Rubber durability: Compounding factors, environmental influences and lifetime prediction using time temperature superposition

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Manchester Polymer Group Rubber Seminar, 16th May 2018.
Agenda

1. Introduction
2. Compounding factors
3. Why do elastomers fail?
4. Lifetime prediction
5. Product testing
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Introduction: The Problem Of Durability

- Service conditions for rubber are becoming ever demanding.
- Need to ensure components can deliver the required service lifetime.
- Required to prove fitness for purpose.
- This is particularly true of rubbers because properties are time and temperature sensitive.
- Properties can also be influenced by any contact media.
- Therefore understanding and predicting long-term changes in properties is essential.
Introduction: The Problem Of Durability

• Compounders often use simple lab tests in order to attempt to predict the behaviour of complex rubber materials.

• These tests have value in terms of identifying suitable materials and establishing a specification, but they lack the ability to predict long term lifetime behaviour.

• Hence in order to ensure that a particular rubber compound is suitable for an application it is necessary to consider multiple aspects of the compound’s properties, its manufacturing and the required service lifetime.

• This presentation provides an overview of some of the important factors relating to rubber durability.
Introduction: The Problem Of Durability

Compounding

Environment

Life Prediction
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Durability: Compounding Factors

Improving durability – key compounding approaches

• Improve fatigue performance.
• Increase endurance.
• Optimise compound modulus
Durability: Compounding Factors

Improving fatigue performance

- A key factor is improving fatigue performance.
- Through compounding this can be addressed in a number of ways:
  - Appropriate polymer selection
  - Better dispersion
  - Smaller particle size fillers
  - Longer mixing times

All of these serve to prevent or delay the onset of crack precursors which form within the compound matrix when the compound experiences load.
Durability: Compounding Factors

Increasing endurance

• A key factor affecting rubber durability is intrinsic compound strength.

• Through compounding improvements in strength can be achieved in a number of ways:
  – Polymer choice
  – Better compound ingredient dispersion
  – Increased loading of reinforcing filler/reduced loading of non-reinforcing filler.
  – Improved polymer filler interaction
  – Optimisation of cross-link density
Durability: Compounding Factors

Controlling compound modulus

• Compound modulus has a significant effect on durability.

• Therefore achieving the optimum modulus during compounding is essential:
  – Lower modulus compounds can have a longer life when under strain as they resist deformation more effectively.
  – Higher modulus compounds are better able to resist higher stresses.
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Why Do Elastomers Fail?

Human Causes Of Failure

- Material misselection and poor specification: 45%
- Poor material process: 20%
- Poor product design: 20%
- Product abuse: 15%
Why Do Elastomers Fail?

Common Service Related Causes Of Failure

- Chemical: 21%
- Heat: 17%
- Fatigue: 12%
- Abrasion: 12%
- Tear: 7%
- Set: 5%
- Ozone: 12%

Note: UV degradation is not usually an issue with carbon black filled rubber.
Durability: Environmental Factors

Effects of service on the rubber compound:

• The effects of service can be complex and profound, they include but are not limited to:

  Cross-linking
  Chain scission
  Chemical reactions
  Change in composition (extraction & absorption)
  Changes in crystallinity
  Cracking
  Crazing
  Discolouration
  Swelling
  Shrinkage
  Property changes
  Fatigue
Durability: Environmental Factors

Chemical attack:

When considering a rubber compound for an application, we need to be aware of any contact media that can cause the following to occur:

- Polymer chain scission leading to molecular weight reduction.
- Increased cross linking of the matrix.
- Polymer chain modification as a result of cyclisation, chlorination or other chain modifications.
Durability: Environmental Factors

Chemical attack:

Chemical attack can have many effects on rubber articles, but often results in:

- Loss of polymer chain flexibility and elastomeric properties.
- Loss of physical properties.
- Change in material strength.
Durability: Environmental Factors

Fatigue:
Fatigue is a complex phenomenon, which can occur through a combination of the following:

- Extreme service
- Cyclic damage
- Chemical attack
- Ozone attack
- Hysteresis heat build-up

It is not a single value, and the probability of failure must be compared against the number of service cycles.
Durability: Environmental Factors

Fatigue:
• A Function of the Polymer
• Time related
• Related to compounding
• Related to duty/service
• Can be affected by design
• Micro cracks start at flaws in the material
• Cracks propagate through the material leading to ultimate failure

Fatigue cracking in a cycle handlebar grip
Durability: Environmental Factors

Ozone Attack:

Ozone is a naturally occurring gas, present in the atmosphere at concentrations of 0.5 - 2 pphm.

- Ozone can be generated by electrical equipment, and is often present in concentrations up to 50 pphm.
- Ozone is also present in higher concentrations in polluted urban environments.
Durability: Environmental Factors

Ozone Attack:

• A golf club grip.
• Material is under strain, cracks at 90° to the strain direction.
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Durability: Lifetime Prediction

The Conventional Approach, *Arrhenius*:

- Arrhenius is the most widely used model for life prediction.

- In this method, the rate of change of a particular property (rate constant) is monitored with time at predetermined temperatures.

- Since the rate of degradation is temperature dependent, an Arrhenius equation can be applied.

- To assist with experimental setup, it is often assumed that the rate of reaction doubles with every 10°C increase in temperature.
Durability: Lifetime Prediction

Problems With Arrhenius:

- Rate constant needs to be calculated for individual ageing temperatures before plotting an Arrhenius curve.

- Assumes a first order reaction.

- The slopes are used to calculate activation energy.

- The amount of data manipulation may lead to inaccuracies in results.

- The Arrhenius methodology assumes the failure mode is identical at all test temperatures and stress levels.
Durability: Lifetime Prediction

Time-Temperature Superposition (TTS), An alternative to Arrhenius:

- In the TTS method, all individual data at all ageing temperatures are used to construct a master curve.
- Fewer stages of data manipulation.
- The lowest ageing temperature is used as the reference temperature.
- For each data set, the experimental times at this temperature is multiplied by a constant shift factor.
Durability: Lifetime Prediction

Time-Temperature Superposition (TTS), An alternative to Arrhenius:

The model can only be used when the form of the curve is essentially the same at the different test temperatures.
Durability: Lifetime Prediction

Time-Temperature Superposition (TTS), An alternative to Arrhenius:

Time shifts can either be done by eye or using mathematical models such as the Williams Landel Ferry (WLF) equation:

$$\ln(a_T) = \frac{a(T - T_0)}{b + (T - T_0)}$$

Where $a_T$ is the shift factor of an isotherm determined at temperature $T$ in relation to the isotherm at the reference temperature $T_0$ and $a$ and $b$ are coefficients dependent on the material.
Durability: Lifetime Prediction

Time-Temperature Superposition (TTS), An alternative to Arrhenius:

Advantages:

• TTS Can be applied when more than one reaction is occurring, hence the reaction is not first order.

• The method allows rapid collection of data.

• TTS can be applied to product specific test methods as well as to simple physical properties.
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Durability: Product Testing

Lifetime Prediction Is Not Enough

• Lifetime prediction techniques alone are insufficient for confirming overall durability.

• Realistic product testing is also required in order to simulate the behaviour of the material in its application and environment.

• This type of testing often requires custom apparatus and specialised laboratories.
Durability: Product Testing

Lifetime Prediction Is Not Enough
Thank-you for your attention

Gary S. Crutchley is Lead Consultant with the Consultancy group at Smithers Rapra. John Manley is Principal Consultant with the Consultancy group at Smithers Rapra.

Smithers Rapra provides a complete range of services which includes:

• Polymer fault & failure diagnosis
• Expert witness services
• Polymer analysis
• Material selection
• Polymer materials and product testing
• Long term data generation and lifetime predictions services.
• Polymer training courses

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