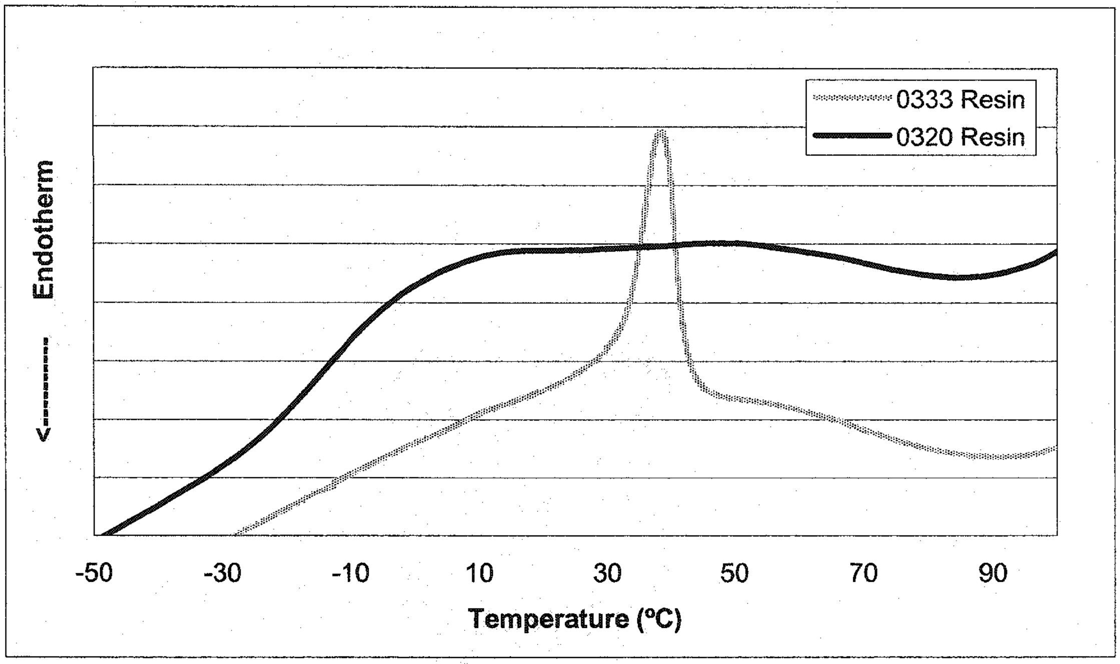

Figure 3.12: DSC Cooling Curve for Resins 0320 and 0333

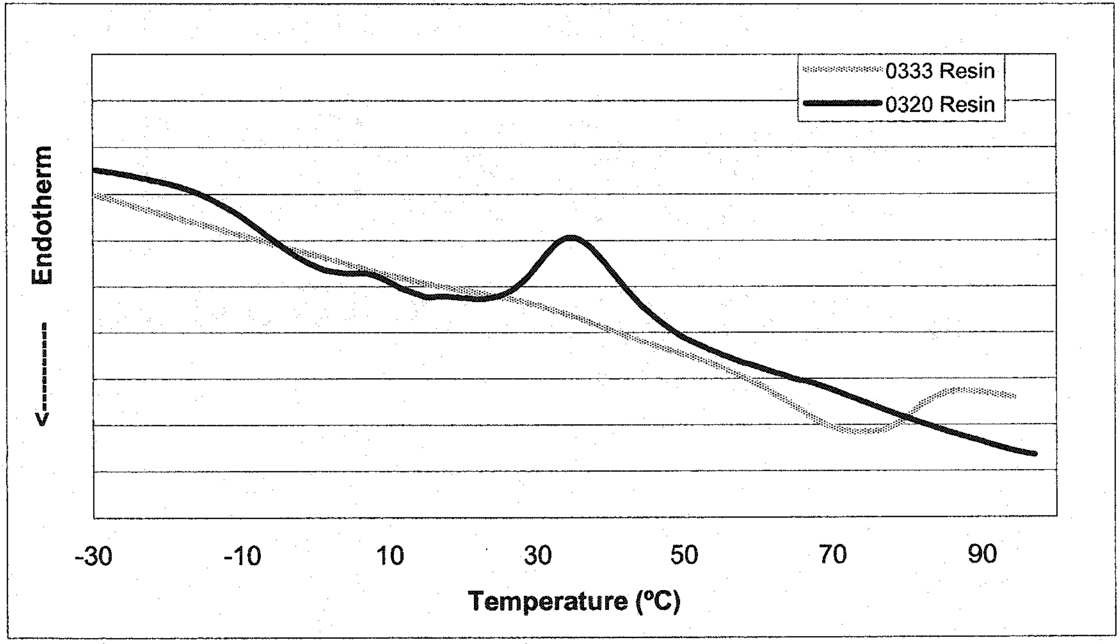

Figure 3.13: DSC Heating Curve for Resins 0320 and 0333

As can be seen from the above figures, there are a large number of transitions occurring over the temperature range tested. Individual components were compared to the resins and it was observed that there are definite contributions from certain components. For example, Component A was responsible for the large crystallization peak as well as the melting trough in Resin 0333. In the combination of components in the resins, transitions seen in individual components have reduced magnitudes or are not seen in the resins due to the components interactions with each other. A good example of this is Component B and Resin 0320.

Resin 0320 and 0333 are definitely different in their transition profile over this temperature range and therefore give a good indication as to the difference in their performance. The drastic crystallization peak at 40°C and melting trough between 60°C and 80°C seen in resin 0333 was likely responsible for an increased failure rate. Once again, this can be related to Component A. Resin 0320 showed a transition at 50°C and melting trough between –10°C and 30°C. This may be due to another component in the resin that was not independently tested. This was possibly the result of the leaching of one of the more volatile components at the above mentioned temperatures. The exact nature of this transition is difficult to determine without a complete description of the additives contained in each component.

Miscibility of the components was confirmed by the presence of a single T_g. The presence of crystallization and melting peaks suggested that there is transitioning over the operating temperature range. All of the transitions noted were dependent on the rates of heating and cooling. This causes difficulty in the determination of transition temperatures that will occur during application, as it is difficult to accurately simulate environmental cooling and heating rates. Since application occurs outdoors in an uncontrolled environment, heating and cooling rates are dependent on the environmental conditions at the time of application causing a variety of cooling rates to which the marking material will be exposed. Therefore, a system, which does not have adverse crystallization or melting properties occurring over the operating temperature range for any cooling or heating rate, would be the ideal system.

The cooling rates also affect the transitions experienced by these components and resins: slower cooling rates result slower transitions of greater magnitude. However, due to the nature of the system and the inability to control application cooling rates or environmental heating and cooling rates, it was not acceptable to solve the cracking problem via variation of cooling rates. It is therefore necessary to reduce transitions within the temperature range independently of cooling rates, via component alteration.

The glass transition of the 0320 resin mixture was seen experimentally on the graph at around 25°C. This was in agreement with that calculated from literature values. Also important was the development of a single glass transition temperature for formulation 0320, indicating that the mixture was miscible. The DSC results for formulation 0333 showed no glass transition temperature. This could indicate that it lies outside of the testing temperature range, but more likely indicates that the resin mixture is highly crystalline and therefore the T_g was not observed for the heating and cooling rates studied. The large melting peak at approximately 75°C and the crystalline peak at 50°C indicate that this formulation became highly crystalline when a rate of 20°C/min was utilized.

The mixing of components can also result in an increase in crystallization if the molecules are such that they "fit" together nicely upon crystallization. This results in a highly crystalline system, which performs poorly as a roadway marking material. T_m and T_c can also be affected as T_g in a miscible system such that there exists a single melting or crystalline temperature, which will be intermediate between the values of the pure components. This could bring the transition temperatures within the operating temperature of the system, which would lead to an increased failure rate.

A slow cooling rate would result in the greatest crystal formation and therefore the worst failure scenario. DSC results at a relatively slow cooling rate show large crystallization and melting peaks. The slower cooling rate will allow for a large amount of time available for the molecules to arrange and thus crystals to form. Faster cooling, which occurs on cooler days, will show less crystallization. Application on a summer day will result in a slow cooling rate and thus high crystallinity. If T_c and T_m occur in the daily temperature cycling range, the result will be a large amount of crystal formation and melting as the temperature fluctuations will be slow and frequent. This will lead to an accumulation of stresses within the system, and therefore, a greater possibility for the cracking of the marking.

3.3.8 Molecular Weight Distribution

Heating of the material above the critical temperatures of the thermoplastic polymer components may result in the breaking of the long chain molecules into smaller molecules. This decrease in M_w would result in the polymer components exhibiting a lower degree of entanglement and thus increase the probability of cracking.

This was observed in the analysis of the molecular weight distribution of components after various heating profiles. The majority of the components were stable for temperatures up to the application temperature. However, at temperatures above the application temperature, degradation of the long chains was more prevalent as can be seen in Table 3.6 and Figures 3.14 and 3.15.

Table 3.6: Molecular Weight Distribution of Components A, B, and C

Component	Heating	M_n	M_w	PDI
A	None	9200	31700	3.4
	Application	9200	31700	3.5
	Overheating	8500	31800	3.8
B	None	1500	16000	10.3
	Application	1500	15800	10.4
	Overheating	1700	14800	8.9
	Burn-off	1300	7100	5.3
C	None	600	1200	1.9
	Application	600	1100	1.9
	Overheating	600	1100	1.8
	Burn-off	635	1100	1.8

Figure 3.14 shows the weight average molecular weight (M_w), which is the average weight of the species in the sample. (Walker, 1999)

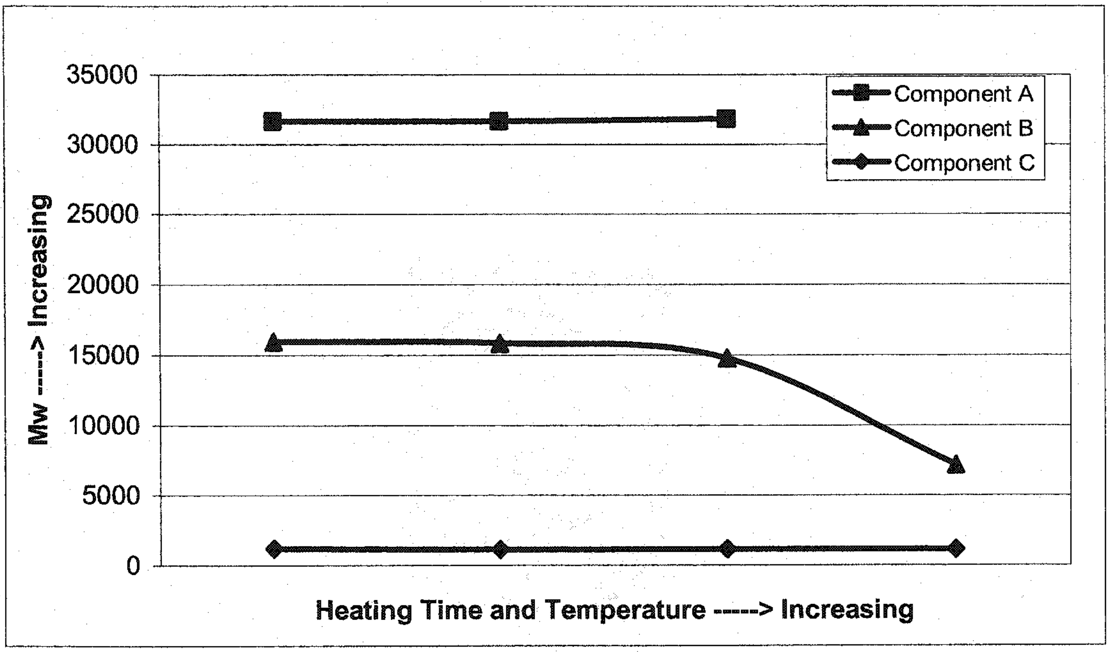

Figure 3.14: Weight Average Molecular Weight (M_w) of Components A, B, and C

M_W can be seen here to remain constant for components A and C as the temperature was increased. A significant difference is noted for component B when it was heated at temperatures much greater than application temperatures for an extended period of time. Component A shows a slight increase as temperatures are raised above application temperatures. However, a large difference was not seen between the virgin polymers and those heated to application temperature.

The number average molecular weight (M_n) is the average number of molecules of each size. (Walker, 1999) Figure 3.15 illustrates that as the temperature experienced by the polymers was increased, Component A showed a decline in M_n values once application temperatures were exceeded. Components B and C showed a slight decline from the virgin polymers to those heated to application temperatures. However, as the temperatures were increased above application temperatures, both showed a slight increase in M_n. Component B once again showed a decrease as extreme temperatures were applied. Component C continued to show an increase. This indicates that some modification to the polymer components with increased temperatures is occurring. To ensure optimal performance of the markings, temperatures should remain low and every effort made to ensure application temperatures are not exceeded.

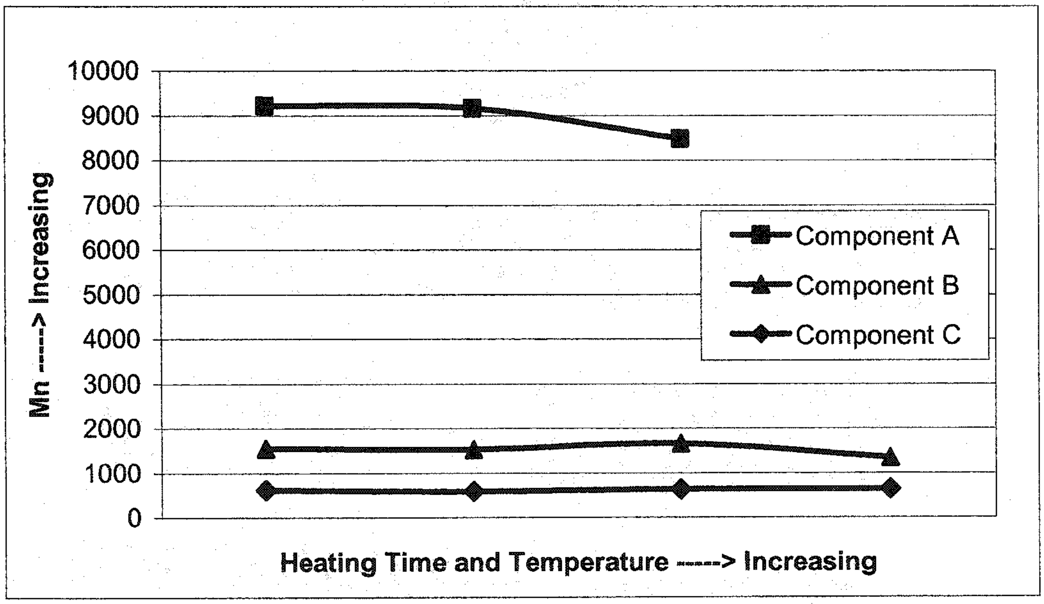

Figure 3.15: Number Average Molecular Weight (M_n) of Components A, B, and C

The other value to take into consideration is the polydispersity (PDI), which is illustrated in Figure 3.16. Component A showed a slightly increasing polydispersity as temperature was increased. This was an indication that as the polymer was exposed to higher temperatures, a greater range of molecular weight components were being generated, possibly due to the break up of the existing components. Components B shows steadily decreasing polydispersity which was an indication that there was some activity in the rearrangement of polymer molecules. It was possible that as the polymer was exposed to higher temperatures, a certain degree of crosslinking occurred. This would lead to a reduction in the smaller molecular weight species. Component B appeared to be particularly susceptible as temperatures were increased above application temperature.

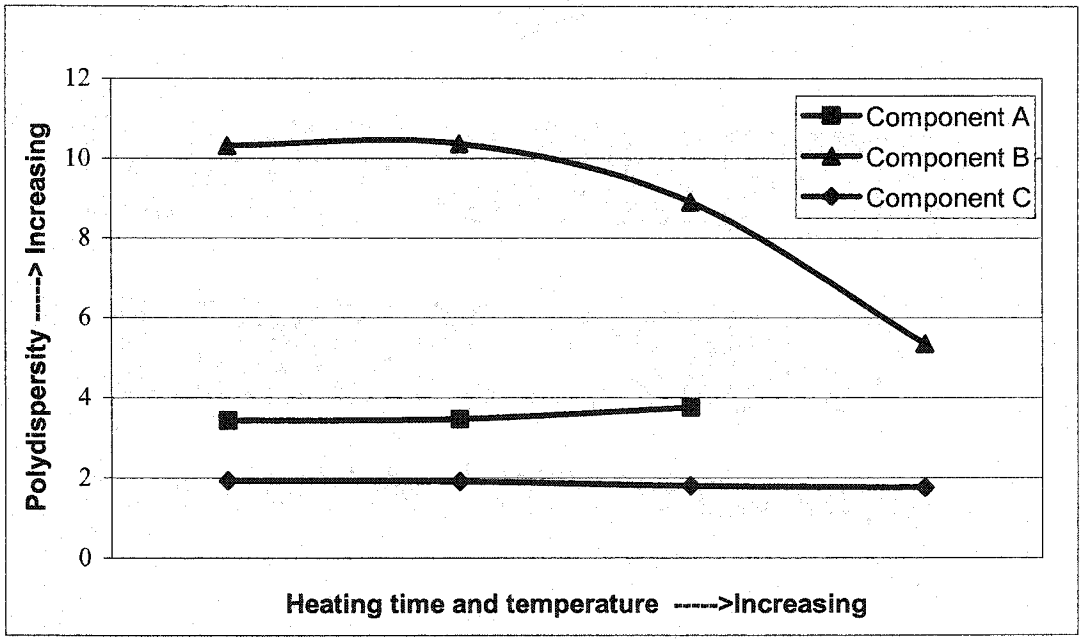

Figure 3.16: Polydispersity of Components A, B, and C

At times, the batches may be overheated either during production or during the re-heating process. This will lead to variations in the properties of the mixture such that it may lead to failure earlier than expected. The thermoplastic polymer components no longer exhibit the properties of the original formulation, which were those that the formulations were based upon. It is important to the function of the marking material that overheating not occur during either the manufacturing or application processes.

3.3.9. Tensile Strength

As stresses are built up within the marking, the tensile strength becomes important as it will determine the magnitude of the stress that the marking can withstand prior to fracture. (Schoff, 2002) When put under tensile strain, the markings fracture in directions perpendicular to the applied force. The fracture begins with microcracking, which grows in the longitudinal direction, as the sample is pulled, until complete transverse fracture occurs. There was no noticeable elongation of the sample. The marking materials exhibit very low tensile strength, which is undetectable with the available equipment. This low tensile strength is due to the high percentage of fillers, aggregates, pigments, etc. This is also in agreement with the asphalt studies discussed. The low tensile strength of the marking materials is an indication that a small magnitude stress can result in fracture. Higher percentages of thermoplastic polymer matrix within the formulation may result in an increased tensile strength. However, it is unlikely that the percentage could be increased such that some elongation of the material would be observed. If an elongation were noted, it would imply that the material was able to absorb a certain loading prior to fracture. This ultimate system would consist of a high percentage of thermoplastic polymer matrix and a low percentage of fillers, aggregates, pigments, etc. This type of system is inadequate in every other aspect.

3.3.10 Taber Abrasion

A better performing abrasion resistant formulation will exhibit a reduced ability to absorb loads from temperature and traffic cycling. However, a better performing stress absorption formulation will show poor abrasion resistance due to the increased percentage of thermoplastic polymer matrix in the formulation. The best performing system will occur with the optimization of the abrasion resistance and stress resistance of the formulation.

Abrasion resistance is an important characteristic for the marking as a cracked line can still be considered functional, but an abraded line is no longer visible and thus not functional. Abrasion is increased in areas of high traffic volumes or at points where traffic tends to pass over the markings (eg. corners, turning lanes, merging lanes). Transverse markings such as crosswalks show high abrasion in the wheel tracks. Winter conditions lead to higher abrasion of the markings, due to the cold temperatures and sand on the roads. Center and side markings are often covered by snow and sand, which also increases abrasive wear.

Snowploughing is particularly abrasive and destructive to the markings. Raised markings are susceptible due to the scraping nature of the snowploughs. The use of profiled markings are therefore not practical in regions where snowploughing occurs. The ploughs not only abrade the marking as they pass over, but also chip at the edges of the marking. Inlaid markings are susceptible to snowplough damage if any erosion has occurred resulting in a space between the marking and the asphalt. As the plough moves along, it will push snow and dirt into the space resulting in a force on the marking as the debris is pushed forward.

Abrasion in the summer differs in that the thermoplastic polymer matrix is softened by the higher temperatures, which allows it to be abraded more easily. Exposed matrix material may also stick to the tires as they pass over, causing material to be carried away on the tires. Abrasion resistance will also be altered as the marking ages. Markings are particularly susceptible to wear when they are new and not completely cured. They are also extremely susceptible to wear when they have significantly aged and are more brittle.

Abrasive wear is also dependant on the type of polymer components utilized in a formulation. Figure 3.17 shows the different weight loss experienced by the two original formulations, 0320 and 0333. It is important to note that the first data point for each formulation represent abrasion testing on beaded surfaces. These results are clearly higher than the City of Edmonton specification of 0.6 g weight loss. Therefore, subsequent testing was conducted on bead free surfaces. As the testing continues into the depth of the samples, the abrasive wear becomes constant with 0333 showing a slightly lower weight loss than 0320.

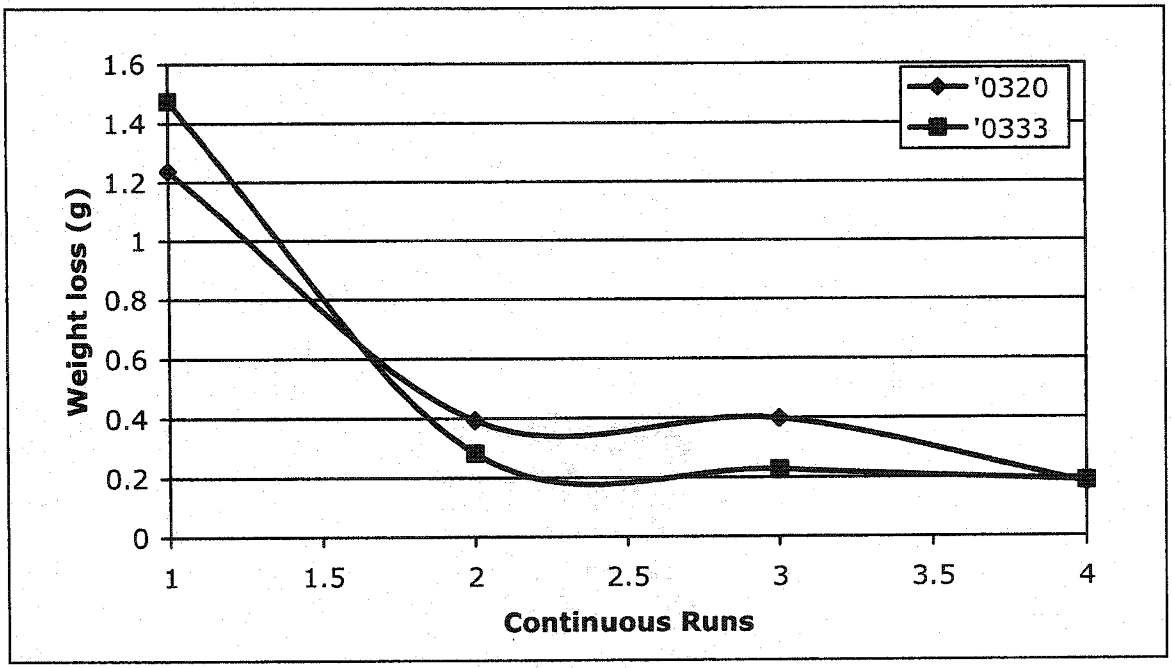

Figure 3.17: Abrasion Resistance of Original Formulations

3.3.11 Adhesion

Even more detrimental to the marking's performance is adhesion failure. When the markings lose adhesion, they are typically destroyed by or removed from the roadway by passing traffic. Adhesion must be sufficient to ensure that the marking fails by other mechanisms prior to adhesive failure. Formulations studied showed good adhesion between the markings and the substrates as seen in Tables 3.7 and 3.8.

Table 3.7: Adhesion on Asphalt Concrete

Sample	Application Temperature (°C)	Adhesion (MPa)
0320-5	0	0.75
		0.50
0320-6	20	1.0
		0.70

0333-5	0	1.0
		1.0
		0.60
0333-6	20	0.7

Table 3.8: Adhesion on Concrete

Sample	Application Temperature (°C)	Adhesion (MPa)
0320-5	0	1.4
		1.3
		1.6
0320-6	20	2.1
		2.5
		2.1
0320-8	60	1.25
		1.4
0333-5	0	0.7
		0.6
		0.9
0333-6	20	1.4
		1.2
		1.2
0333-8	60	1.0
		1.95
		2.0

Adhesion failure did not occur between the coating and the asphalt, but instead in the top layer of the asphalt, when tests were conducted on the asphalt rounds. Since the adhesion bond between coating and asphalt was strong, the result was the cohesive failure of the asphalt substrate. The asphalt cohesive forces tended to be rather low (0.5-1.0 MPa). This showed that the adhesion properties of the coating system were sufficient to ensure the bond between coating and asphalt. However, the strength of the bond between the asphalt and coating could not be determined.

Due to the time required to produce the asphalt rounds and the difficulty in the determination of the bond strength, paving stone concrete blocks were used for further testing. The paving stone concrete blocks were not high quality concrete and thus exhibit lower cohesive strength than would be expected from concrete used in roadway construction. Tests were conducted to determine if the substrate temperature on application was a factor in the adhesive bond. Cohesive failure of the concrete was noted on all samples applied to concrete blocks at 60ºC. Markings applied at 0ºC and 20ºC, showed adhesive failure consistently between 1.2 N/mm^2 and 2.0 N/mm^2 depending on the formulation. This is an indication of the magnitude of the marking-substrate bond. Both formulations showed increased adhesion on the concrete at room temperature.

This was an expected result given that lines applied to concrete blocks at higher temperatures had a slower cooling rate. Therefore, more time was available for the bond formation between the substrate and the thermoplastic. Markings applied to cold substrates had a faster cooling rate and thus a reduced time for bond formation. It is suspected that the markings applied to concretes at 60ºC had even more significant bond formation thus resulting in cohesive failure prior to adhesive failure.

The optimal adhesion temperature varied depending on the formulation and the substrate upon which the markings were applied, as can be seen in Figures 3.18 and 3.19.

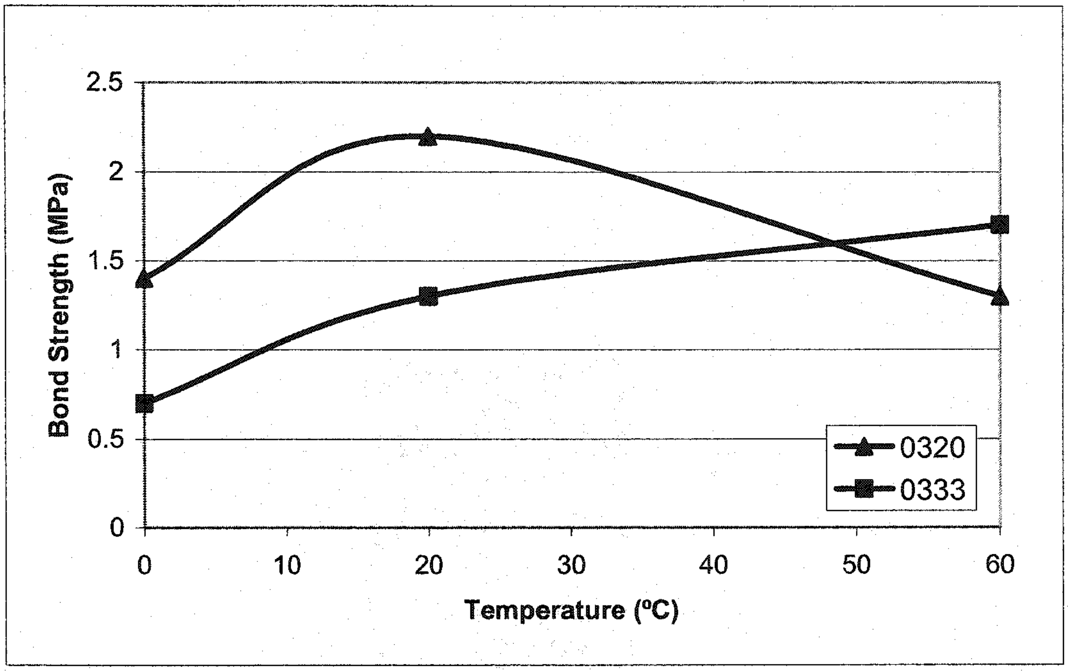

Figure 3.18: Optimal Adhesion Temperature on Concrete

Typically, three tests were conducted for each formulation at each temperature with results obtained ± 0.25 MPa. Formulation 0320 showed the highest adhesion when applied to concrete at 20°C, Figure 3.18. Whereas, formulation 0333 showed steadily increasing adhesion to the concrete substrate over the temperature range studied. However, when testing was completed on the asphalt substrate (Figure 3.19) the reverse was noted, with 0333 showing steadily decreasing adhesion. 0320 shows no maximum adhesion temperature, but instead a steadily increasing trend. It must be noted that the majority of samples studied on the asphalt substrate resulted in cohesive failure of the asphalt. Thus, the results are likely affected by the asphalt cohesive strength dependence on temperature.

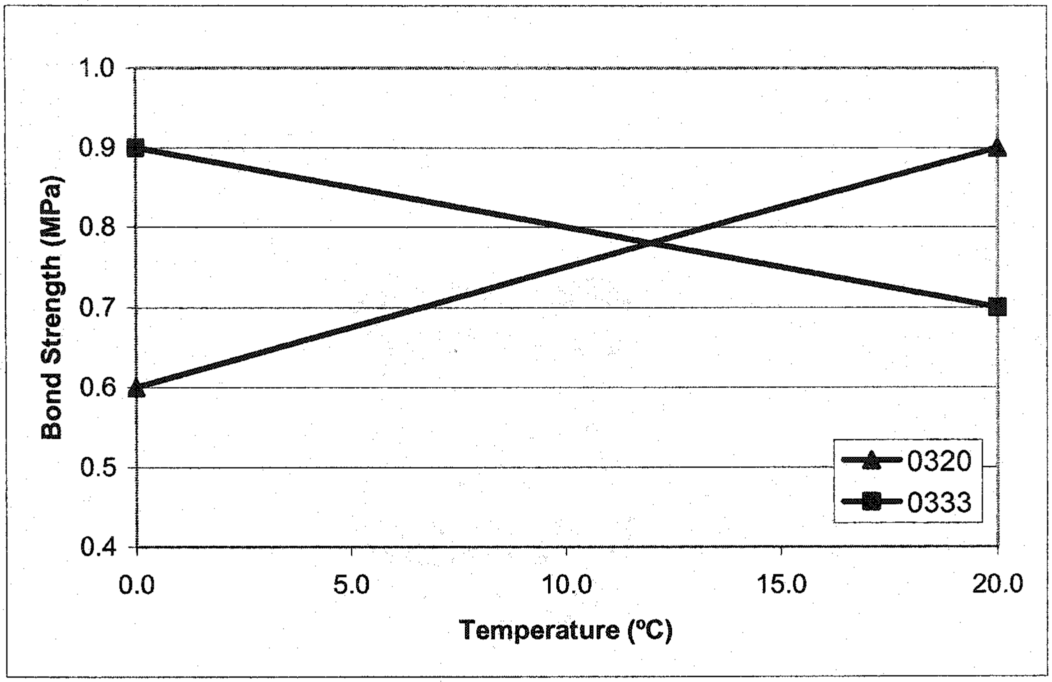

Figure 3.19: Optimal Adhesion Temperature on Asphalt Concrete

Due to the strength of the adhesive bond between the marking and the substrate, there is no slippage occurring as the materials expand and contract at different rates. Reduced adhesion would allow for some slippage, which would reduce the build up of stresses within the marking material. However, the failure would then occur as a result of a loss of adhesion.

Even after fracture has occurred, the pieces remain adequately adhered to the asphalt concrete substrate. The edges of the lines often crack away due to reduced adhesion and voids forming under the edges of the marking. As traffic passes over the lines, they simply snap. After fracture, moisture and dirt can get under the edges of the fractured sections also causing a loss of adhesion. Similarly, as traffic passes over, the edges are cracked and snap away. The effects of snowploughing also leave the edges susceptible to attack by dirt, etc.

3.3.12 Water Absorption and Elimination

Further aiding in the erosion of the adhesive bonds is the presence of water. Water not only aids in the edge erosion, but can also be absorbed by the marking materials. Water causes the markings to swell. (Schoff, 2002) Cycling between wet and dry conditions increases the internal stress of the marking. (Gaughen, 2000) For this reason, low water absorption is preferred. The original formulations studied showed water absorption and elimination as represented in Tables 3.9 and 3.10.

Table 3.9: Water Absorption

Time (hr)	0.25	24.25	120.25	192.25	312.25	336.25
Sample						
0333-4-1	0.09%	0.13%	0.23%	0.25%	0.28%	0.35%
0333-4-2	0.07%	0.13%	0.17%	0.24%	0.27%	0.29%
0333-4-3	0.09%	0.10%	0.18%	0.22%	0.26%	0.28%
0333-4-4	0.08%	0.11%	0.22%	0.23%	0.26%	0.34%
0320-6-1	0.27%	0.30%	0.44%	0.42%	0.49%	0.54%
0320-6-2	0.07%	0.12%	0.16%	0.17%	0.22%	0.19%
0320-6-3	0.06%	0.06%	0.15%	0.23%	0.26%	0.25%
0320-6-4	0.06%	0.10%	0.13%	0.17%	0.17%	0.17%

The systems studied show a high absorption rate, but also a fast elimination rate. However, after significant drying time, the samples continued to show an increase in weight from initial values. This implies that water is being withheld in the sample. This retention of water will further enhance the effect of expansion and contraction resulting from temperature cycling.

Table 3.10: Water Elimination

Time (hr)	0.17	0.33	0.50	0.67	1.0	2.0	2.5	24	72	96	192
Sample											
0333-4-1	0.27%	0.26%	0.26%	0.26%	0.25%	0.24%	0.24%	0.23%	0.22%	0.22%	0.22%
0333-4-2	0.21%	0.21%	0.20%	0.20%	0.20%	0.19%	0.18%	0.16%	0.16%	0.16%	0.16%
0333-4-3	0.20%	0.19%	0.18%	0.18%	0.17%	0.17%	0.16%	0.15%	0.14%	0.14%	0.14%
0333-4-4	0.26%	0.25%	0.25%	0.24%	0.24%	0.23%	0.23%	0.21%	0.20%	0.20%	0.20%
0320-6-1	0.48%	0.47%	0.46%	0.46%	0.45%	0.45%	0.45%	0.43%	0.43%	0.42%	0.42%
0320-6-2	0.12%	0.12%	0.11%	0.11%	0.11%	0.11%	0.11%	0.09%	0.09%	0.08%	0.08%
0320-6-3	0.18%	0.17%	0.17%	0.16%	0.16%	0.15%	0.14%	0.13%	0.13%	0.13%	0.12%
0320-6-4	0.11%	0.10%	0.10%	0.10%	0.10%	0.09%	0.09%	0.07%	0.07%	0.07%	0.07%

Formulations 0320 and 0333 followed a similar trend when exposed to water. Figure 3.20 represents the uptake of water by formulations 0320 and 0333. Initial uptake of water is rapid, within 15 minutes. Continued exposure results in a steady increase in water absorption. Formulation 0333 showed a slightly lower uptake than 0320; however, it showed a rapid increase near the end of the test. This was consistent throughout the samples, indicating that a deterioration of the system may be occurring after prolonged exposure to water. A maximum was not reached such that the graph would level off within the 350 hours for which the study was run. However, Figure 3.20 does show a slowing of the rate of absorption over the study. It is possible that over an increased time study, the maximum absorption would be reached.

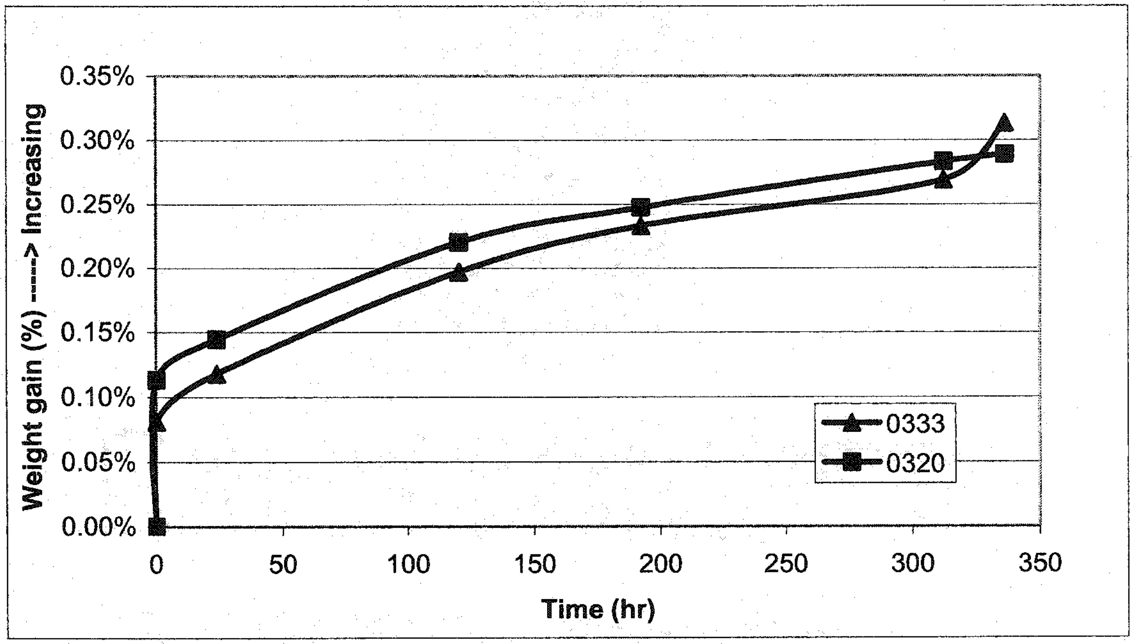

Figure 3.20: Water Absorption of Formulations 0320 and 0333

Elimination of the water was also rapid, occurring within 10 minutes, as seen in Figure 3.21. However, following this elimination, the weight gain remained constant at approximately 0.18%. The amount of water absorbed is not large with less than 0.35% being observed for both formulations. The overall retention of approximately 0.18% in both formulations will be detrimental to the lifetime of the marking. Additional stresses will be accumulated over the heating / cooling and traffic cycling as the water contracts and expands. Also, with this retention of water in the system, a greater opportunity will exist for the water molecules to attack and possibly deteriorate the resin – aggregate bonds.

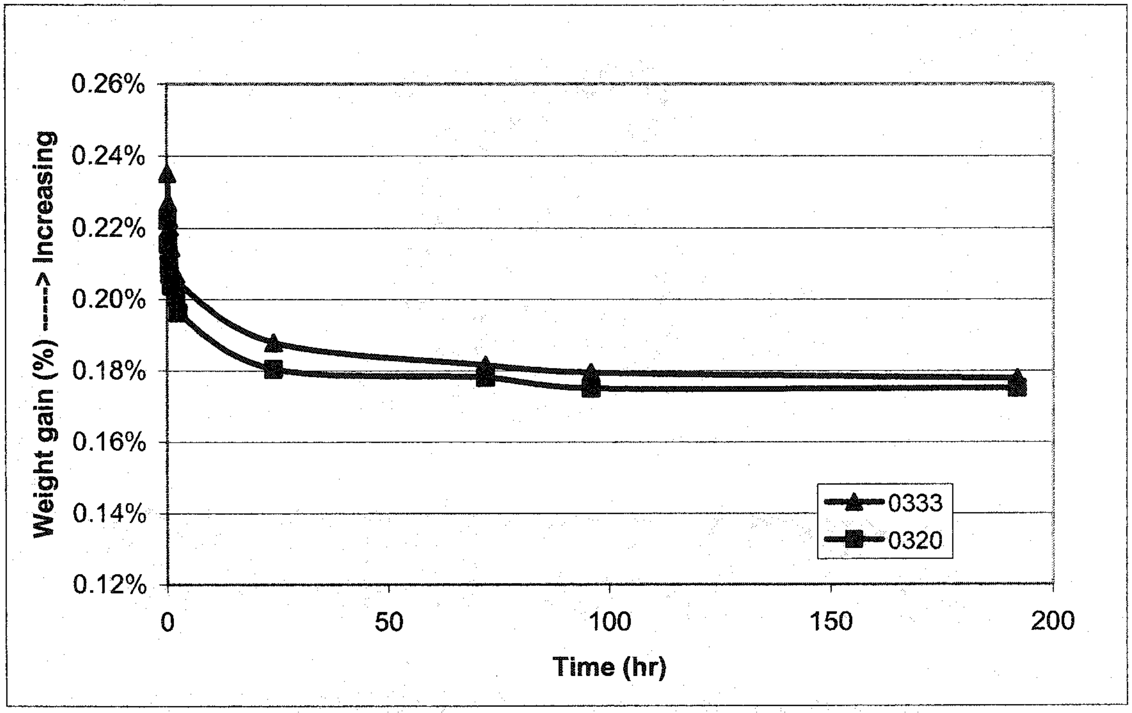

Figure 3.21: Water Elimination of Formulations 0320 and 0333

The presence of popped air bubbles were noted on the surface of the samples: an indication that the water may be attacking the thermoplastic polymer matrix or dissolving one of the fine fillers. This is similar to the asphalt concrete system in that the water can attack the bonds causing them to dissolve.

If microcracking is already present, the water will be able to further penetrate the system, resulting in a greater effect on the system. Microcracks will be forced open as heating and cooling causes contraction and expansion of the water. It is important that the lines not be applied in wet or damp conditions, which would result in the trapping of water between the marking and the asphalt causing the deterioration to begin immediately upon application.

3.3.13 Application Procedures

These mechanisms of failure are enhanced by improper application, as a well formulated marking will show poor performance if applied incorrectly. Alternately, an adequately formulated marking will show satisfactory performance if applied correctly. Substrate properties also affect marking performance.

New asphalt concrete is susceptible to bleeding of the asphalt cement and it can therefore be difficult for the markings to adhere due to the bituminous film covering the aggregate surfaces. Bubbling of the oils can also result on application causing potholes in the marking. New asphalt concrete is also soft and tender in comparison to the strength obtained when they have been given the opportunity to cure. Markings applied to fresh asphalt concrete are often lost due to traffic loading, which results in the failure of the asphalt concrete under the marking, causing the marking to crack due to loss of adhesion. The marking will remove the layer of asphalt concrete beneath it. Allowing new asphalt concrete sufficient time to cure and age prior to application will increase the service life of the marking, however, unmarked roadways are inconsistent with safety. Therefore, a balance must be found in which the optimal performance of the markings is possible while ensuring traffic safety. (Dale, 1988)

Alternately, old asphalt concrete has a tendency to exhibit polished aggregates. This occurs due to repetitive traffic cycling and the wearing away of the top layer of asphalt cement. Mechanical adhesion of the markings to polished aggregate is poor and also results in premature failure due to adhesive failure. (Dale, 1988)

Similarly, as the markings are extruded, the ends may show reduced adhesion, which leads to cracking due to traffic loading. Reduced adhesion is due to a cooling in the material while it is in the holding tank prior to application, or overheating at the shoe. If the markings are applied too hot, they will be brittle due to overheating of the thermoplastic polymer matrix, which will also show a burnt yellow colour. If the markings are applied at temperatures below the application temperature, they will have reduced viscosity and thus will not flow as required. They will not appear flat, but instead, pitted with pull marks throughout. They show higher wear and collect dirt, which reduces their visibility. It is important that adequate time be allowed for the markings to cure prior to allowing traffic to pass over them. This will ensure that the thermoplastic polymer matrix has had sufficient time to dry, which will limit the damage to the marking as well as the amount of dirt that will stick to the marking.

Markings applied to dirty surfaces will not exhibit adequate adhesion due the adhesion of the marking material to the dirt particles instead of the asphalt concrete surface. Ideally, depressions and crevices should be clean so that the marking material can penetrate and make an ideal mechanical and in some cases, chemical, bond. The surface condition is crucial in the thermoplastic bonding due to the high viscosity and therefore, higher difficulty in wetting the surface. It is imperative that the surfaces be clean and dry as there will only be partial adhesion to dirty surfaces, and essentially no adhesion to wet surfaces. When application is done correctly, the asphalt concrete and thermoplastic marking weld themselves together. (Dale, 1988)

3.3.14 Summary of Transverse Cracking Mechanisms

Table 3.11 is a summary of the various mechanisms working to cause the transverse cracking of thermoplastic roadway markings.

Table 3.11: Mechanisms of Thermoplastic Roadway Markings Failure

Types of Failure	Causes of Failure	
	Primary	Contributing
Disintegration	Low abrasion resistance	-insufficient binder -brittle binder due to aging or deterioration -soft binder, aggregates, or fillers -high sanding to prevent icing -studded tires or chains -high traffic flow over markings (merging lanes)
	Debonding of marking/asphalt	-poor asphalt cohesion -deterioration by water and debris -inadequate application -displacement by heavy loading
Fracture	Shrinkage / Expansion	-temperature fluctuations -aging of the polymer resins
	Brittleness	-overheated or too many reheats of the marking material -embrittlement (crystallization) of polymer resins -aging and oxidation or polymer resins -low temperature exposure

	Fatigue	-reduced stiffness or “springy” asphalt concrete substrate -cracks in the asphalt concrete -debonding of marking and asphalt -high traffic loading -low tensile strength -reduction of built up stresses from various other mechanisms -uneven thickness causing temperature gradients

Chapter 4

Experimental Formulations

4.1 Formulations and Results

Due to difficulties with on road, in-environment testing of the markings, a number of formulations were prepared for in-lab testing. Actual preparation of the formulations provided an indication of the viability of the various components in the mixture. The production process required that any addition of new components not alter the current manufacturing or application process. This necessitated the formulation of samples in the lab to ensure that new components could be added without adverse affects to these processes.

A set of samples was formulated in the lab to determine if the addition of certain components would result in improved performance. Variations in resin content and component content were also tested to establish the optimal resin conditions for the systems. Tables 4.1 to 4.4 are a summary of the samples completed for each of the formulations. Actual component names and concentrations are not included due to confidentiality. The following system was utilized in sample identification:

eg. 0320 – MX3 – 2

where 0320 represents the formulation the sample is based upon, M is a concentration identifier: M – mid resin content, H – high resin content, L – low resin content, L1, L2, L3 represent an increasing resin content in a low resin content system, X1, X2, X3, etc.

represent the new components, C1, C2, etc. represent various component ratios, and 2 represents the run number.

Table 4.1: Summary of Samples for Formulation 0320

Sample Identification	Sample Type	Distinguishing Characteristic
0320-1	Complete	Original formulation
0320-2	Complete	Original formulation
0320-3	Resin	Original formulation
0320-4	Complete	Original formulation
0320-5	Complete	Original formulation
0320-6	Complete	Original formulation
0320-7	Resin	Original formulation
0320-8	Complete	Original formulation
0320-LR-1	Complete	Very low resin content
0320-MR1-1	Complete	Mid resin content
0320-MR1-2	Complete	Mid resin content
0320-MR2-1	Complete	Higher resin content than MR1
0320-MR3-1	Complete	Higher resin content than MR2
0320-MR4-1	Complete	Higher resin content than MR3
0320-HR-1	Complete	Very high resin content
0320-MC1-1	Complete	Low component ratio
0320-MC1-2	Resin	Low component ratio
0320-MC2-1	Complete	Higher than MC1 component ratio
0320-MC2-2	Resin	Higher than MC1 component ratio
0320-MC3-1	Complete	Higher than MC2 component ratio
0320-MC3-2	Resin	Higher than MC2 component ratio
0320-MC4-1	Complete	Higher than MC3 component ratio
0320-MC4-2	Resin	Higher than MC3 component ratio
0320-L1X1-1	Complete	Low percentage of X1 added
0320-L2X1-1	Complete	Higher percentage of X1 than L1
0320-L3X1-1	Complete	Higher percentage of X1 than L2
0320-MX1-1	Complete	Mid percentage of X1 added
0320-MX1-2	Resin	Mid percentage of X1 added
0320-H1X1-1	Complete	High percentage of X1 added
0320-H2X1-1	Complete	High percentage of X1 than H1
0320-MR3-L1X1-1	Complete	Mid level resin content, low percentage of X1
0320-MR3-L2X1-1	Complete	Mid level resin content, higher percentage of X1
0320-MR3-H2X1-1	Complete	Mid level resin content, high percentage of X1
0320-MX2-1	Complete	Mid percentage of X2 added
0320-MX2-2	Resin	Mid percentage of X2 added
0320-L2X3-1	Complete	Low percentage of X3 added

0320-L2X3-2	Resin	Low percentage of X3 added
0320-MX3-1	Complete	Mid percentage of X3 added
0320-MX3-2	Resin	Mid percentage of X3 added
0320-LX4-1	Resin	Low percentage of X4 added
0320-LX4-2	Complete	Low percentage of X4 added
0320-HX4-1	Resin	Higher percentage of X4
0320-HX4-2	Complete	Higher percentage of X4
0320-LX5-1	Resin	Low percentage of X5 added
0320-LX5-2	Complete	Low percentage of X5
0320-HX5-1	Resin	Higher percentage of X5
0320-LX6-1	Resin	Low percentage of X6 added
0320-LX6-2	Complete	Low percentage of X6 added
0320-HX6-1	Resin	Higher percentage of X6
0320-HX6-2	Complete	Higher percentage of X6

Table 4.2: 0320 Observations

Sample Identification	Observations
0320-LR-1	Very low viscosity, unable to liquefy for application
0320-MR1-1	Overheated on heating to application temperature
0320-MR1-2	Not comparable to original formulations – too thin
0320-MR2-1	Visually comparable – promising formulation
0320-MR3-1	Visually comparable – promising formulation
0320-MR4-1	Not comparable to original formulations – too thick
0320-HR-1	Very high viscosity, far to liquid for application
0320-L1X1-1	X1 did not dissolve or mix with the main components
0320-L2X1-1	X1 did not dissolve or mix with the main components
0320-L3X1-1	X1 did not dissolve or mix with the main components
0320-MX1-1	X1 did not dissolve or mix with the main components
0320-MX1-2	X1 did not dissolve or mix with the main components
0320-H1X1-1	X1 did not dissolve or mix with the main components
0320-H2X1-1	X1 did not dissolve or mix, unable to liquefy
0320-MR3-L1X1-1	X1 did not dissolve or mix with the main components
0320-MR3-L2X1-1	X1 did not dissolve or mix with the main components
0320-MR3-H2X1-1	X1 did not dissolve or mix, unable to liquefy
0320-MX2-1	X2 did not dissolve or mix with the main components
0320-MX2-2	X2 did not dissolve or mix with the main components
0320-L2X3-1	Not comparable to original formulation – overall
0320-MX3-1	Visually comparable – promising formulation
0320-LX4-2	Not comparable to original formulation – overall
0320-HX4-2	Not comparable to original formulation – too thick
0320-LX5-2	Not comparable to original formulation – overall
0320-HX5-1	Not comparable to original formulation – too thick
0320-LX6-2	Not comparable to original formulation – overall
0320-HX6-2	Not comparable to original formulation – overall

Table 4.3: Summary of Samples for Formulation 0333

Sample Identification	Sample Type	Distinguishing Characteristic
0333-1	Complete	Original formulation
0333-2	Complete	Original formulation
0333-3	Resin	Original formulation
0333-4	Complete	Original formulation
0333-5	Complete	Original formulation
0333-6	Complete	Original formulation
0333-7	Resin	Original formulation
0333-8	Complete	Original formulation
0333-MR1-1	Complete	Mid resin content
0333-MR2-1	Complete	Higher resin content than MR1
0333-MR3-1	Complete	Higher resin content than MR2
0333-MR4-1	Complete	Higher resin content than MR3
0333-A1-1	Resin	Component A1 added
0333-A2-1	Resin	Component A2 added
0333-A3-1	Resin	Component A3 added
0333-A4-1	Resin	Component A4 added
0333-A4-2	Complete	Component A4 added
0333-A5-1	Resin	Component A5 added
0333-A5-2	Complete	Component A5 added
0333-A6-1	Resin	Component A6 added
0333-A7-1	Resin	Component A7 added
0333-A7-2	Complete	Component A7 added
0333-L1X1-1	Complete	Low percentage of X1 added
0333-L2X1-1	Complete	Higher percentage of X1 than L1
0333-MX1-1	Complete	Mid percentage of X1 added
0333-MX1-2	Resin	Mid percentage of X1 added
0333-HX1-1	Complete	High percentage of X1 added
0333-MX2-1	Complete	Mid percentage of X2 added
0333-MX2-2	Resin	Mid percentage of X2 added
0333-L2X3-1	Complete	Low percentage of X3 added
0333-L2X3-2	Resin	Low percentage of X3 added
0333-MX3-1	Complete	Mid percentage of X3 added
0333-MX3-2	Resin	Mid percentage of X3 added
0333-LX4-1	Resin	Low percentage of X4 added
0333-LX4-2	Complete	Low percentage of X4 added
0333-HX4-1	Resin	Higher percentage of X4 added
0333-HX4-2	Complete	Higher percentage of X4 added
0333-LX5-1	Resin	Low percentage of X5 added
0333-LX5-2	Complete	Low percentage of X5 added
0333-LX6-1	Resin	Low percentage of X6 added
0333-LX6-2	Complete	Low percentage of X6 added

Table 4.4: 0333 Observations

Sample Identification	Observations
0333-A1-1	A1 did not dissolve or mix, Melt Index too low
0333-A2-1	A1 did not dissolve or mix, Melt Index too low
0333-A3-1	A1 did not dissolve or mix, Melt Index too low
0333-A4-2	Not comparable to original formulation – too thick
0333-A5-2	Not comparable to original formulation – too thick
0333-A6-1	A1 did not dissolve or mix, Melt Index too low
0333-A7-2	Not comparable to original formulation – too thick
0333-L1X1-1	X1 did not dissolve or mix with the main components
0333-L2X1-1	X1 did not dissolve or mix with the main components
0333-MX1-1	X1 did not dissolve or mix with the main components
0333-MX1-2	X1 did not dissolve or mix with the main components
0333-HX1-1	X1 did not dissolve or mix with the main components
0333-MX2-1	X2 did not dissolve or mix with the main components
0333-MX2-2	X2 did not dissolve or mix with the main components
0333-L2X3-1	Visually comparable – promising formulation
0333-MX3-1	Not comparable to original formulation – too thick
0333-HX4-2	Not comparable to original formulation – too thick
0333-LX4-2	Visually comparable – promising formulation
0333-LX5-2	Visually comparable – promising formulation
0333-LX6-2	Visually comparable – promising formulation

While mixing and applying the experimental formulations, it was observed that some of them were not comparable to the original. As can be seen from Tables 4.2 and 4.4, a large number of new components used in the experimental formulations did not melt at mixing temperatures and therefore, were not considered as functional. The addition of others resulted in the increase in the mixtures viscosity such that it was not possible to extrude them. Alternately, others exhibited a low viscosity and were unable to retain their shape after extrusion.

The general appearance of the extruded marking was also important. If the marking did not extrude smoothly or exhibited pitting, they were not comparable to the original formulations and thus not further investigated. Certain formulations required additional heating to enable extrusion. This led to yellowing of the marking, also causing the formulation to be eliminated.

A list of promising formulations was compiled for further testing. However, the majority of the additional components did not result in the development of promising formulations due to their incompatibilities with the existing components.

4.2 Taber Abrasion

These tests were designed to give an indication of the wear performance that could be expected from each of the formulations. Tests were completed as described in Chapter 2 on bead free surfaces. The following results appear to exceed requirements; however, this is a function of the weighing technique used, which was described in Chapter 2. When these results are corrected for wet weighing, they fall within the City of Edmonton weight loss limit of 0.6 g.

Tables 4.5 and 4.6 are summaries of the abrasion testing carried out on the promising experimental formulations. Also included are a number of the samples prepared using new components that exhibited good abrasion resistance. Testing was completed to determine if these components would enhance abrasion resistance even though they did not dissolve into the sample. The values have not been corrected as they are comparable to the experimental formulations and the original formulations which were also tested using the alternate weighing method described in Chapter 2.

Table 4.5: Taber Abrasion of Additional Components to Formulation 0320

Component	Weight loss (g) – dry weights
0320-2	0.7329
0320-MR3-L1X1-1	0.9754
0320-MR3-L2X1-1	0.9677
0320-L1X1-1	0.6948
0320-L2X1-1	0.9033
0320-MX1-1	0.8275
0320-MX2-1	0.9358
0320-MX3-1	0.9571
0320-LX4-2	0.7834
0320-LX5-2	0.9161
0320-LX6-2	0.8431
0320-MC1-2	0.9126
0320-MC2-2	0.8634
0320-MC3-2	0.8035
0320-MC4-2	0.8656

Table 4.6: Taber Abrasion of Additional Components to Formulation 0333

Component	Weight loss (g) – dry weights
0333-4	0.8445
0333-MR1-1	0.8665
0333-MR2-1	0.9396
0333-MR3-1	0.8258
0333-MR4-1	0.8889
0333-MX1-1	0.9762
0333-MX2-1	0.9601
0333-MX3-1	1.0284
0333-LX4-2	0.9653
0333-LX5-2	0.9431
0333-LX6-2	0.8913

The addition of a number of new components to the formulations was done in order to not only increase wear resistance, but also improve stress absorption, thus reducing cracking. Due to incompatibilities noted with a number of the new components, abrasion resistance testing was conducted to determine if indeed the addition of the new components resulted in a formulation that met the City of Edmonton standards for abrasion as it is a determining factor in the formulations success. Figures 4.1 and 4.2 are a representation of the data shown in Tables 4.5 and 4.6. Weight loss varied depending on both the type and amount of component added. Formulations 0320-L1X1-1 and 0333-MR3-1 show slightly lower abrasion resistance when compared to the original formulations. However, due to these formulations being observed to be incomparable with the original formulations, as seen in Tables 4.2 and 4.4, further analysis was not conducted.

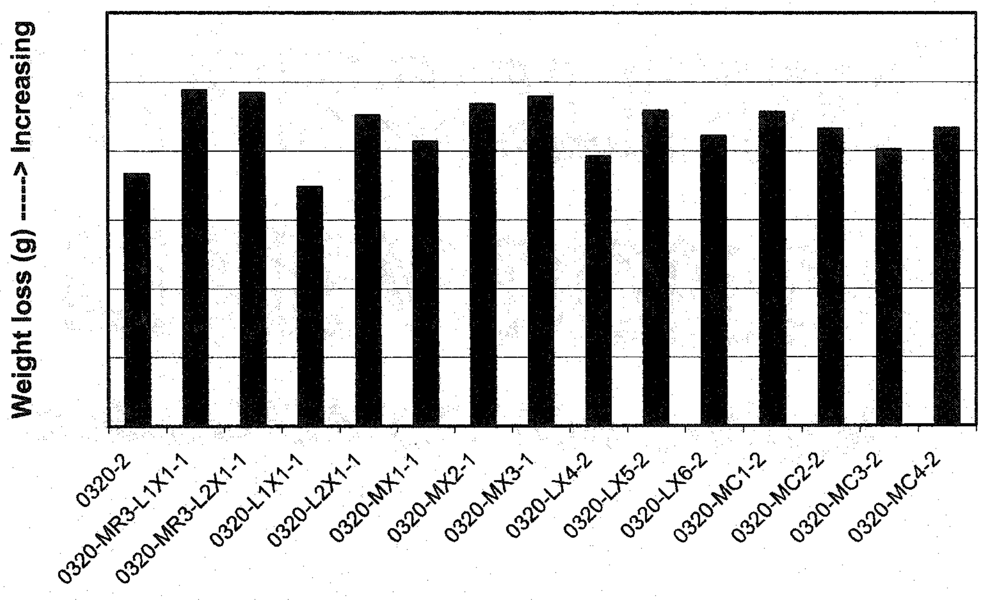

Figure 4.1: Taber Abrasion Analysis of Additional Components to Formulation 0320

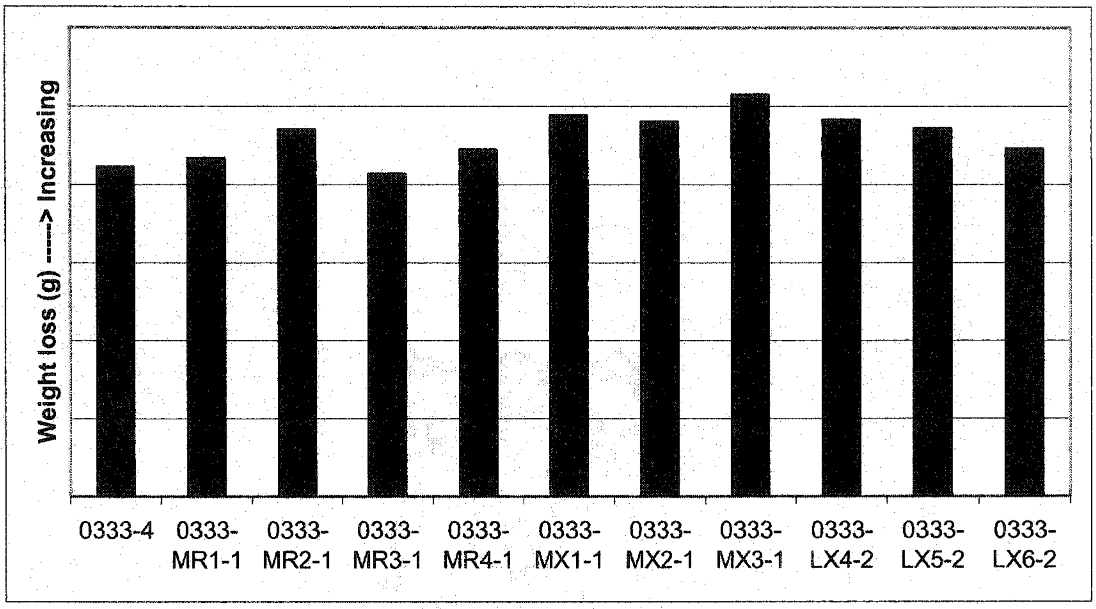

Figure 4.2: Taber Abrasion Analysis of Additional Components to Formulation 0333

Table 4.7 is a summary of three different formulations tested for abrasion resistance into the depth of the samples. Table 4.8 represents the abrasion as a function of the resin content. Both Tables 4.7 and 4.8 are corrected to the values which are comparable with the City of Edmonton specifications and are additive throughout the testing.

Table 4.7: Taber Abrasion Depth Study (Corrected Values)

Cycles	Total Weight Loss (g)		
	0320-MR2-1	0320-MR3-1	0333-4
200	0.4907	0.4282	0.2430
400	0.9138	0.7603	0.5508
600	1.3371	1.1322	0.8651
800	1.7547	1.5360	1.1842
1000	2.2360	1.9233	1.4350

Table 4.8: Taber Abrasion as a Function of Resin Content (Corrected Values)

Formulation	Weight Loss (g)	Formulation	Weight Loss (g)
0320-MR2-1	0.4472	0333-MR2-1	0.3142
0320-MR3-1	0.3847	0333-MR3-1	0.2761
0320-2	0.3926	0333-MR4-1	0.2972
		0333-4	0.2824

Taber abrasion as a function of the depth in the sample was tested to ensure that as the line wore, adequate abrasion resistance was maintained throughout the samples. Figure 4.3 shows that wear was uniform throughout the depth of the sample. This also indicates that mixing was adequate to create a homogeneous mixture. There was no settling of heavy aggregates or fillers.

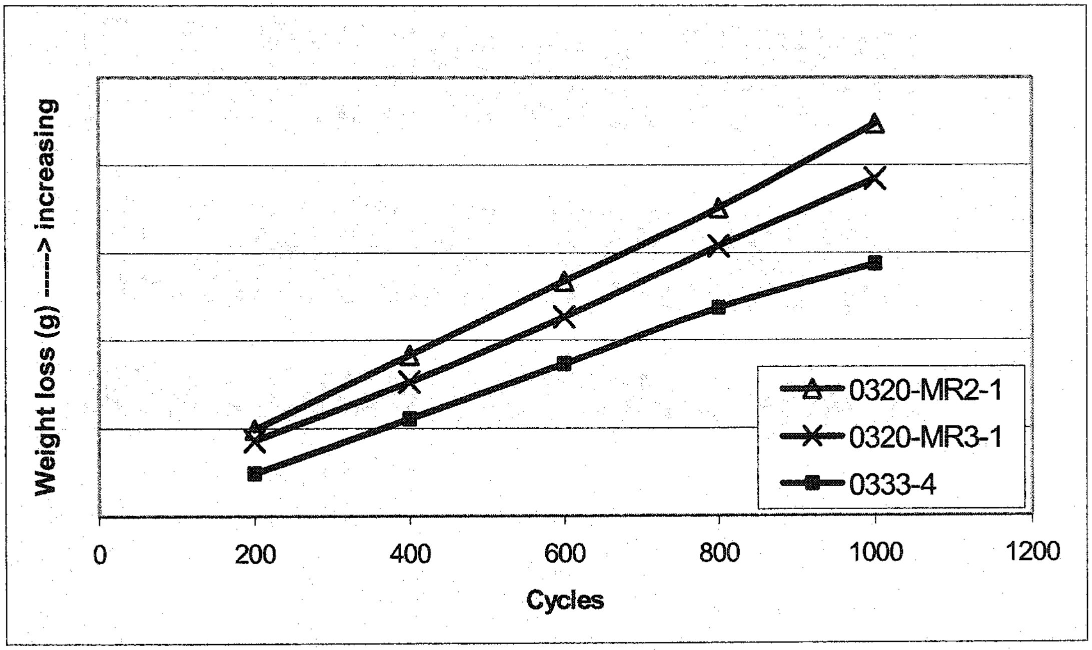

Figure 4.3: Taber Abrasion Depth Study

Formulation 0333-4 exhibited slightly increased abrasion resistance than the resin content altered 0320 formulations. This is similar to the results obtained for the original 0320 formulations.

Abrasion as a function of resin content was studied to determine if the percentage of resin could be reduced without adversely affecting the abrasive wear of the formulation. Figure 4.4 shows that the formulations as designed currently offer the highest abrasion resistance, or lowest abrasive wear. The decrease in wear is minimal for formulations with a resin content slightly lower than the original; however, formulations with resin contents much lower than the original show an increase in abrasive wear.

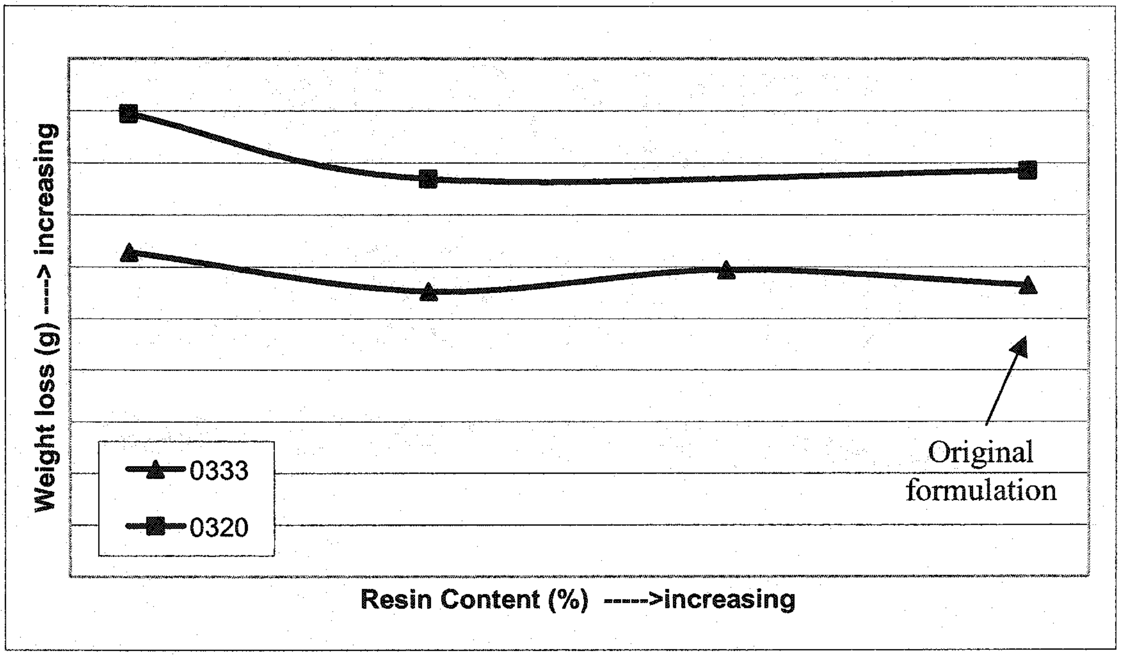

Figure 4.4: Taber Abrasion Weight Loss as a Function of Resin Content

Abrasion resistance is simply one factor in the determination of a promising formulation. 0333 formulations for differing resin contents were not considered to be promising formulations as they are not comparable to the original formulations when observed while formulating, extruding and in overall appearance. 0320 formulations for reduced resin content were promising for mid level resin content, however, the increase in abrasion resistance is not sufficient to warrant a change to the currently used formulation without further testing.

Further testing was not required for the formulations identified in Tables 4.2 and 4.4 or those tested using Taber abrasion. It was determined that these formulations did not meet the City of Edmonton's standards for abrasion resistance and thus were not considered viable as alternative formulations.

4.3 Summary

Multiple formulations were prepared to see if the manipulation of the existing formulations by various techniques would result in a better performing material. Studies on the percent resin in the formulation revealed that in order to meet the City of Edmonton specifications for Taber abrasion wear, the existing formulations must be utilized without variation in the percent resin. When the percentages of the current components were altered, the resulting formulations were also sub-standard in the Taber abrasion testing. Once again, it can be concluded that the ratios of the components currently in use are optimized for Taber abrasion.

The addition of various additional components was explored to determine if their presence would result in superior performing marking materials. These components included polyurethanes, ethylene vinyl acetate, fibres and waxes. Polyurethanes were considered to be an excellent option as they have superior wear, thermal, and tensile properties over a large temperature range. However, the polyurethane samples utilized were incompatible with the current systems, in that they did not melt at the mixing temperature and therefore, did not allow for adequate mixing with the other components. It is possible that a two component system would provide better mixing properties; however, this would lead to the need for significant changes in the production process due to the safety concerns associated with these types of systems.

Ethylene vinyl acetate was added as it also has excellent abrasion, elasticity, and temperature stability over a range of temperatures. However, as the vinyl acetate content was increased, the result was a system in which the fine aggregates, fillers and pigments were chemically bonded to the vinyl acetate in a very rigid system. (Choi et al, 1991) The higher vinyl acetate content was preferred as it shows better temperature stability; however, once again, performance was not comparable to the original formulations.

Fibres were added in hopes of reducing wear as a result of Taber abrasion. However, the affordable and compatible fibres were not well rated for abrasive wear. The more abrasion resistant fibres were very expensive and acted as a filler or aggregate, therefore, reducing the amount of aggregate, filler, etc, required. This resulted in a very high viscosity material. Optimization led to very small percentages of these fibres incorporated, thus no appreciable reduction in wear was noted.

Waxes were added to increase the materials ability to absorb stresses built up as a result of various mechanisms. The waxes tested were very soft and pliable at ambient temperatures and also exhibited very low abrasion resistance. Their addition resulted in a significant increase in Taber abrasion wear. This is not acceptable as the lines may not crack with the addition of waxes, but they would certainly abrade off very quickly. An abraded line is definitely a failed line, whereas, a cracked line is still functional.

A high percent thermoplastic polymer matrix system would show very poor wear as the polymer components are generally very soft and easily abraded. Systems exhibiting a high percentage of fillers, aggregates, pigments, etc would show better abrasion. However, there exists a critical matrix percentage at which optimal wear is achieved. Above this percentage, wear is poor due to the easily abraded matrix and below, wear is poor due to chipping and pitting of the fillers, aggregates, pigments, etc due to insufficient matrix to hold the material together.

Additives, such as polyurethane, which have good abrasion characteristics, may provide a better overall abrasion resistance for the mixture. However, compatibility of these additives limits their usefulness within the systems. Since abrasion resistance is one of the major criteria for the grading of these systems, it is necessary that they perform to specification. New formulations that do not meet abrasion wear standards are not acceptable.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

The mechanisms of failure were determined to be numerous and dependent on one another. Transverse cracking occurs when the internal stresses exceed the cohesive strength of the marking. Cracking will also result if the stresses are larger than the cohesive strength of the asphalt concrete, which will result in the asphalt concrete cracking. This results in the cracking of the marking as the marking material is not sufficiently strong to remain intact once the substrate support has failed.

Stresses are accumulated in the marking due to a variety of events including: (1) temperature cycling causing thermal expansion and contraction, transitioning through the glass transition temperature causing the material to go from soft and rubbery to hard and brittle and vice versa, and crystal formation increasing brittleness, (2) traffic cycling causing load cycling, (3) environmental conditions such as sun and rain which deteriorate the polymer components, and (4) environmental aging of the material over time which reduce its ability to absorb stresses due to increased brittleness and hardness.

The extent of the cracking is dependent on the frequency and magnitude of these events. Increased failure rates and smaller distances between cracks will be noted in areas of higher frequency. Markings may show no transverse cracking in areas of lesser traffic activity even when environmental conditions are similar.

Failure due to abrasive wear is increased when markings are perpendicular to traffic flow, or driven on as in the case of turning or merging lanes. Abrasive wear is also increased when there are additional abrasive materials on the roadway, as seen in winter driving conditions, when sand is applied to provide traction in icing conditions. Snowploughing is particularly abrasive to the markings as the plough scrapes them as it passes over. The material properties also affect abrasive wear such that a more brittle marking will show increased wear, as will a marking which is softened due to high temperatures.

The adhesive strength of the formulations must remain high as markings that show cracking are still functional if they remain attached to the roadway. The current formulations show high adhesion to the substrates, however, the asphalt concrete substrate has low cohesive strength. This results in the loss of the marking material along with the top layer of the asphalt concrete.

Experimental formulations in which components were added to current formulations did not result in the development of a superior formulation. The additional components were either incompatible with current components, required alterations to the current manufacturing and application procedures, or did not exhibit comparable performance.

A superior marking material requires that it perform well in the Edmonton environment. This implies that the formulation exhibit both high and low temperature stability as well as transitioning, which occurs outside of the operational temperature range. It must be sufficiently tough to show excellent abrasion resistance while remaining amorphous enough to absorb any stresses that accumulate due to such things as traffic cycling. It must also show adequate adhesion over a large range of substrate application temperatures to allow for application during the spring, summer, and fall.

Finally, manufacturing and processing should be consistent with techniques currently in use.

5.2 Future Work

As the mechanisms of failure have been defined, the future work in this area should focus on the development of a superior formulation. The manipulation of the current formulations did not yield an exceptional formulation; therefore, future efforts should be directed towards a formulation independent of current formulations. The new formulation should be developed based on the established criteria for failure reduction as noted earlier. This will lead to a formulation uniquely designed for superior performance in the Edmonton area.

Further testing on the polymer components utilized in the formulations would provide valuable information on temperature limits that the marking material would be capable of withstanding. Differential Scanning Calorimetry (DSC) at various heating and cooling rates would provide an indication of the material's performance over a range of application temperatures, both environmental and substrate. This would allow for the development of a set of application guidelines based on the outside temperature and the temperature of the asphalt concrete. Further testing at various heating and cooling rates would also be valuable in the evaluation of the reproducibility of the data by ensuring that the phenomena observed were as a result of the transitions actually occurring within the sample and not due to error or an anomaly observed at a specific rate.

Due to the similarities between this system and the asphalt concrete system, further in-lab testing may be conducted using methods developed for the asphalt concrete systems. This would include tensile testing to determine the cohesive strength of the marking material. Accelerated aging tests, which would simulate both environmental aging as well as load-induced aging, would be useful in the determination of critical stress limits for the marking material.

Finally, field evaluation studies should be conducted to ensure the performance of new formulations as in-lab testing can not accurately simulate the environmental conditions that the marking will experience. This testing would be best accomplished with strip testing on roads in the Edmonton area. The results obtained for the new formulations could then be correlated with data obtained by the City of Edmonton for other thermoplastic roadway marking materials to determine the suitability of the new formulations for use.

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Appendix A

Sample Calculations

1. Change in length of marking on cooling after application.

Given: $L = 1 \text{ m} = 1000 \text{ mm}$

$\Delta T = 160°C$

$\alpha_{polymer} = 12 \times 10^{-5} /°C$

Substitute values into:

$$\Delta L = (\alpha_{polymer})(\Delta T)(L)$$

$$= (12 \times 10^{-5})(160)(1000)$$

$$= 0.0192 \text{ m}$$

2. Thermal stress resulting from a 40°C temperature increase.

- For a marking without adhesion to a substrate, self-restrained

Given: $\alpha_{marking} \cong 1.9 \times 10^{-5} /°C$

$E = 1000 \text{ MPa}$

$\Delta T = 40°C$

Substitute values into:

$$\sigma_{restrained} = (E)(\alpha_{marking})(\Delta T)$$

$$= (1000)(1.9 \times 10^{-5})(40)$$

$$= 0.76 \text{ MPa}$$

- For a marking restrained by the asphalt concrete (AC) substrate

Given: $\alpha_{marking} \cong 1.9 \times 10^{-5}$ /°C

$\alpha_{AC} \cong 2.5 \times 10^{-5}$ /°C

$E = 1000$ MPa

$\Delta T = 40$°C

Substitute values into:

$$\sigma_{ACrestrained} = (E)(\Delta\alpha)(\Delta T)$$

$$= (1000)(2.5 \times 10^{-5} - 1.9 \times 10^{-5})(40)$$

$$= 0.24 \text{ MPa}$$

3. Force exerted by thermal expansion and contraction.

- For a summer cycle inlaid marking

Given: $\alpha_{polymer} = 12 \times 10^{-5}$ /°C

$L = 1$ m

$\Delta T = 40$°C

$E = 1000$ MPa

Width = 0.1 m

Thickness = .008 m

Substitute values into:

$$\Delta L = (\alpha_{polymer})(\Delta T)(L)$$

$$= (12 \times 10^{-5})(10)(1)$$

$$= .0012 \text{ m}$$

Substitute values into:

$$\sigma = E\ (\Delta L/L)$$

$$= 1000\ (.0012/1)$$

$$= 1.2\ \text{MPa} = 1200\ \text{Pa}$$

Substitute values into:

$$F = (\sigma)\ (\text{Area})$$

$$= (1200)(0.1 \text{ x } 0.008)$$

$$= 0.96\ \text{N}$$