RELATIONSHIPS BETWEEN CHEMICAL AND MECHANICAL PROPERTIES OF POLYETHYLENE

STRUCTURAL APPLICATIONS AND MECHANICAL MODELLING

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OUTLINE

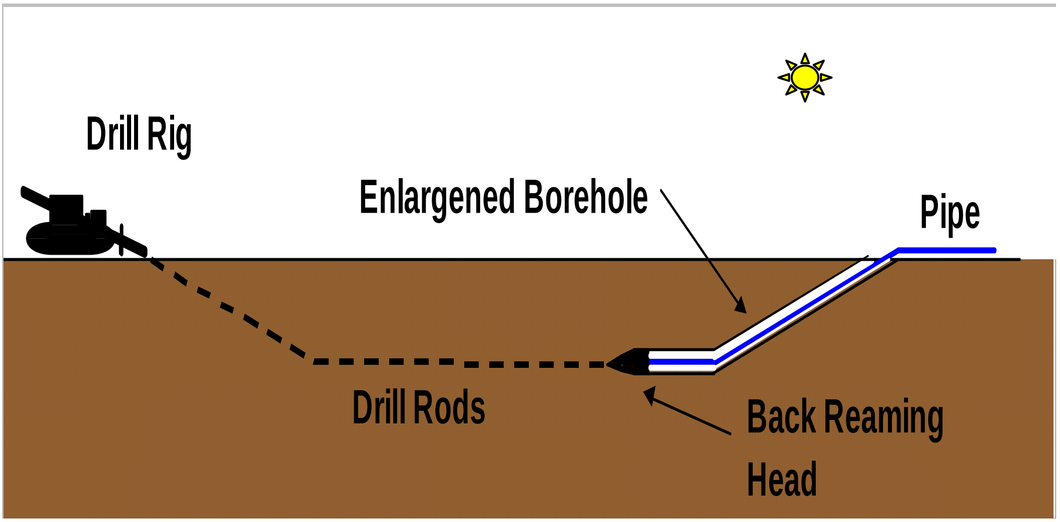
- Motivation for the work
- Research objectives
- Organization of the project
- Background information

- Experimental and theoretical work:
  - Chemical,
  - Micromechanical
  - Macromechanical

- Summary and Conclusions

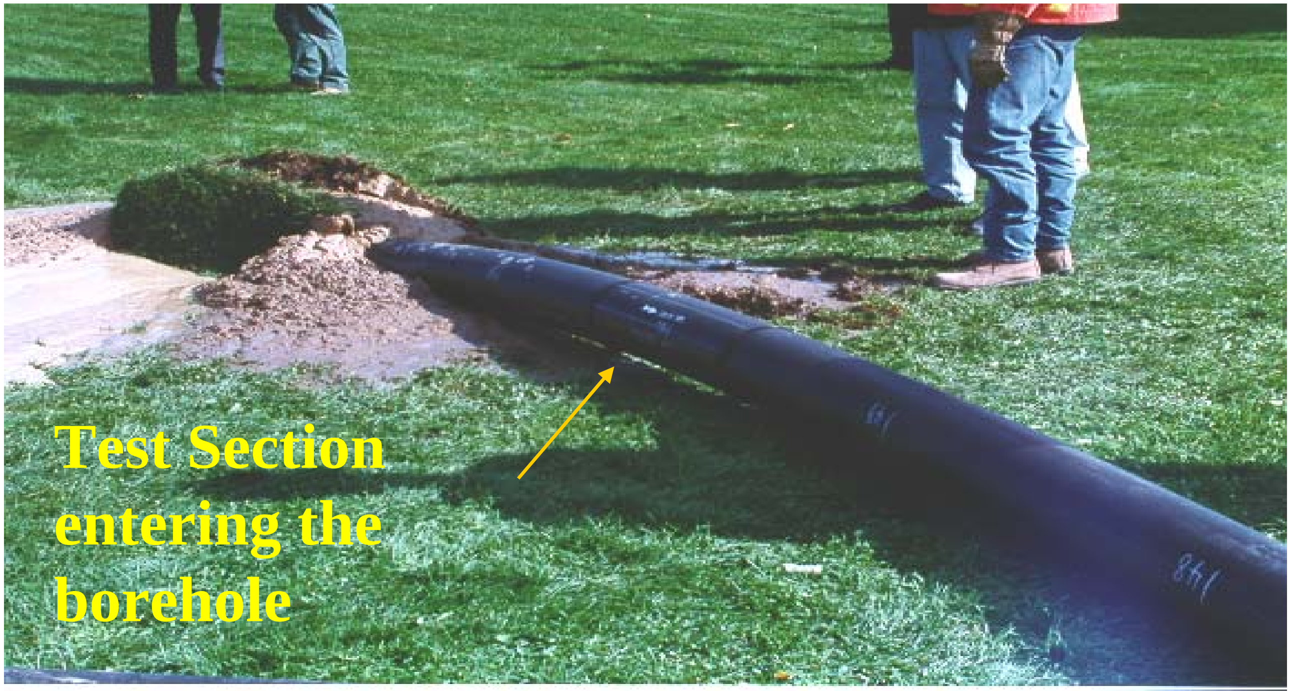
MOTIVATION FOR THE WORK

- Installation of polyethylene pipes using trenchless methods
- Example - *Back Ream/Pull Back phase of horizontal directional drilling*



TRENCHLESS ENGINEERING RESEARCH PROGRAM:

- **Field testing of the pipes**
- **Development of a numerical predictive model for pulling forces: PipeForce 2005**



Installation of Instrumented Test Pipe

GOALS OF THE RESEARCH PROGRAM

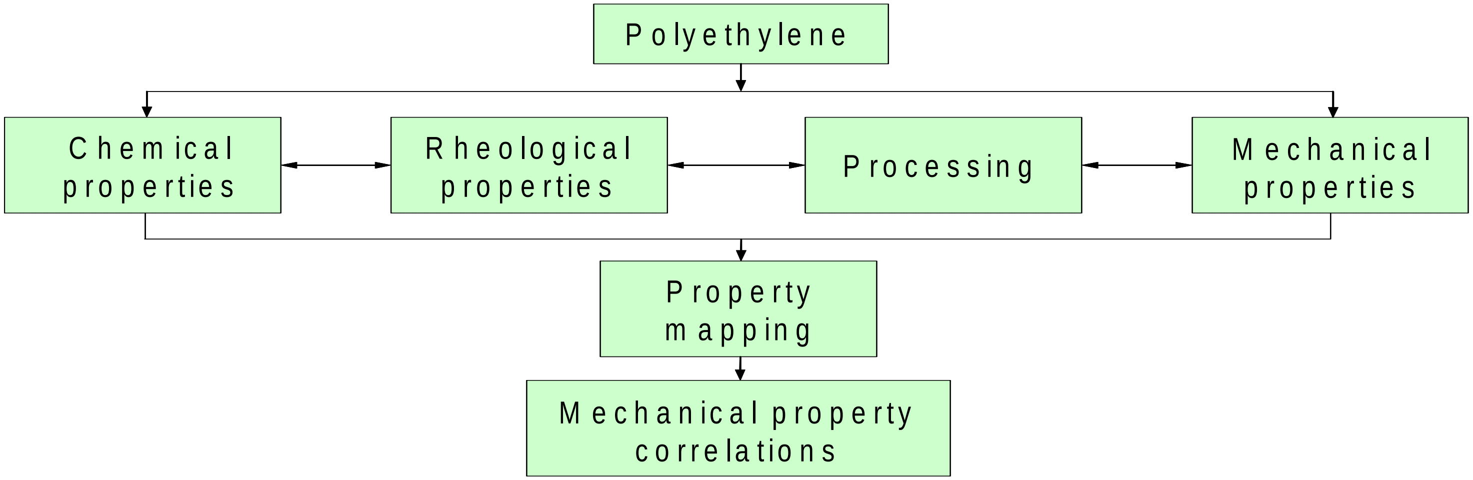
- Model for predicting *mechanical* properties of polymers based on *chemical* composition
  - understanding of the relationship between the chemical processes of producing a polymer and its mechanical constitutive properties

- Polymer applicability for structural applications
  - Production of materials for specific applications.
  - Specification of appropriate manufacturing and molding processes when the required mechanical properties are known.

OVERVIEW OF THE PRESENTED RESEARCH PROGRAM

- **Chemical analysis of polyethylene**
  - **Relating chemical to rheological and mechanical properties**
  - **Creation of ‘maps’ of relations between microstructure and mechanical properties.**
- **Micromechanical properties and modelling of polyethylene**
  - **Modifying the existing constitutive equations to incorporate *damage*.**
- **Macromechanical properties and modelling of polyethylene**
  - **Development of time dependent material modelling formulations for finite element analysis**

Chemical–mechanical Relationships



Polyethylene

Chemical properties

Rheological properties

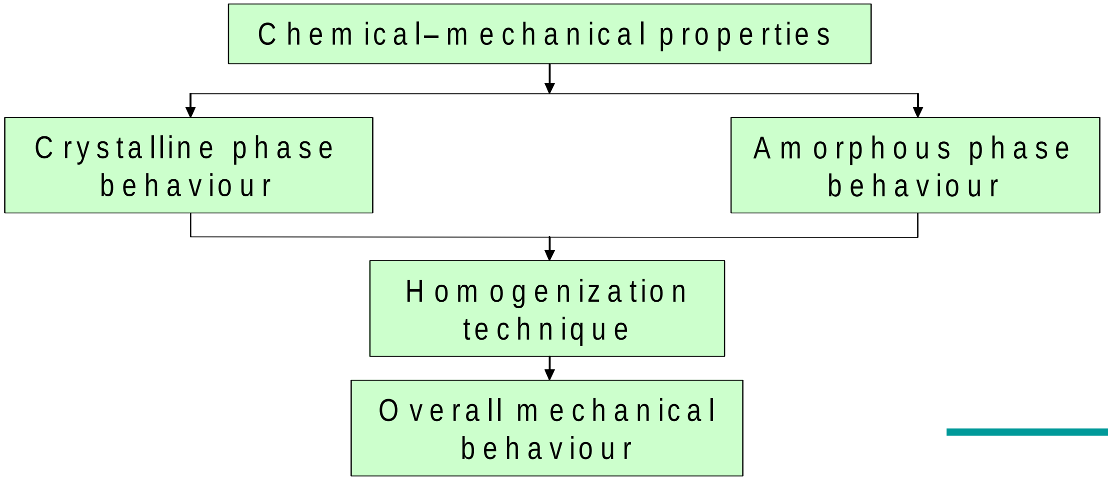
Processing

Mechanical properties

Property mapping

Mechanical property correlations

Micromechanical modelling



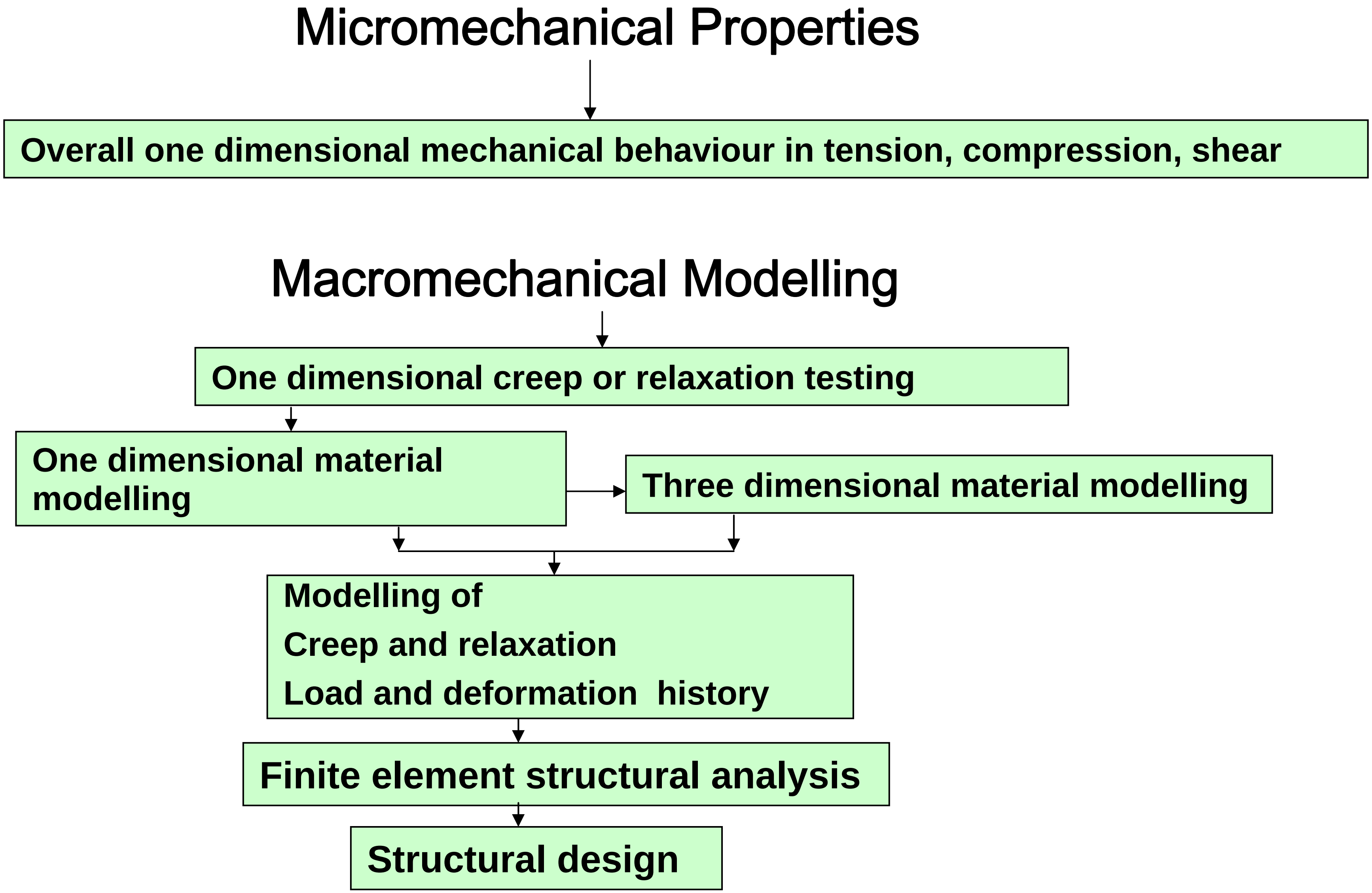
Chemical–mechanical properties

Crystalline phase behaviour

Amorphous phase behaviour

Homogenization technique

Overall mechanical behaviour



Micromechanical Properties

Overall one dimensional mechanical behaviour in tension, compression, shear

Macromechanical Modelling

One dimensional creep or relaxation testing

One dimensional material modelling

Three dimensional material modelling

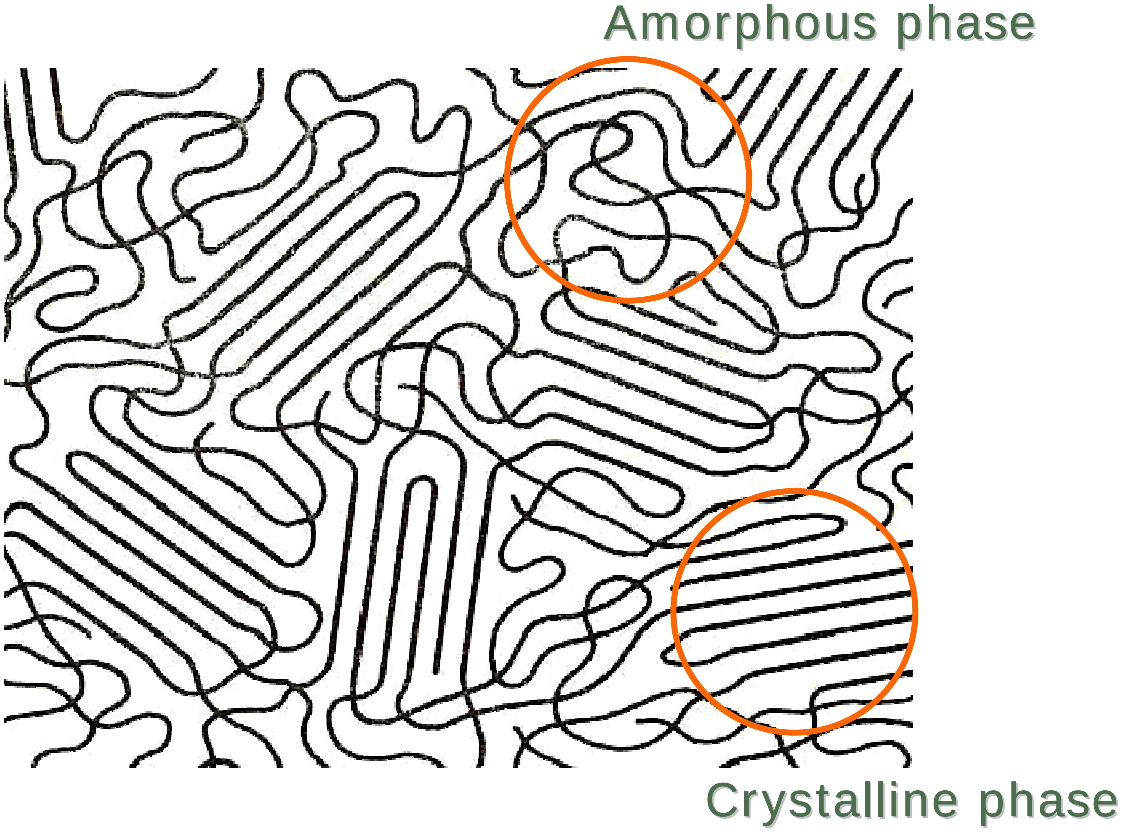
Modelling of
Creep and relaxation
Load and deformation history

Finite element structural analysis

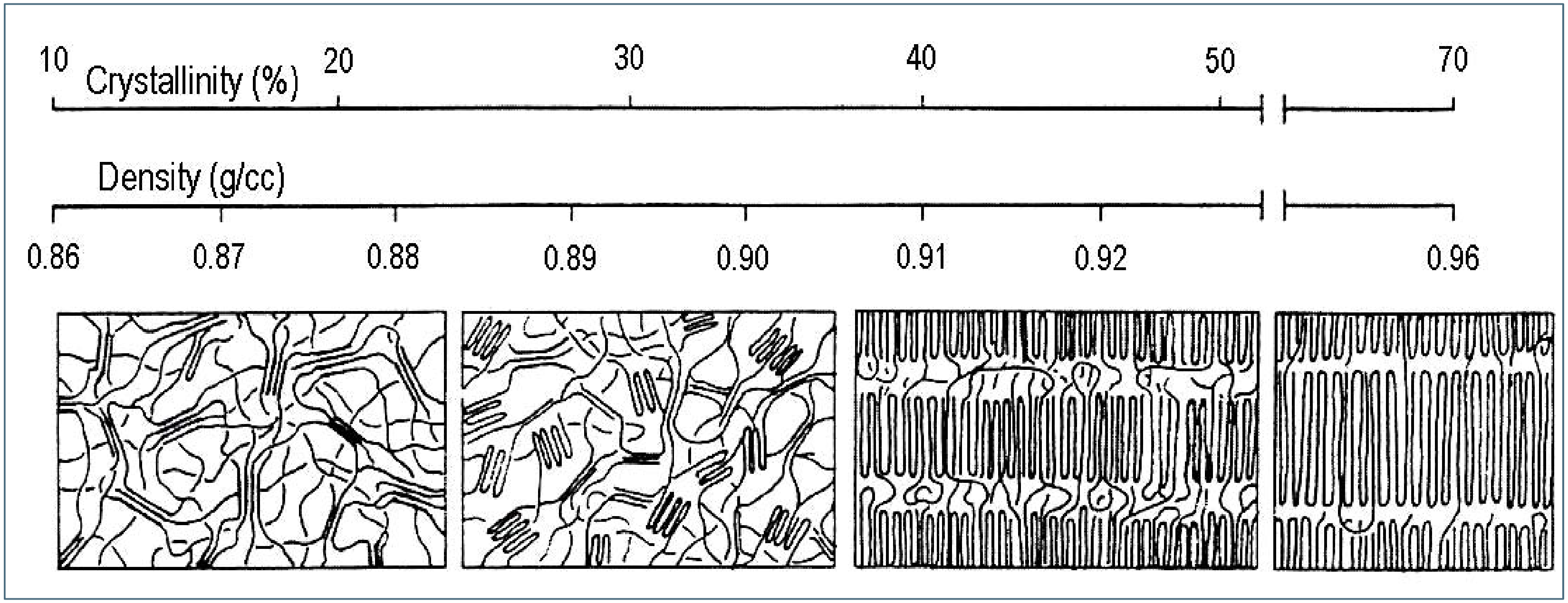
Structural design

POLYETHYLENE PHASES

Polyethylene structure



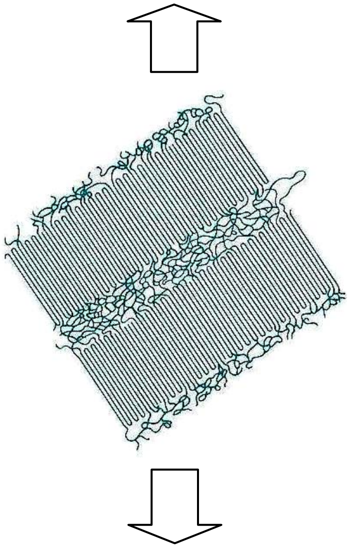
STRUCTURE OF POLYETHYLENE



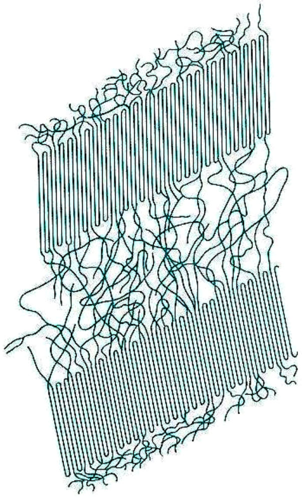
- Semicrystalline polymer

DEFORMATION MECHANISMS

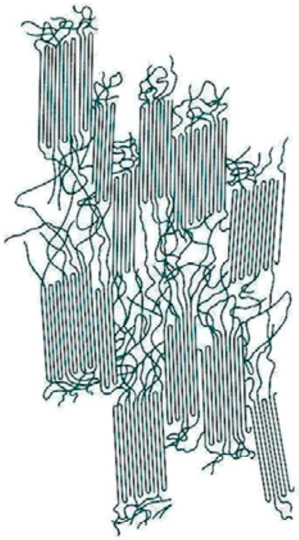
Polyethylene structure



Unstrained inclusion



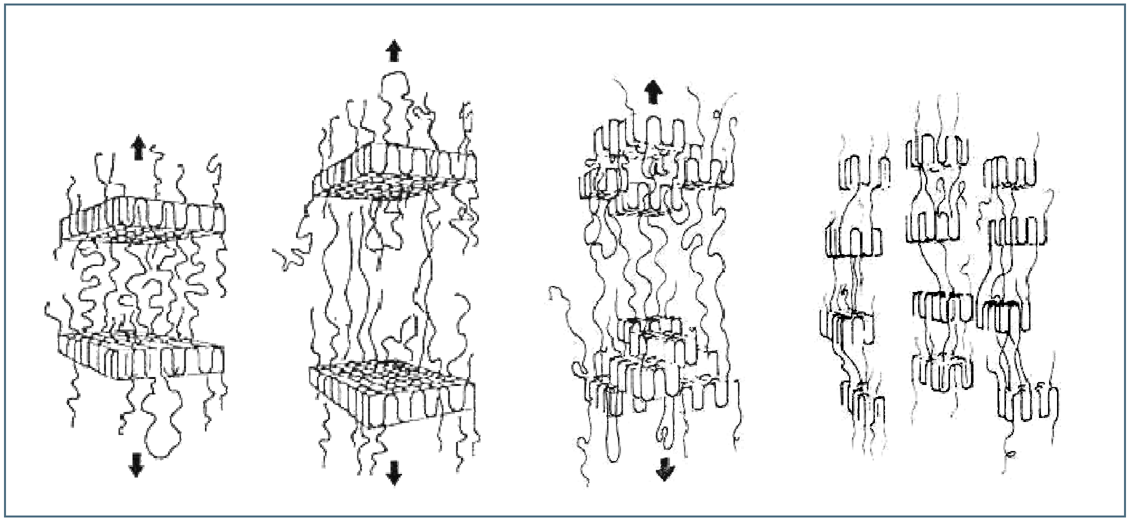
Elongation and tilting

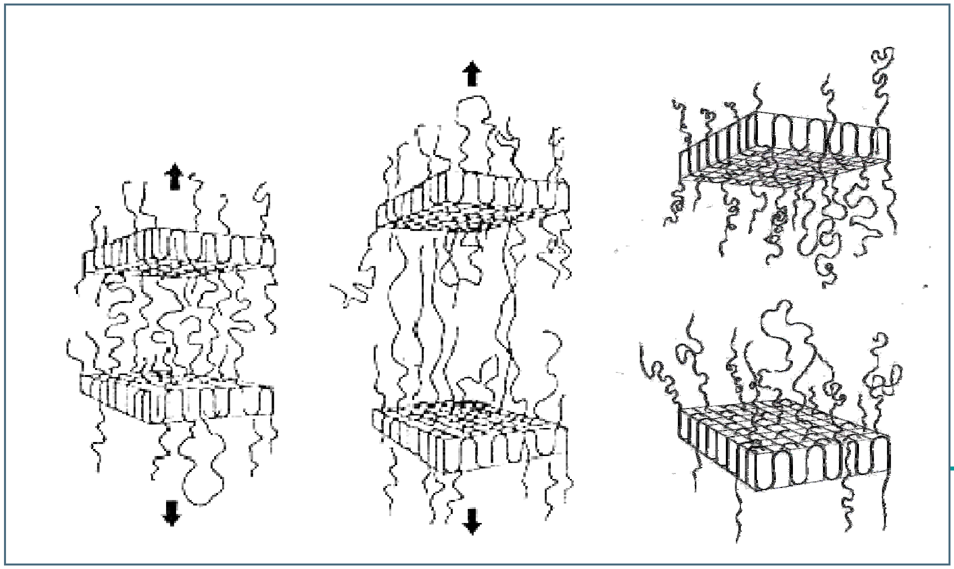


Fragmentation

FAILURE MECHANISMS

- Ductile failure
  - “Necking” of material
  - Rough fibrous surface





- Brittle failure
  - clean break with little material deformation
  - fracture surface appears smooth

STRESS CRACKING OF POLYETHYLENE

- Increase in molecular weight (MW) increases strength
- Increase in short chain branching (SCB) increases ESCR

- Bimodal polyethylene
  - More tie-molecules and chain entanglements
  - Better mechanical properties

CHEMICAL PROPERTIES OF HIGH DENSITY POLYETHYLENE

Doctoral Candidate: Joy Cheng
Chemical Engineering

Objectives:

Relationships between chemical and mechanical properties for polyethylene

Produce ‘maps’ describing relations between key micro molecular and physical/mechanical properties

Develop method for predicting slow crack growth

CHEMICAL PROPERTIES

- Molecular Weight
- Molecular Weight Distribution
- Short Chain Branching
- Long Chain Branching

- Crystallinity
- Density

EXPERIMENTAL TECHNIQUES

Test Methods	Material Properties
GPC (gel permeation chromatography)	Molecular weights and distribution Long chain branching indicators
DSC (differential scanning calorimetry)	Percentage crystallinity
CRYSTAF (Crystallization analysis fractionation)	Short chain branching and its distribution
C^{13}NMR (nuclear magnetic resonance)	Short/Long chain branching
NCLT (notch constant load test)	ESCR (environmental stress cracking resistance)
Tensile creep	Tensile properties
Capillary rheometry	Molecular weight and distribution Long chain branching level
Oscillating shear analysis	Long chain branching, shear modulus, shear viscosity

ExxonMobil resins

Chemical Properties	**PE1**	**PE2**	**PE3**
Density (company)	0.95	0.963	0.963
Melt index (company)	0.3	0.73	0.25
Melt point (°C) (measured)	130.1	134.8	134.5
% crystallinity (measured)	53.68%	56.32%	59.81%
SCB (/1000C) (measured)	29.03	3.33	2.85
LCB (/1000C) (measured)	1.18	1.45	1.18
Mechanical Properties			
Tensile modulus (MPa) (company)	1790	2620	2324
Environmental Stress Crack Resistance (hours) (company)	65	10	15

BRANCH MEASUREMENTS

SCB

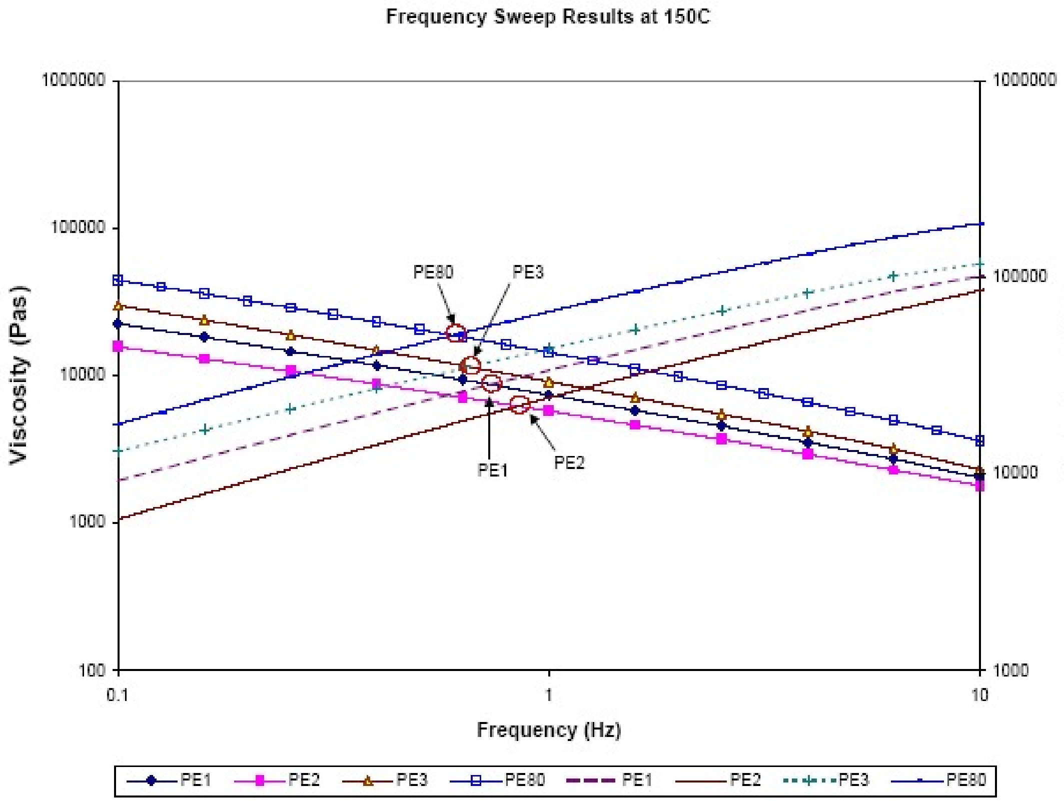
Resin	SCB content (75°C -85°C)	ESCR (hours)
2	0.1631	10
3	0.1632	15
1	0.3438	65

LCB

Resin	LCB (/1000C)	Tensile modulus (Mpa)
1	1.18	1790
3	1.18	2340
2	1.45	2620

RELATING RHEOLOGICAL PROPERTIES WITH MW and MWD

Oscillatory shear analysis

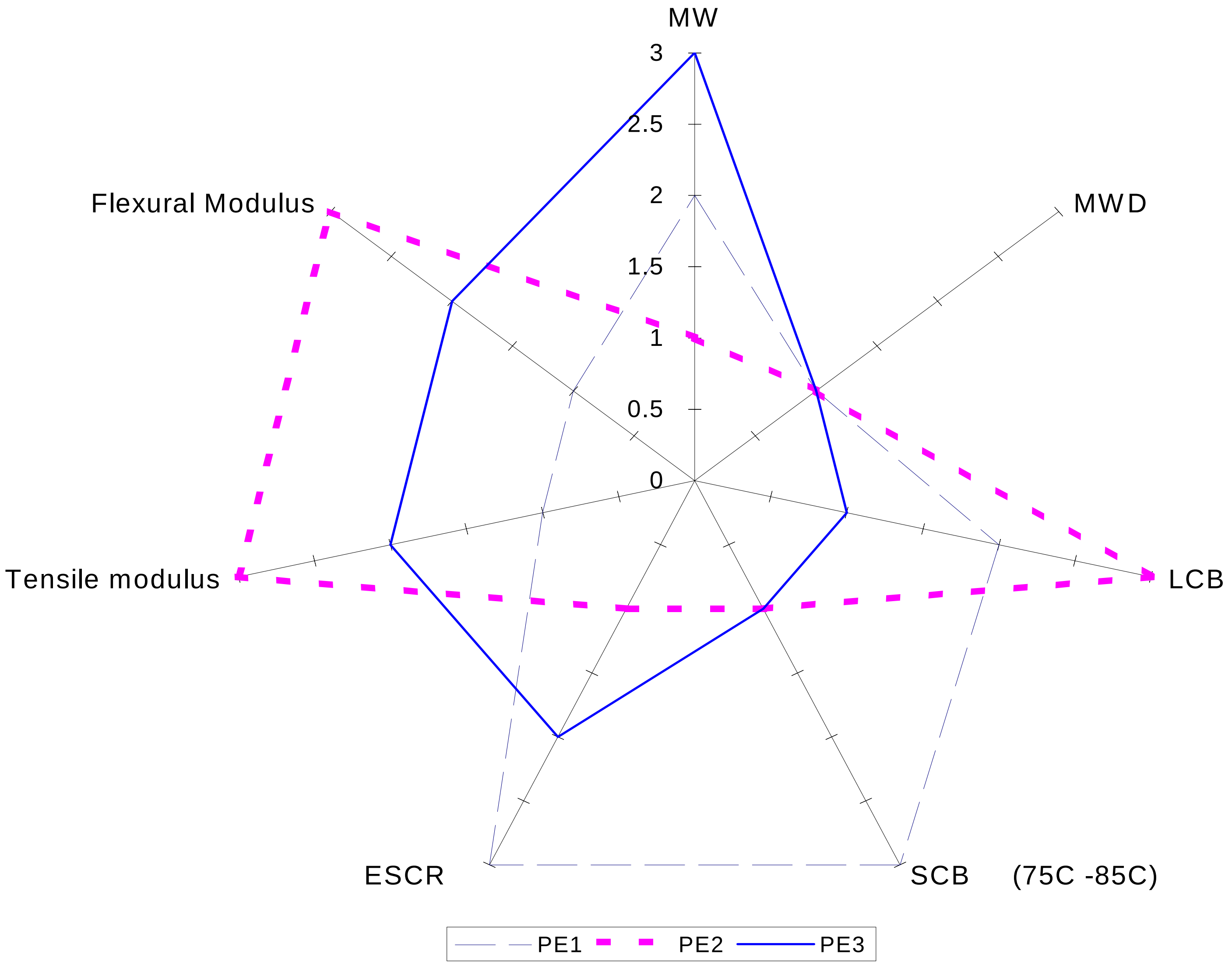


- Polymer with higher MW shows a higher intersection point.

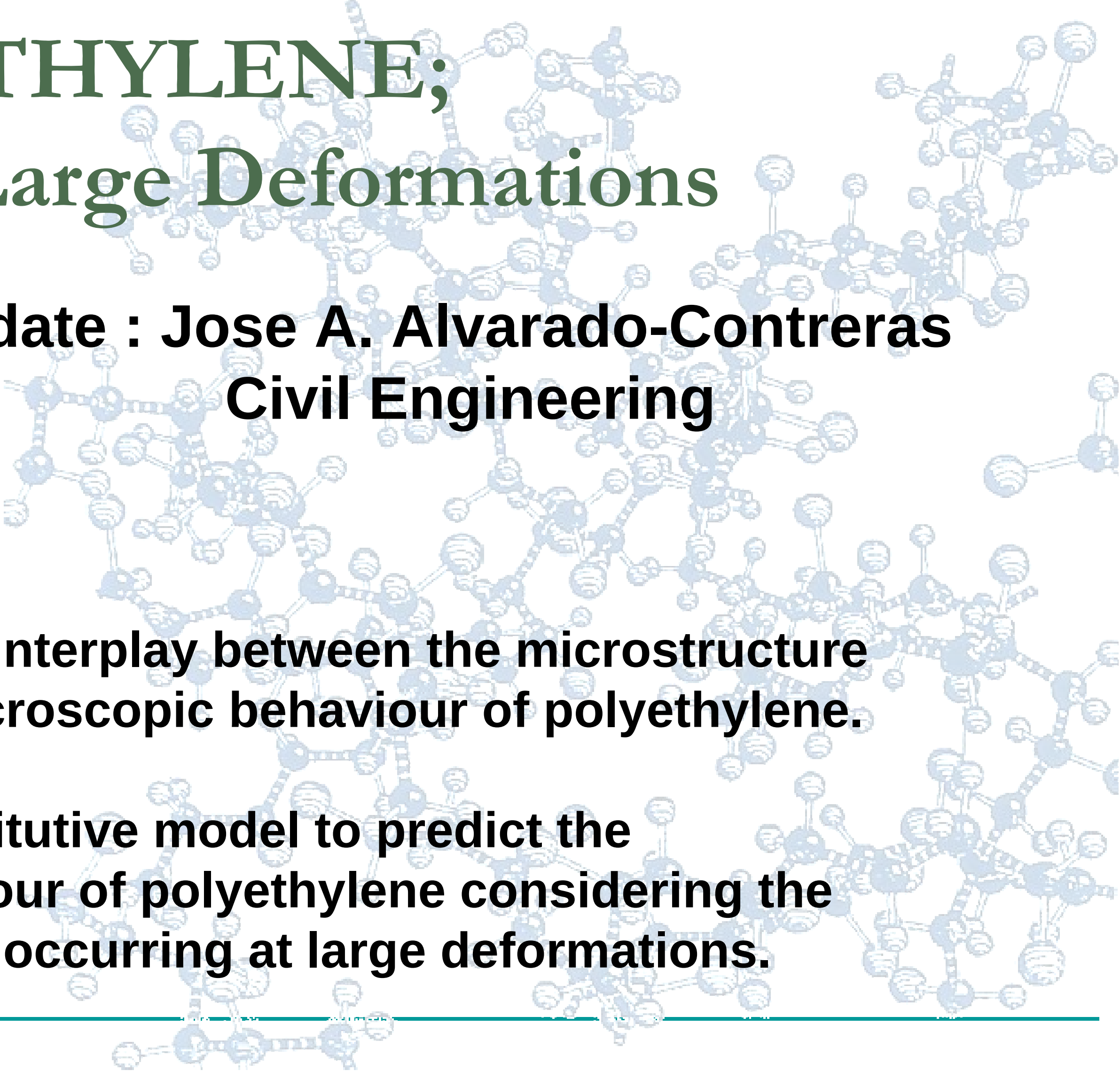
- Increase in breadth of MWD is shown by the intersection moving towards the right of the graph

- In mechanical analysis, resin with higher MW is expected to have better mechanical strength, while broader MWD means better processability.

Property map for blow molding resins



MICROMECHANICAL MODELLING OF POLYETHYLENE;
Damage at Large Deformations



Doctoral Candidate : Jose A. Alvarado-Contreras
Civil Engineering

Motivation

To understand the interplay between the microstructure and the overall macroscopic behaviour of polyethylene.

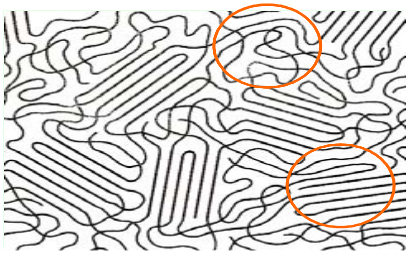
Goal

To develop a constitutive model to predict the mechanical behaviour of polyethylene considering the damage processes occurring at large deformations.

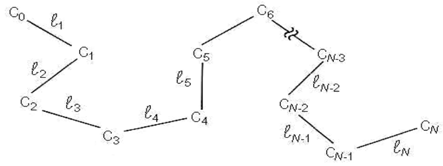
Micromechanical Modelling

Polyethylene structure

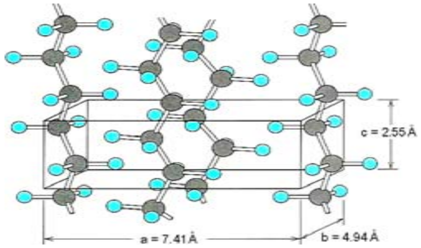
Amorphous phase



Crystalline phase

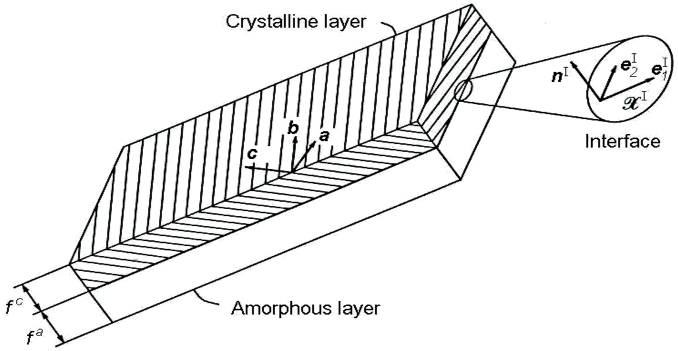


Idealized PE molecule

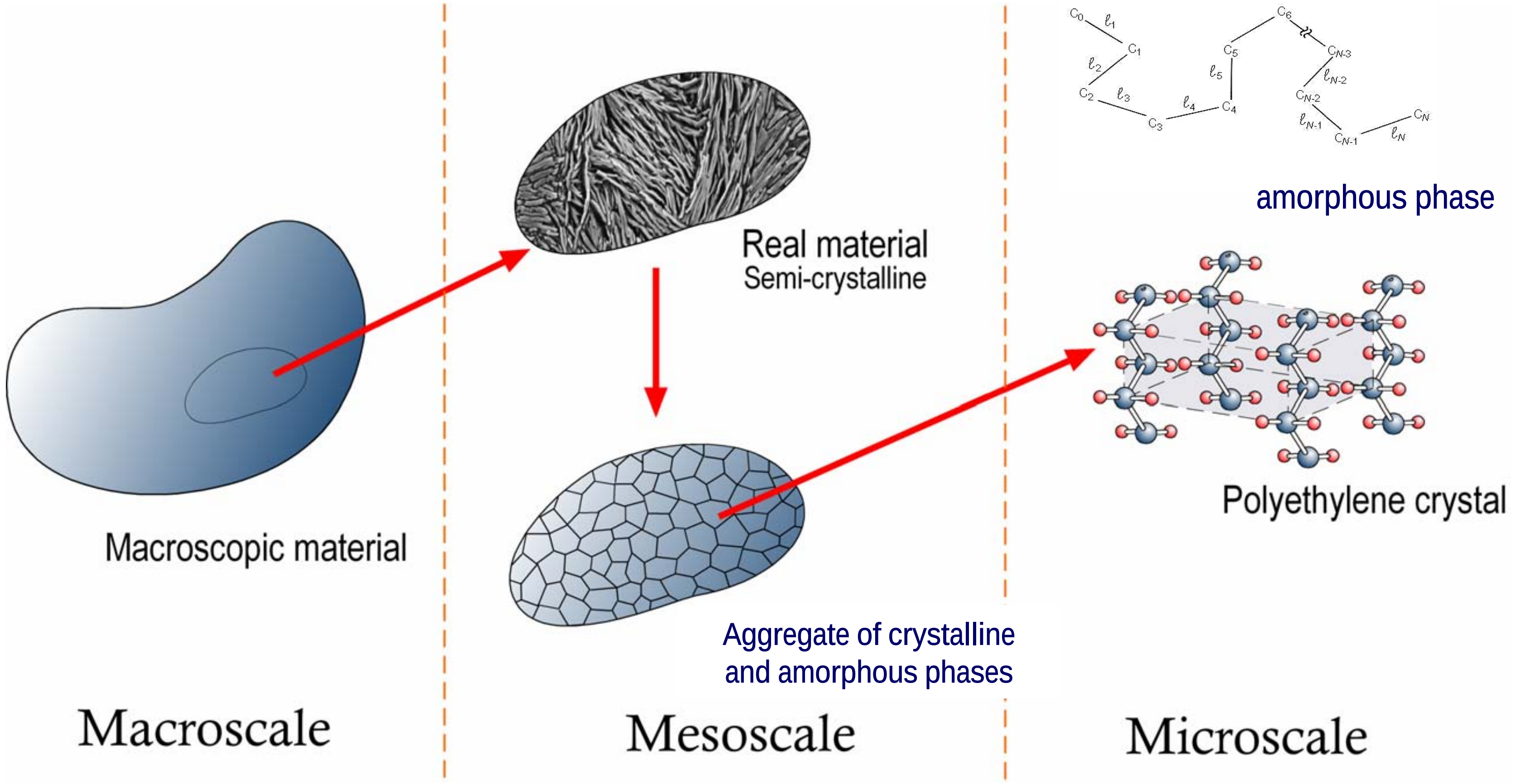


Idealized PE crystal

Inclusion volume-averaging



MICROMECHANICAL APPROACH



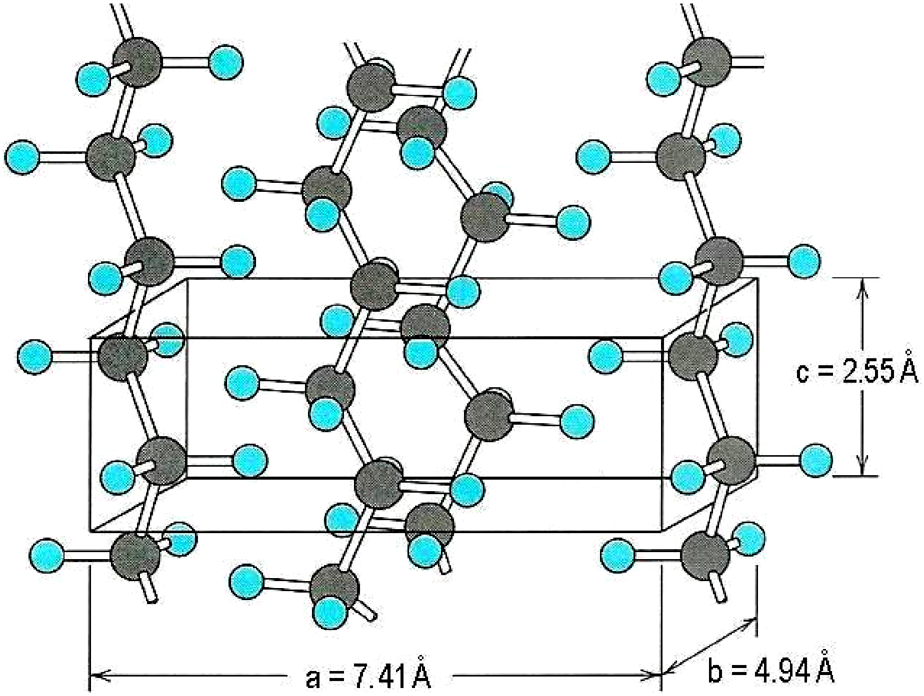
Homogenization technique

Inclusion constitutive model

Constitutive equations

CRYSTALLINE POLYETHYLENE

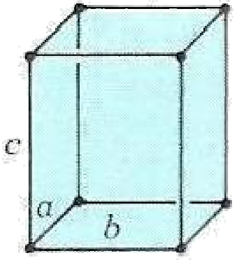
Crystalline cells



Orthorhombic crystal lattice

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^{\circ}$



Lattice parameters:

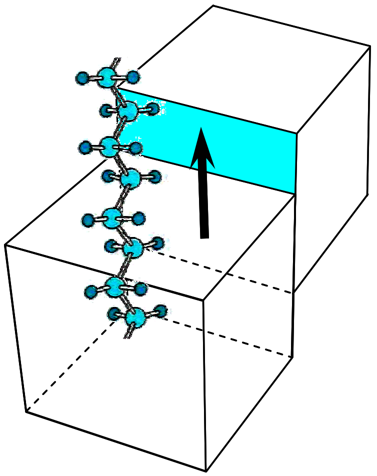
a = 7.4 x 10^{-10} m

b = 4.93 x 10^{-10} m

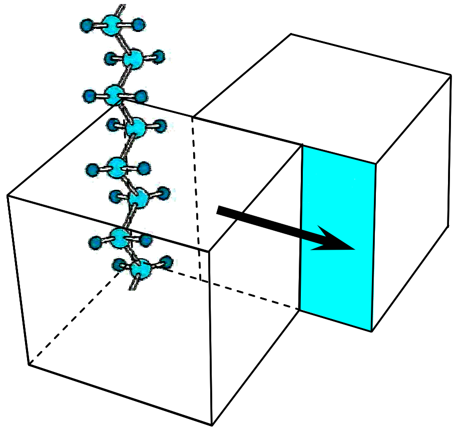
c = 2.54 x 10^{-10} m

CRYSTALLINE POLYETHYLENE

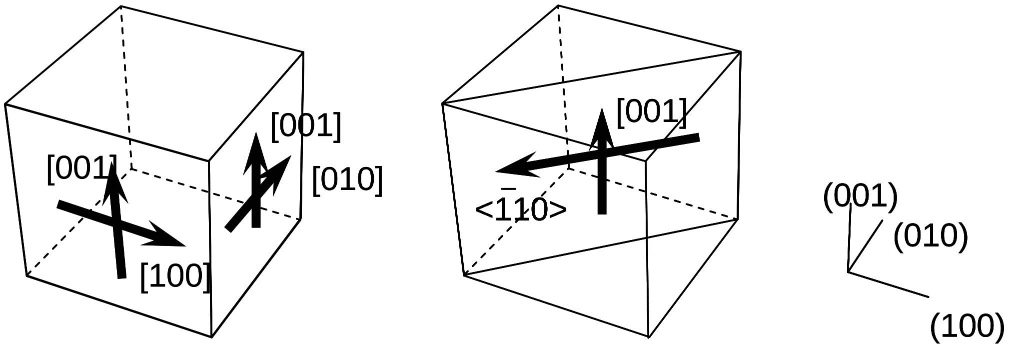
Deformation mechanisms - Slip systems



Chain slip



Transverse slip



Crystallographic slip systems

Slip system	g^{α}(MPa)
(100) [001]	7.2
(010) [001]	15.6
{110} [001]	13.0
(100) [010]	12.3

Critical shear strength

Bartczak *et al*, 1992

CRYSTALLINE POLYETHYLENE

Summary - Viscoplastic model

Schmid tensor

$$R^{\alpha} = \tfrac{1}{2}(n^{\alpha} \otimes s^{\alpha} + s^{\alpha} \otimes n^{\alpha})$$

$$A^{\alpha} = \tfrac{1}{2}(n^{\alpha} \otimes s^{\alpha} - s^{\alpha} \otimes n^{\alpha})$$

EQUILIBRIUM
Resolved shear stress

$$\tau^{\alpha} = S : R^{\alpha}$$

Stress-strain relationship

$$\dot{\gamma}^{\alpha} = \dot{\gamma}_0 \left(\frac{\tau^{\alpha}}{g^{\alpha}} \right)^{n}$$

$\dot{\gamma}^{\alpha}$ Shear strain rate
τ^{α} Resolved shear stress

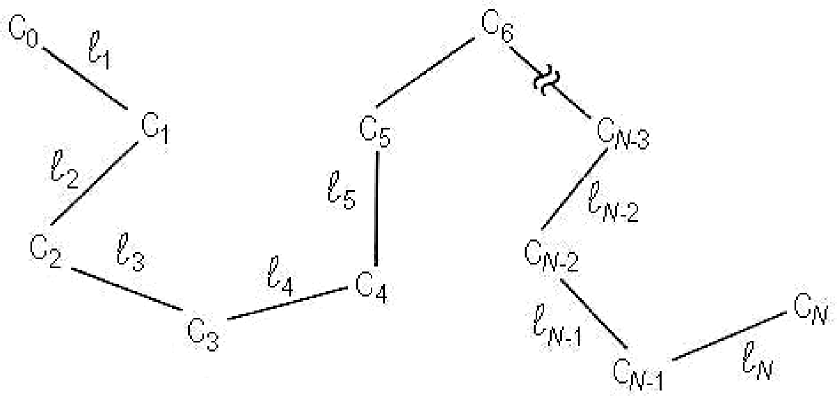
COMPATIBILITY
Deformation rate and spin

$$D^{p} = \sum_{\alpha=1}^{N} \dot{\gamma}^{\alpha} R^{\alpha} \qquad W^{p} = \sum_{\alpha=1}^{N} \dot{\gamma}^{\alpha} A^{\alpha}$$

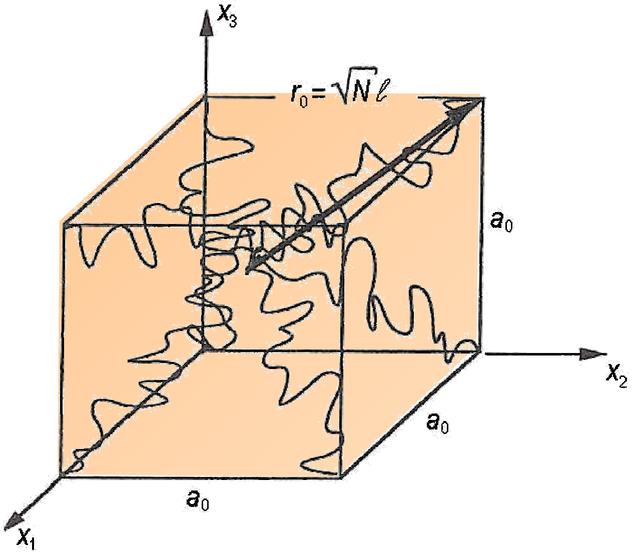
W^{p} Spin

D^{p} Deformation rate

AMORPHOUS POLYETHYLENE



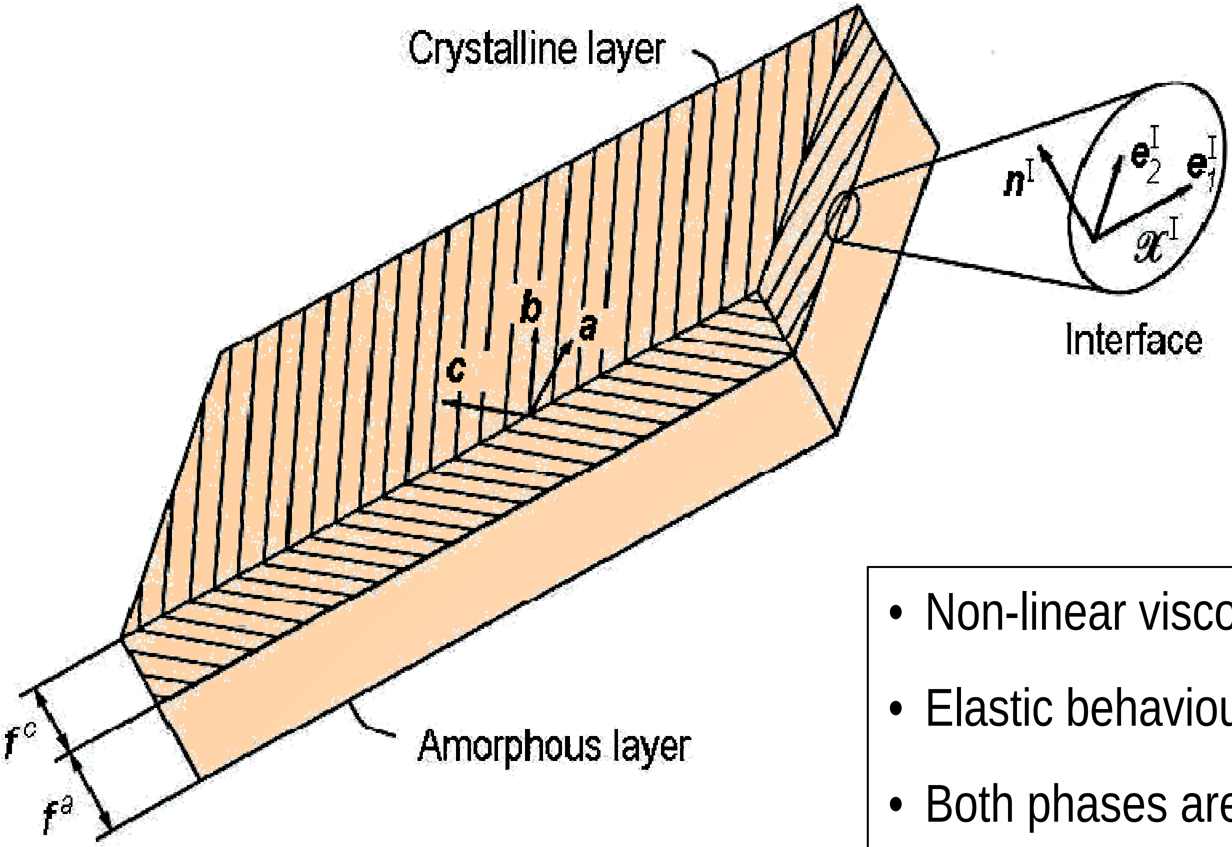
Idealized molecule



The eight-chain model

COMPOSITE INCLUSION

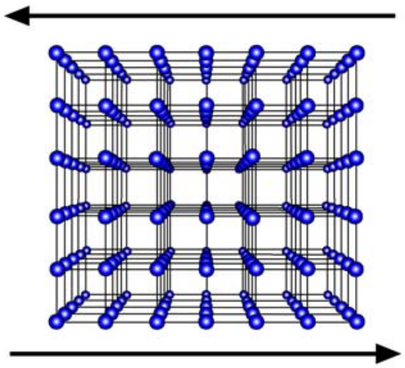
Inclusion constitutive model



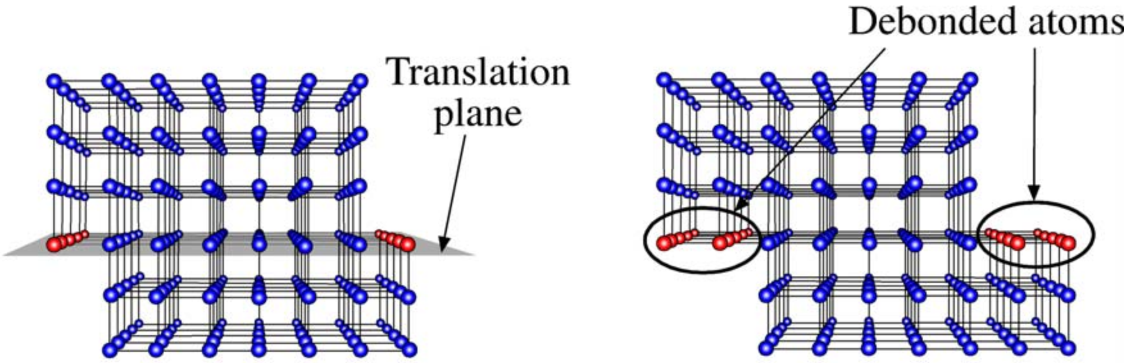
- Non-linear viscoplastic behaviour.
- Elastic behaviour is not included.
- Both phases are incompressible.
- Insensitive to pressure deformation
- Deformation and stress are uniform.

DEFORMATION MECHANISMS

Stress-strain relationship



Unstrained crystal



Fragmentation

$$\dot{\gamma}^{\alpha} = \dot{\gamma}_0 \left(\frac{\tau^{\alpha}}{g^{\alpha}} \right)^{n}$$

Classic viscoplastic model

$$\dot{\gamma}^{\alpha} = \dot{\gamma}_0 \left(\frac{\tau^{\alpha}}{(1-\Omega^{\alpha})g^{\alpha}} \right)^{n}$$

$$\Omega^{\alpha} \equiv \frac{\text{No. atomic debonds}}{\text{Initial No. atomic bonds}}$$

Proposed damage model

DAMAGE MODEL

Stress-strain state in single crystals

$$\dot{\gamma}^{\alpha} = \dot{\gamma}_0 \left(\frac{\tau^{\alpha}}{g^{\alpha}} \right)^{n}$$

Classic viscoplastic model

$$\dot{\gamma}^{\alpha} = \dot{\gamma}_0 \left(\frac{\tau^{\alpha}}{(1-\Omega^{\alpha})g^{\alpha}} \right)^{n}$$

Stress-strain relationship

$$\frac{d\Omega^{\alpha}}{d\tau^{\alpha}} = \dot{\Omega}_0 \left(\frac{\tau^{\alpha}}{(1-\Omega^{\alpha})g^{\alpha}} \right)^{m}$$

Damage evolution law

$$\frac{d\dot{g}^{\alpha}}{d\dot{\gamma}^{\alpha}} = C$$

Hardening law

Damage model

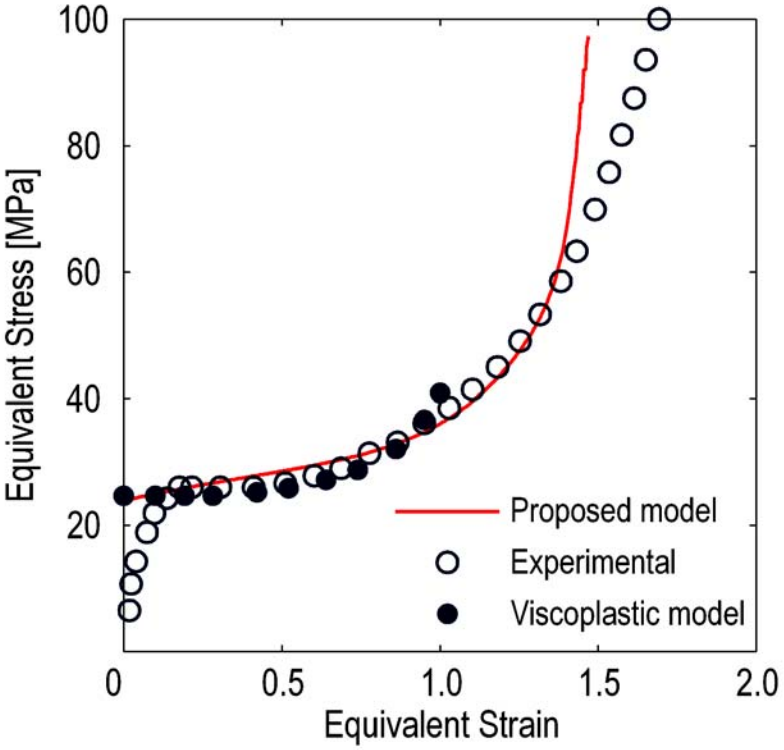
PRELIMINARY RESULTS

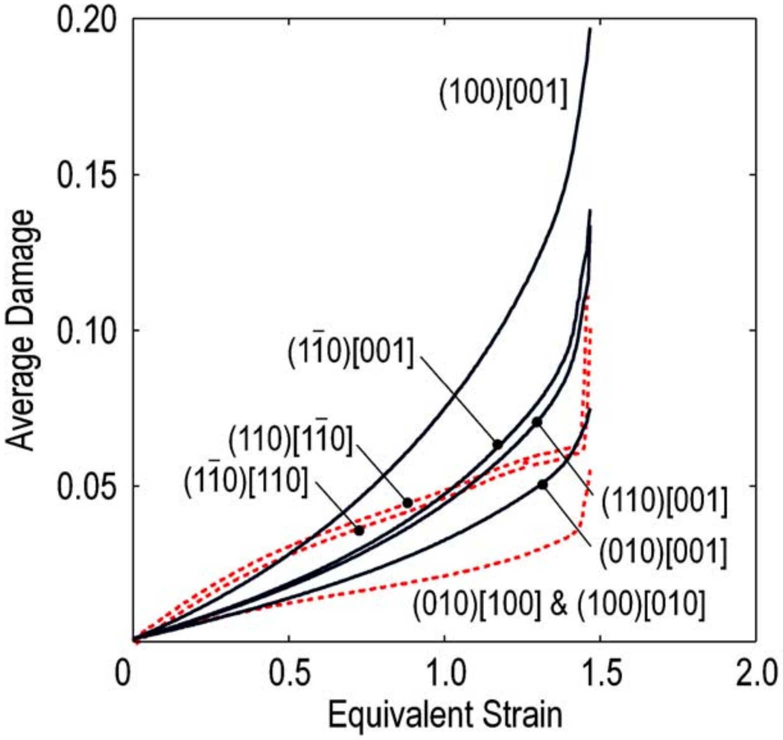
Numerical implementation of existing models

- Idealized 100% crystalline polyethylene.
- 100 randomly oriented crystals.
- Initially isotropic texture.
- Uniaxial tension and simple shear

UNIAXIAL TENSION

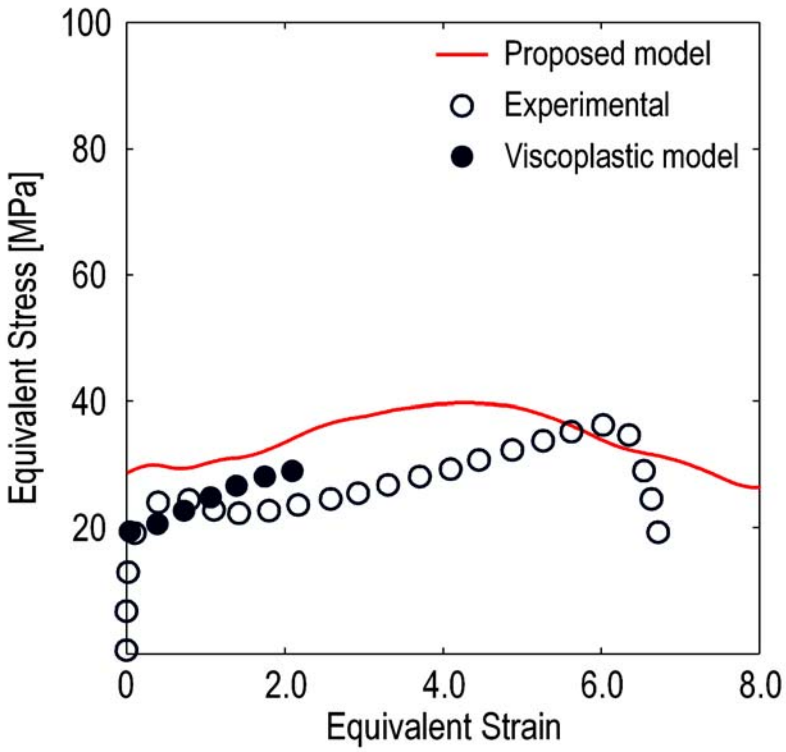
Stress-strain behaviour and damage evolution

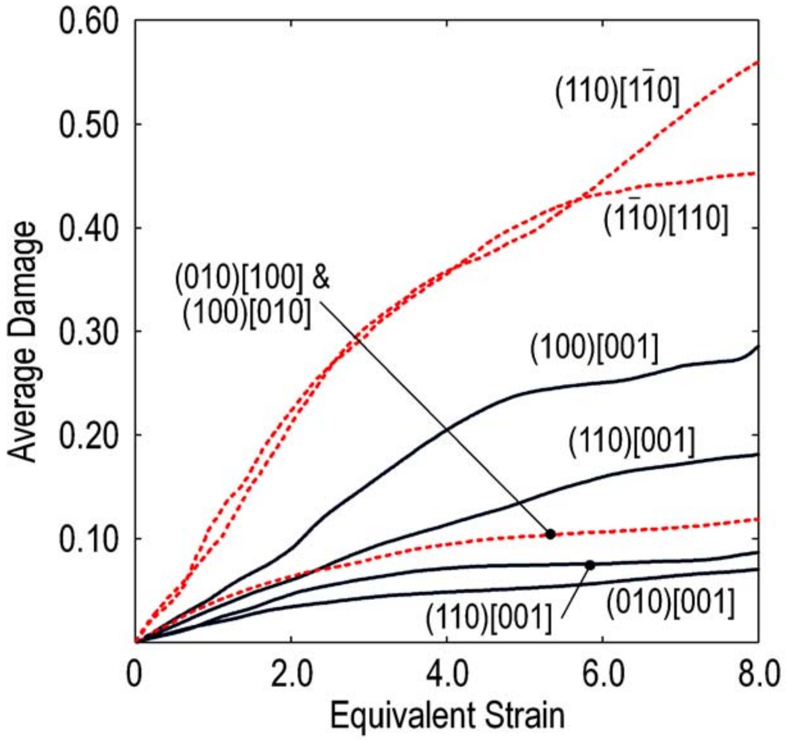




SIMPLE SHEAR

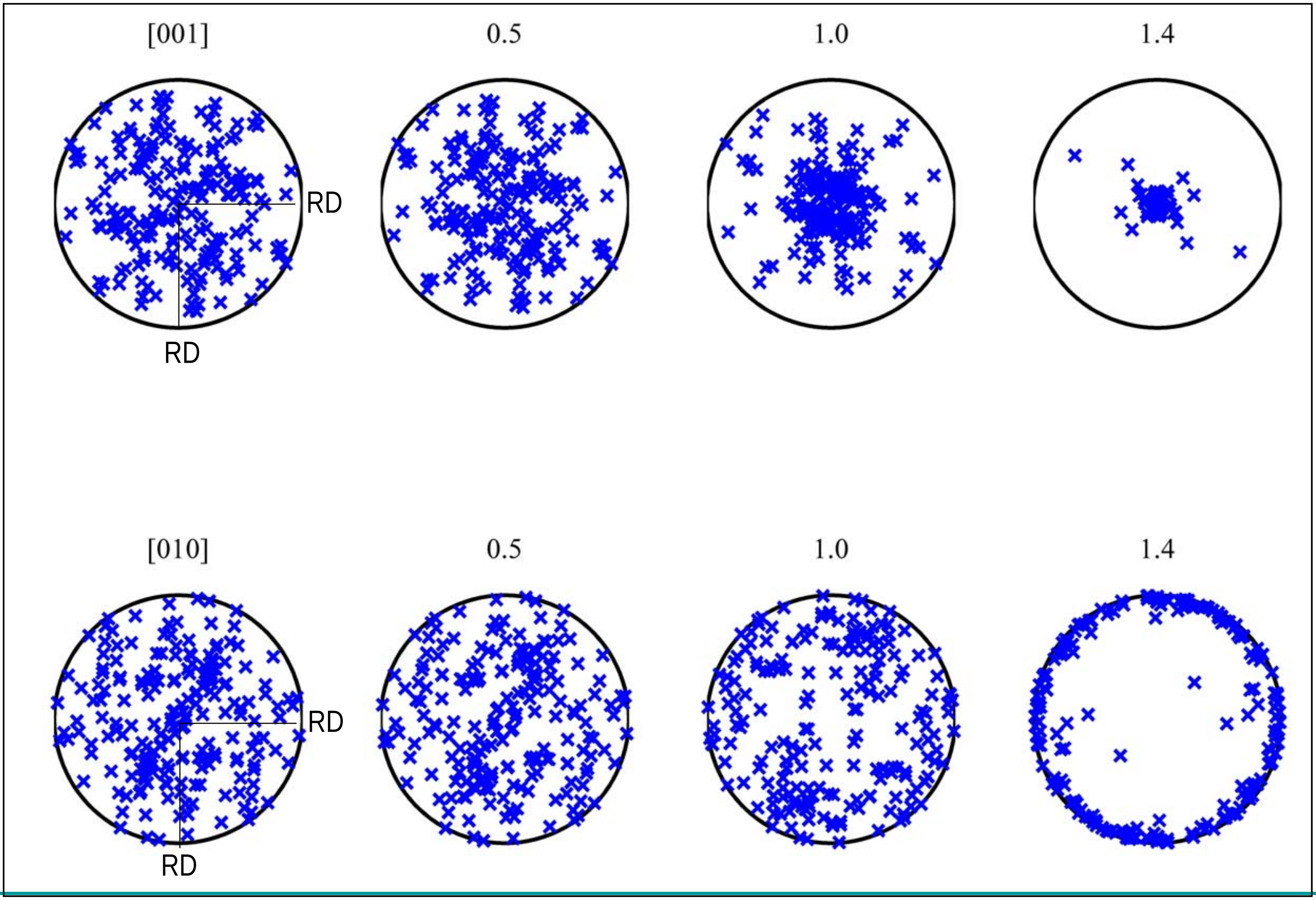
Stress-strain behaviour and damage evolution





NUMERICAL RESULTS – UNIAXIAL TENSION

Crystallographic textures in 100% crystalline polyethylene



Projection plane perpendicular to the loading direction

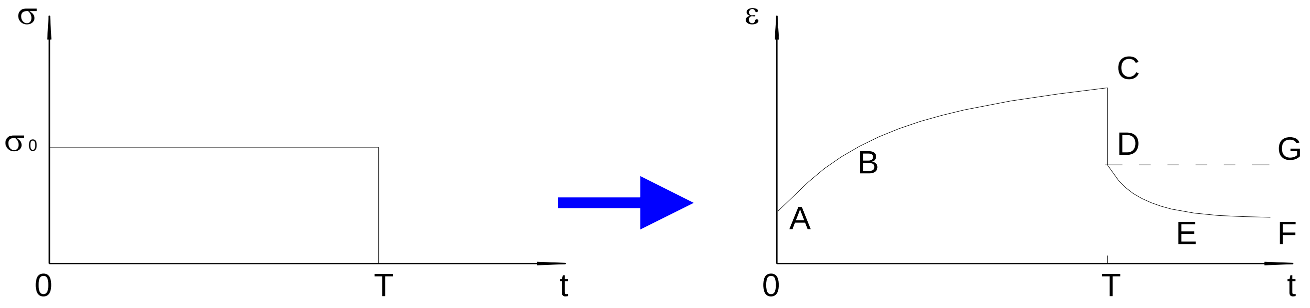
MACROMODELLING OF POLYETHYLENE MATERIALS

Doctoral Candidate: Hongtao Liu
Civil Engineering

Objective:

To develop a nonlinear viscoelastic model to be used in finite element analysis for polyethylene structures

BEHAVIOUR OF POLYETHYLENE MACRO-MECHANICAL CREEP RESPONSE



(a)

(b)

LOADING

- instantaneous elastic response
- delayed elastic response
- viscous flow

UNLOADING

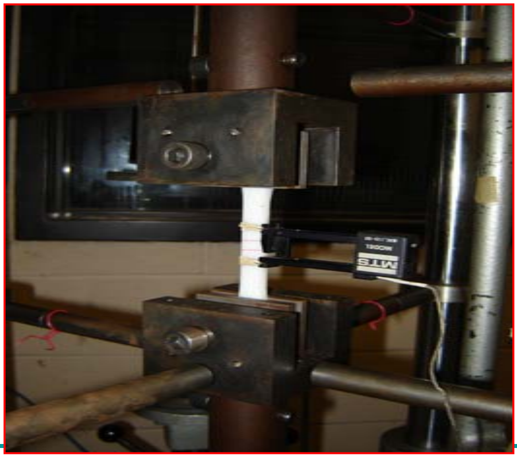
- instantaneous elastic drop
- delayed recovery
- permanent (plastic) deformation

MATERIAL TESTING

- **Creep tests**
  - Short – 24 hr (used in model calibration)
  - Long – 14 day, 7 day
- **Tensile load rate tests**
  - Load(stress) rate
  - Strain rate
- **Complex tests**
  - Combinations of load rate and creep

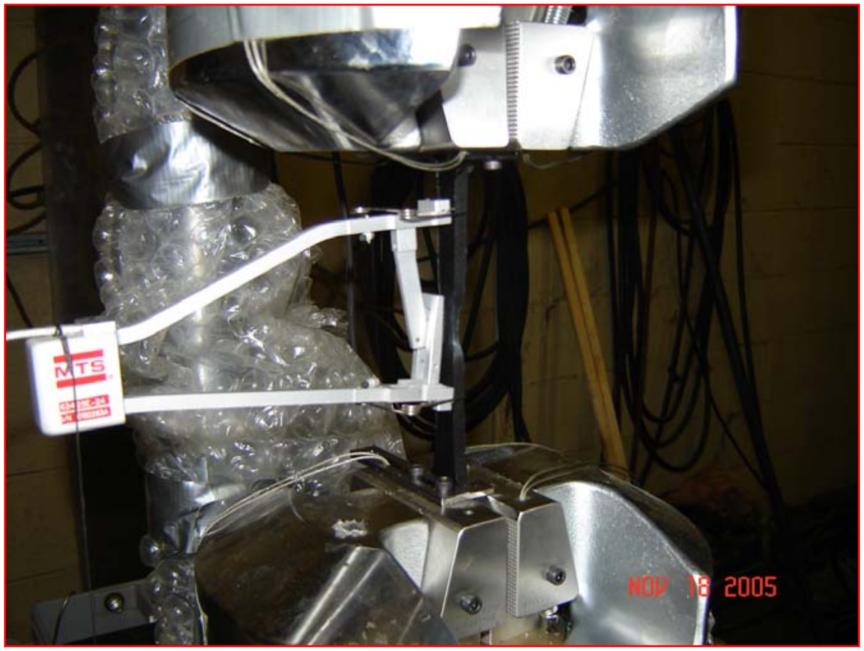
TEST SET-UP FOR CREEP

- Loading is applied by dead weights through a lever
- Clip-on strain gage is used
- Strain history is recorded

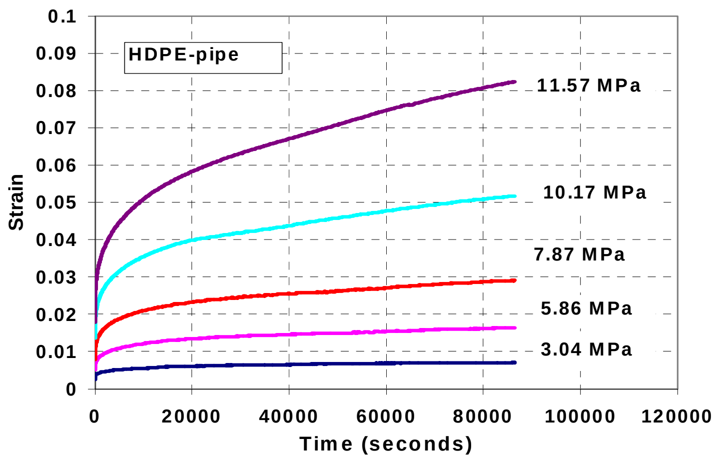


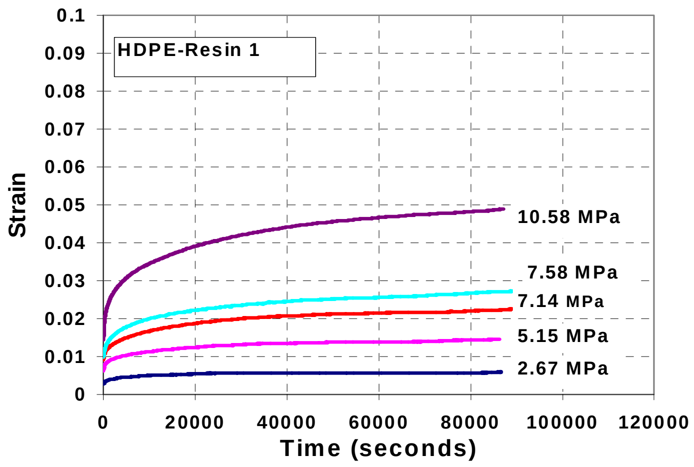
MATERIAL TESTING

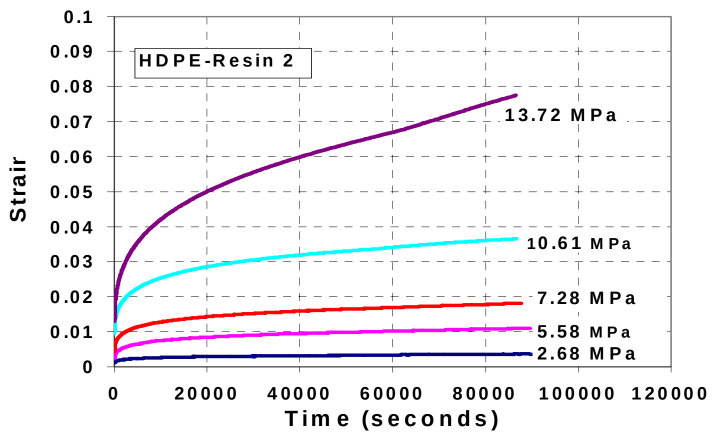
- MTS tester

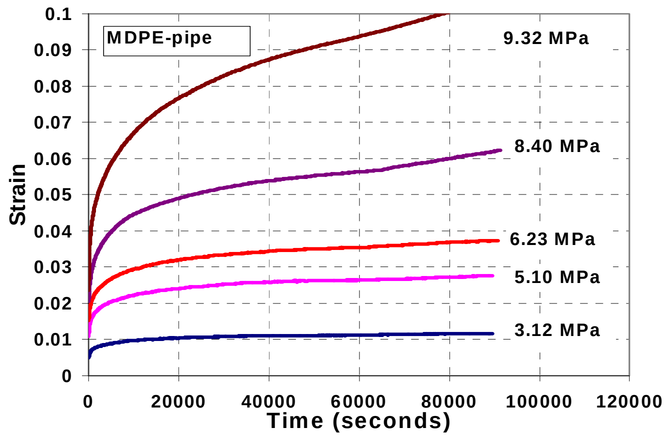


EXPERIMENTAL CREEP RESPONSE OF FOUR POLYETHYLENES TESTED IN THE RESEARCH PROGRAM.

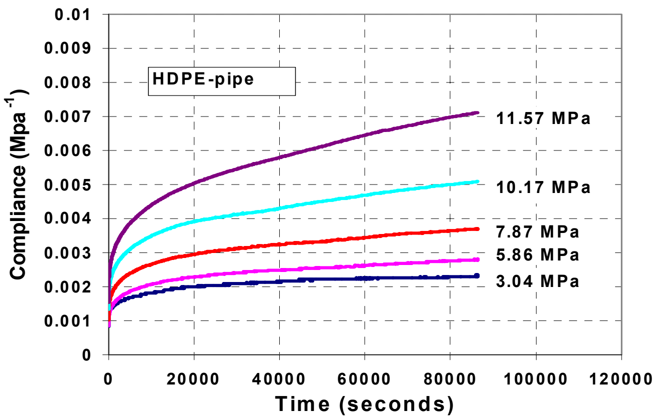


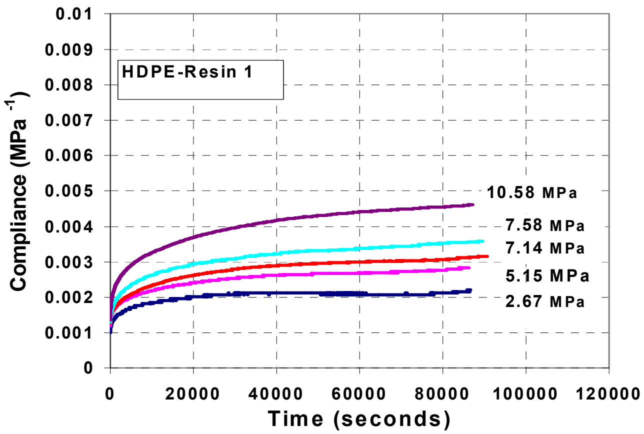


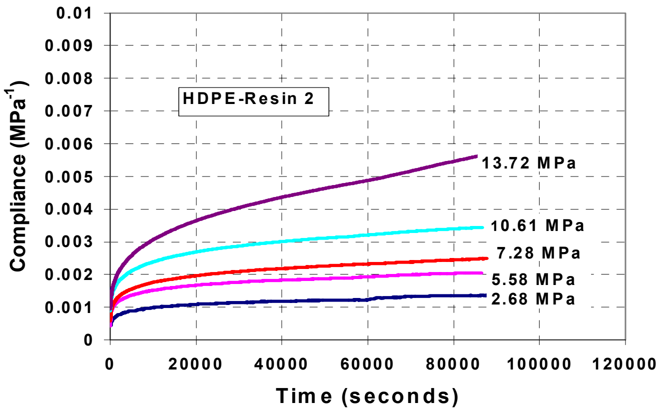


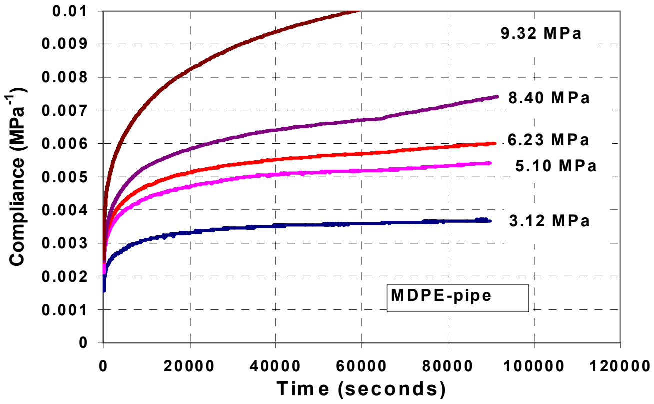


EXPERIMENTAL COMPLIANCE CURVES FOR FOUR POLYETHYLENES TESTED IN THE RESEARCH PROGRAM.

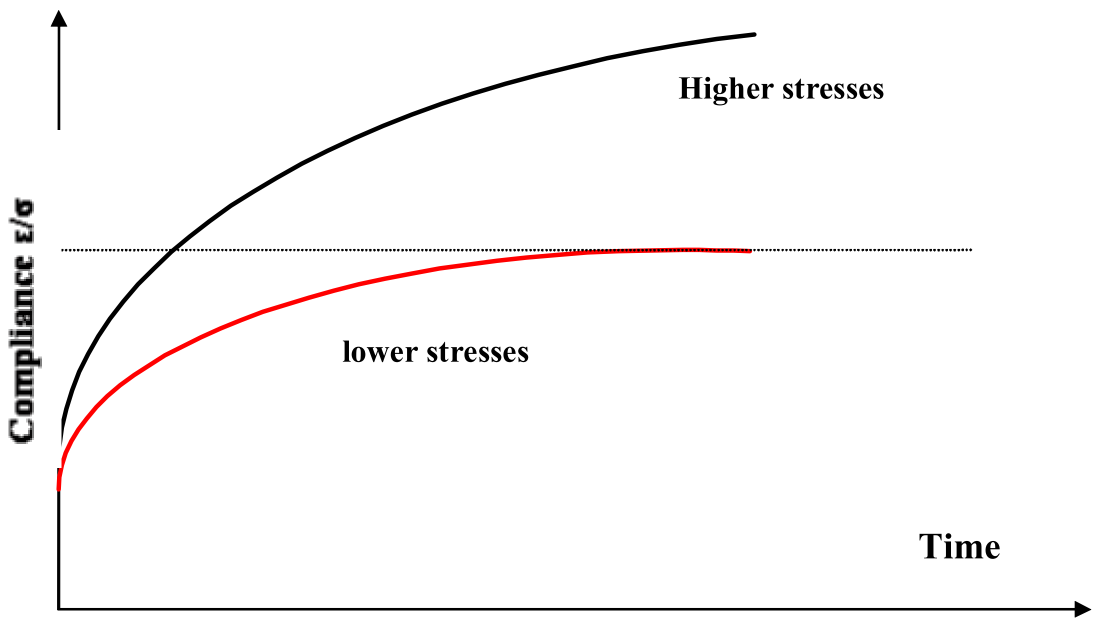








TYPICAL CREEP COMPLIANCE CURVES FOR POLYETHYLENE SUBJECT TO LOW AND HIGH LEVELS OF STRESSES.



MODEL GENERATION

Viscoelastic Models

Integral formulation: $$\varepsilon(t) = \int_0^t \psi(t-\tau)\,\dot{\sigma}(\tau)\,d\tau$$

For constant stress: $$\varepsilon(t) = \psi(t)\sigma$$

- Multi-Kelvin Approach; exponential functions

$$\psi(t)=\psi_e+\psi_v(t)=\frac{1}{E_0}+\sum_{i=1}^{n}\frac{1}{E_i}\left\{1-\exp\left(-\frac{t}{\tau_i}\right)\right\}$$

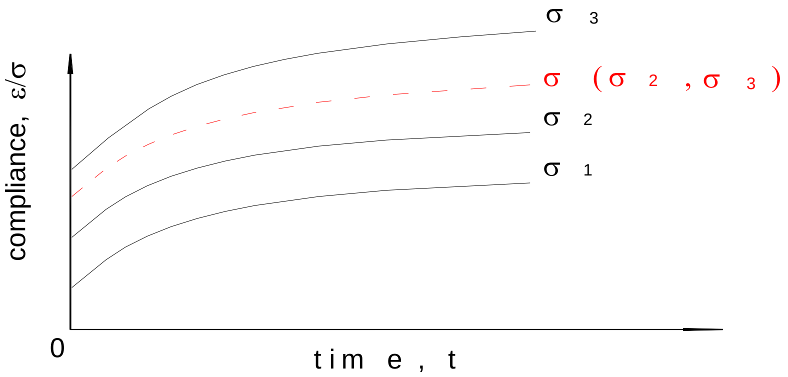
- Power Functions

$$\psi(t)=\psi_e+\psi_p(t)=\frac{1}{E_0}+C_0t^{C_1}$$

MODEL GENERATION

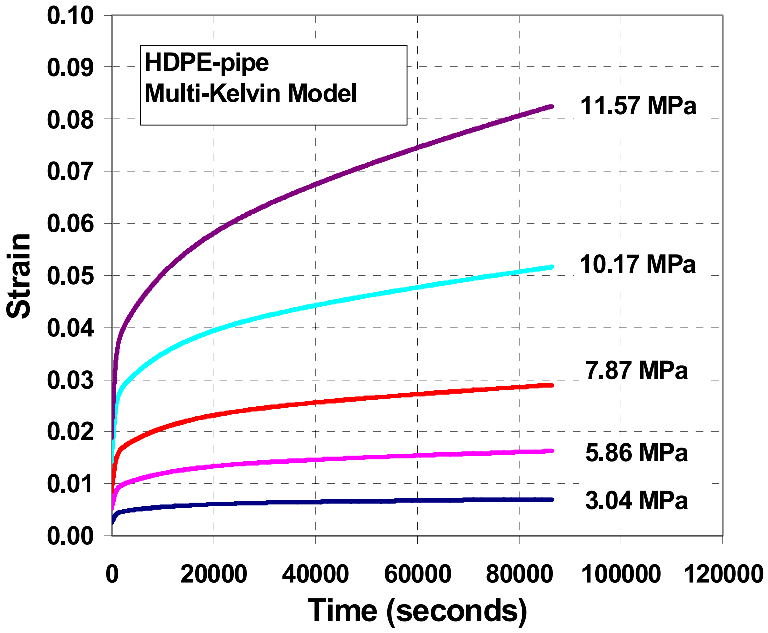
- Nonlinear least-squares fitting creep data
- Linear interpolation to include stress effects
- The model for a given PE is presented in a table form

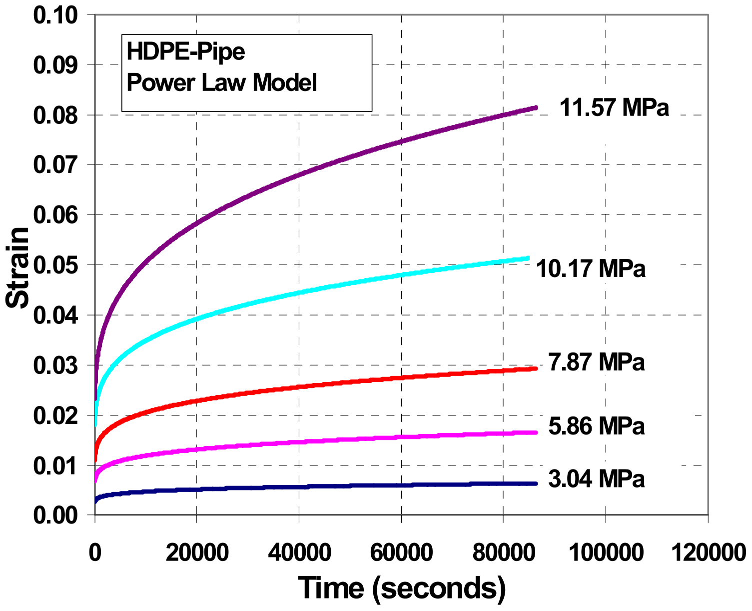
$$\varepsilon(t)=\int_0^t\left\{\frac{1}{E_0(\sigma)}+\sum_{i=1}^{n}\frac{1}{E_i(\sigma)}\left\{1-\exp\left(-\frac{t-\tau}{\tau_i(\sigma)}\right)\right\}\right\}\dot{\sigma}(\tau)\,d\tau$$



Number of Kelvin elements		3		
		τ_1	τ_2	τ_3
stress	E_0	500	10000	200000
		E_1	E_2	E_3
2.97	650	797.3889	2320.3566	925.0882
5.97	580	913.5936	1212.2605	695.0461
7.71	520	1224.7911	1104.9922	385.8572
10.31	500	1034.2045	694.1084	226.4555
12.19	470	1128.4448	806.0972	140.6875

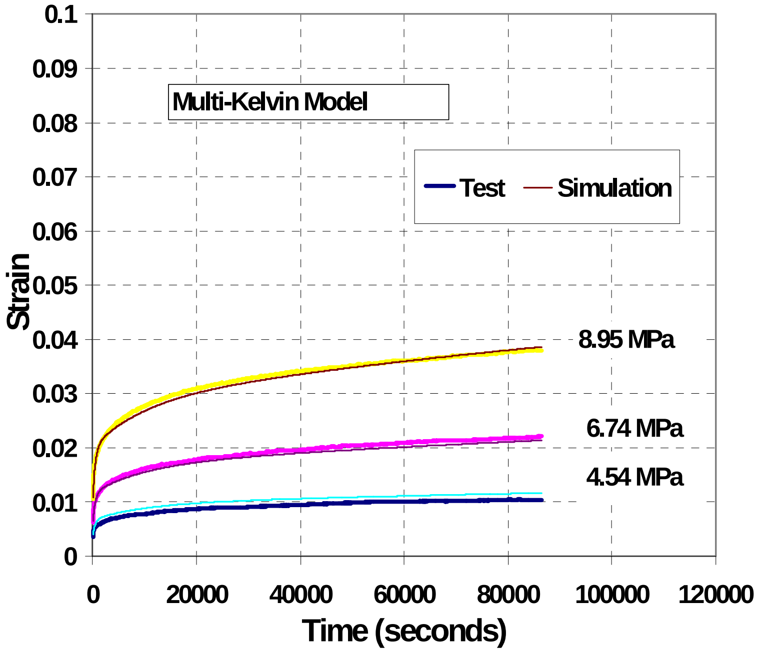
SIMULATED CREEP TESTS

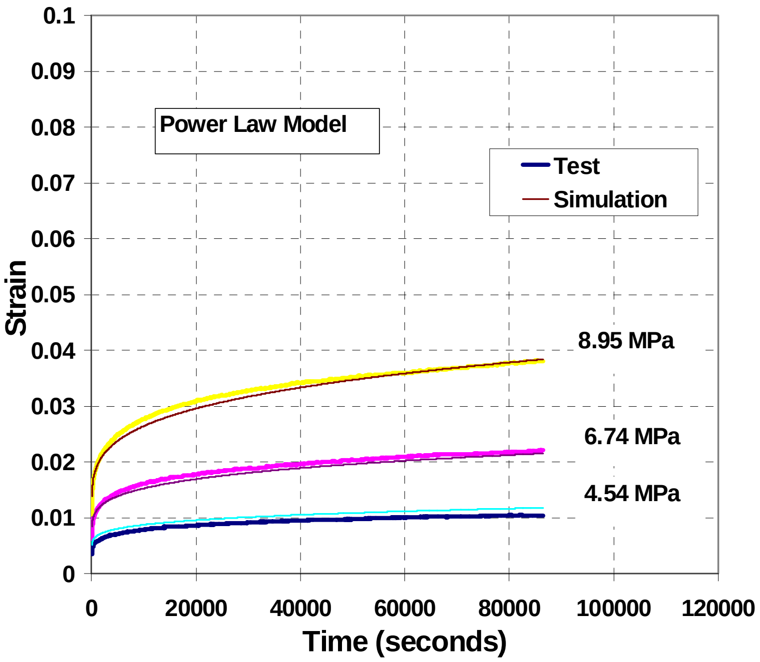




SIMULATED AND EXPERIMENTAL CREEP CURVES FOR STRESSES OTHER THAN THE ONES USED FOR MODEL CALIBRATION.

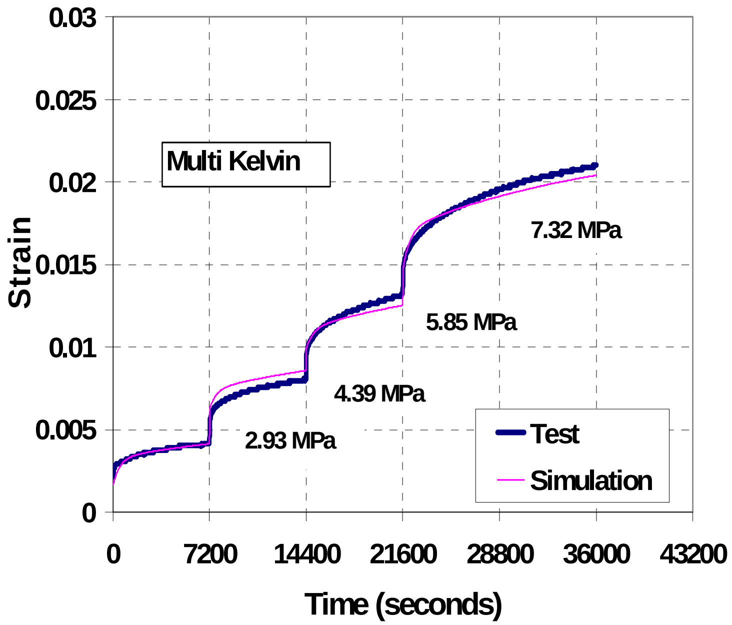
HDPE-PIPE

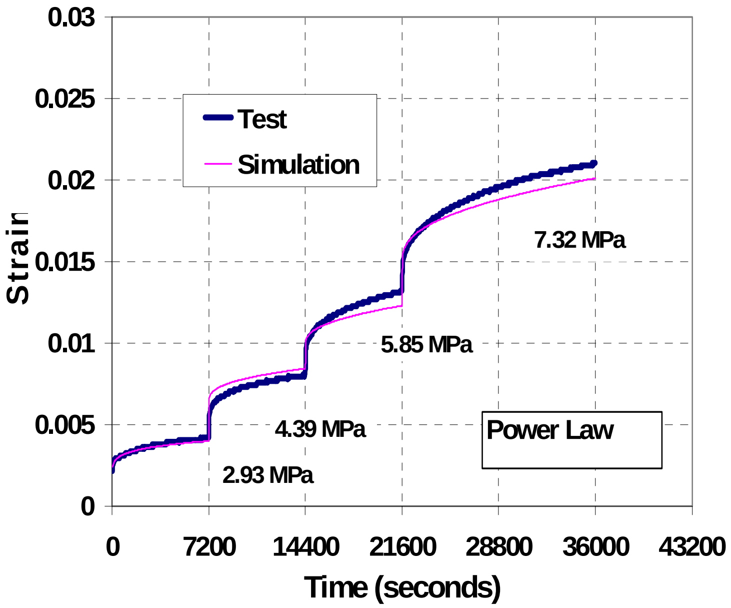




RESPONSE TO TENSILE STEP-LOADING

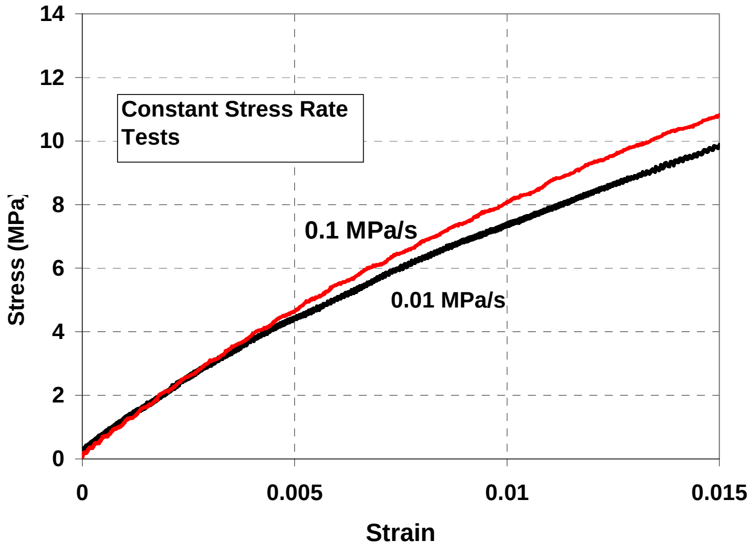
HDPE-PIPE

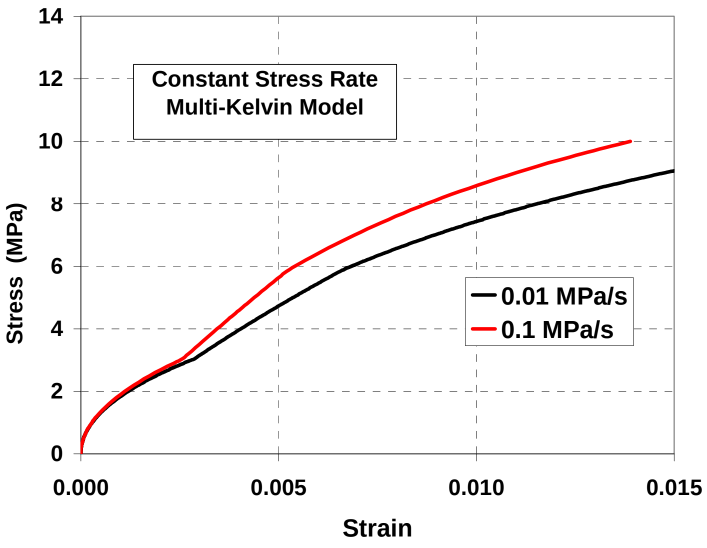




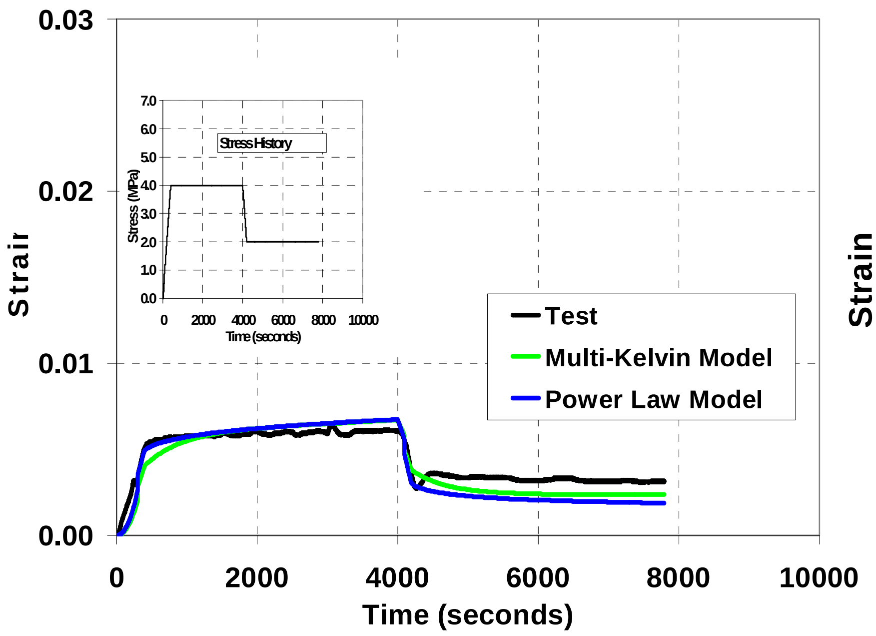
TESTS AND MODELLING LOAD RATE EFFECTS

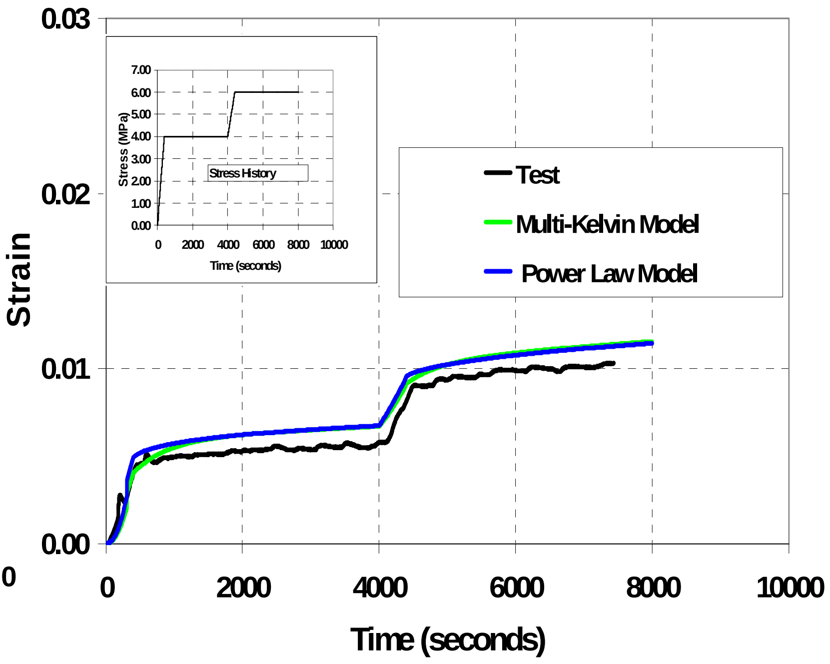
Stress-Strain Relationships





COMPLEX LOAD HISTORIES; LOAD RATES AND CREEP





RELAXATION FUNCTION FROM CREEP COMPLIANCE

$$\varepsilon(t) = \int_0^t \psi(t-\tau)\dot{\sigma}(\tau)d\tau \qquad \sigma(t) = \int_0^t \phi(t-\tau)\dot{\varepsilon}(\tau)d\tau$$

$$\boxed{t = \int_0^t \psi(t-\tau)\varphi(t)d\tau}$$

Numerical procedure to calculate hereditary integral

FINITE ELEMENT MODELLING

3-D APPLICATIONS

- Isotropic and incompressible material
- Extend creep compliance (relaxation function) to 3-D elastic equations
- Using ABAQUS
  - Material User Subroutine (UMAT) can be programmed to include new material models

$$\sigma_{eff}(t)=\sqrt{(\sigma_{11}^2+\sigma_{22}^2+\sigma_{33}^2)-(\sigma_{11}\sigma_{22}+\sigma_{22}\sigma_{33}+\sigma_{33}\sigma_{11})+3(\sigma_{12}^2+\sigma_{23}^2+\sigma_{31}^2)}$$

$$\varepsilon_{eff}(t)=\frac{2}{3}\sqrt{(\varepsilon_{11}^2+\varepsilon_{22}^2+\varepsilon_{33}^2)-(\varepsilon_{11}\varepsilon_{22}+\varepsilon_{22}\varepsilon_{33}+\varepsilon_{33}\varepsilon_{11})+3(\varepsilon_{12}^2+\varepsilon_{23}^2+\varepsilon_{31}^2)}$$

SUMMARY AND CONCLUSIONS

- **Polyethylene is a nonlinear and time dependent material**
- **Different polyethylenes behave differently under stress and strain**

- ***Chemical analysis* , combined with its rheological testing can be used to correlate chemical and mechanical properties of PE**
  - **Molecular weight , molecular weight distribution and branching influence both deformation and failure of polyethylene.**

SUMMARY AND CONCLUSIONS

- *Micromechanical* modelling provides information on the role of physical structure of PE on the macroscopic behaviour
    - Realistic results were obtained by implementing damage mechanics concepts into viscoplastic modelling of PE
- *Macromechanical* modelling was presented.
    - The method can be easily used for modelling any material and can be adapted for finite element analysis

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