EFFECT OF DEGRADATION DURING PROCESSING ON THE MELT VISCOSITY OF A THERMOPLASTIC POLYURETHANE

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OUTLINE

Thermoplastic Polyurethanes

Thermal Degradation

Influence of Polymer Processing Parameters

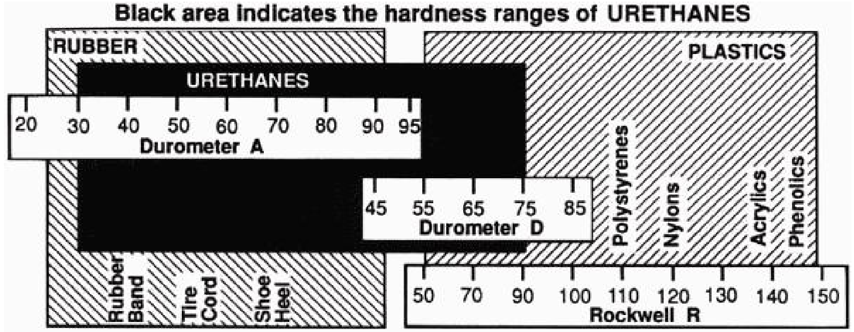
Rheometry

Viscosity Model

Conclusions

THERMOPLASTIC POLYURETHANES

- High performance elastomers
- Tough thermo-plastics
- Bridges the material gap between rubbers and plastics.



Engineering:

- high impact strength
- abrasion resistance
- solvent and oil resistance
- good adhesión
- soft-electronics

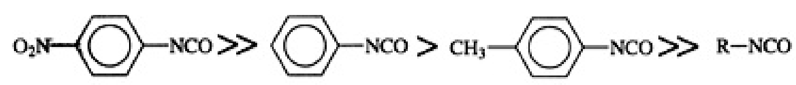
Biomedical:

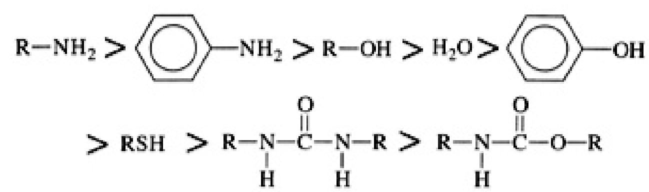
- biomimetic
- antithrombotic
- surgical implants
- soft prothesis

http://www.sdplastics.com/polyuret.html

THERMOPLASTIC POLYURETHANES

- linear segmented copolymers
- micro-phase separated hard and soft segments
- hard segments held together by hydrogen bonds (physical crosslinks).
- thermally labile at melt temperatures
- processed like other thermoplastics via extrusion, injection molding, etc.
- covalent urethane bonds in the TPU backbone are also prone to dissociate at elevated temperatures.





Physical Property Ranges

aromatic TPUs		ASTM	polyester 80A	polyester 65D	polycaprolactone 80A	polyether 80A	polyether 65D
Tensile Strength	psi	D412	5400	6000	5000	5000	6400
Elongation	%	D412	575	400	500	600	390
Tear Strength	Die C pli	D624	600	1300	650	500	1500
Taber Abrasion	H-22		range 10-20	50-60	20-30	20-30	80-100

aliphatic TPUs		ASTM	polyester 80A	polyester 55D	polyether 75A	polyether 60D
Tensile Strength	psi	D412	8000	5000	3000	4500
Elongation	%	D412	430	350	350	360
Tear Strength	Die C pli	D624	400	550	300	700

http://www.polyurethane.org/

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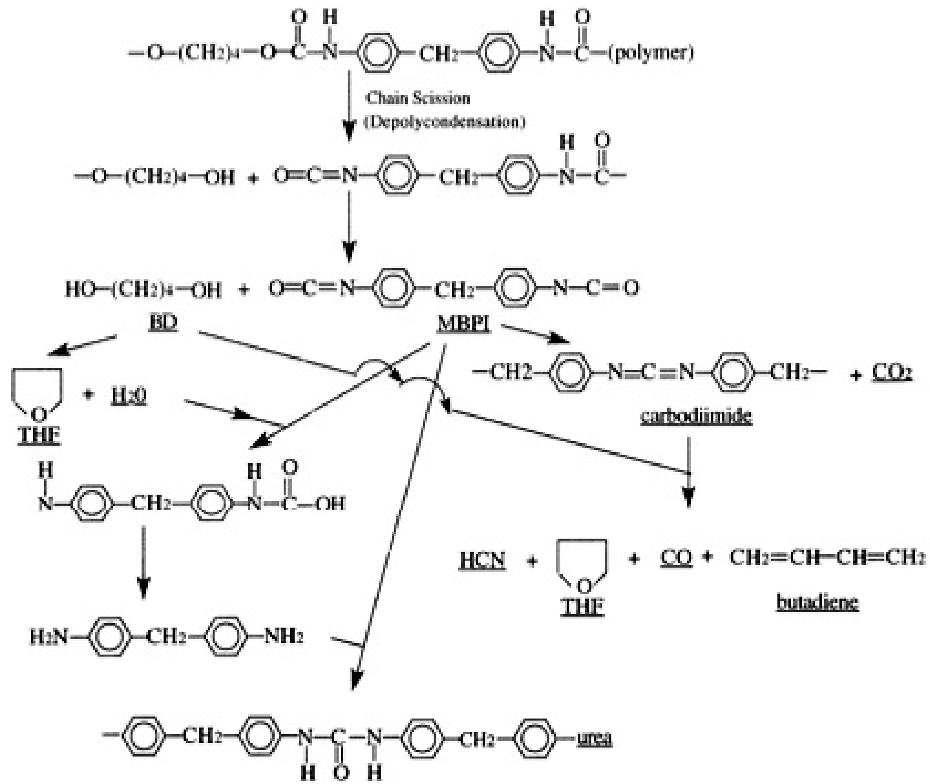
THERMAL DEGRADATION

- widely investigated and are well understood.
- melting usually occurs around or beyond the stability temperature of the urethane linkages
- under ‘mild’ conditions (temperature below 250 ºC), equilibrium is quickly established between urethane linkages and free isocyanate and hydroxyl end-groups.



Grassie, N.; Zulfiqar, M. *J. Polym. Sc., Pol. Chem. Ed* **1978**, *16*, 1563-1574.

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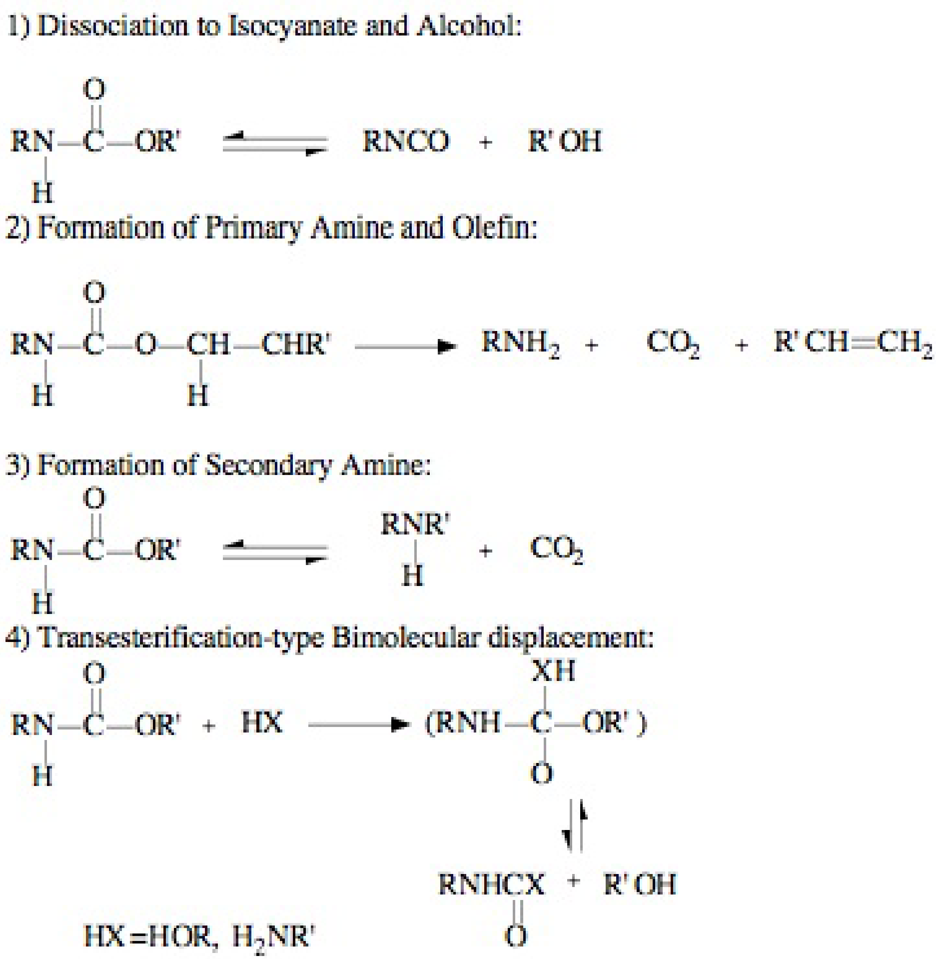
THERMAL DEGRADATION

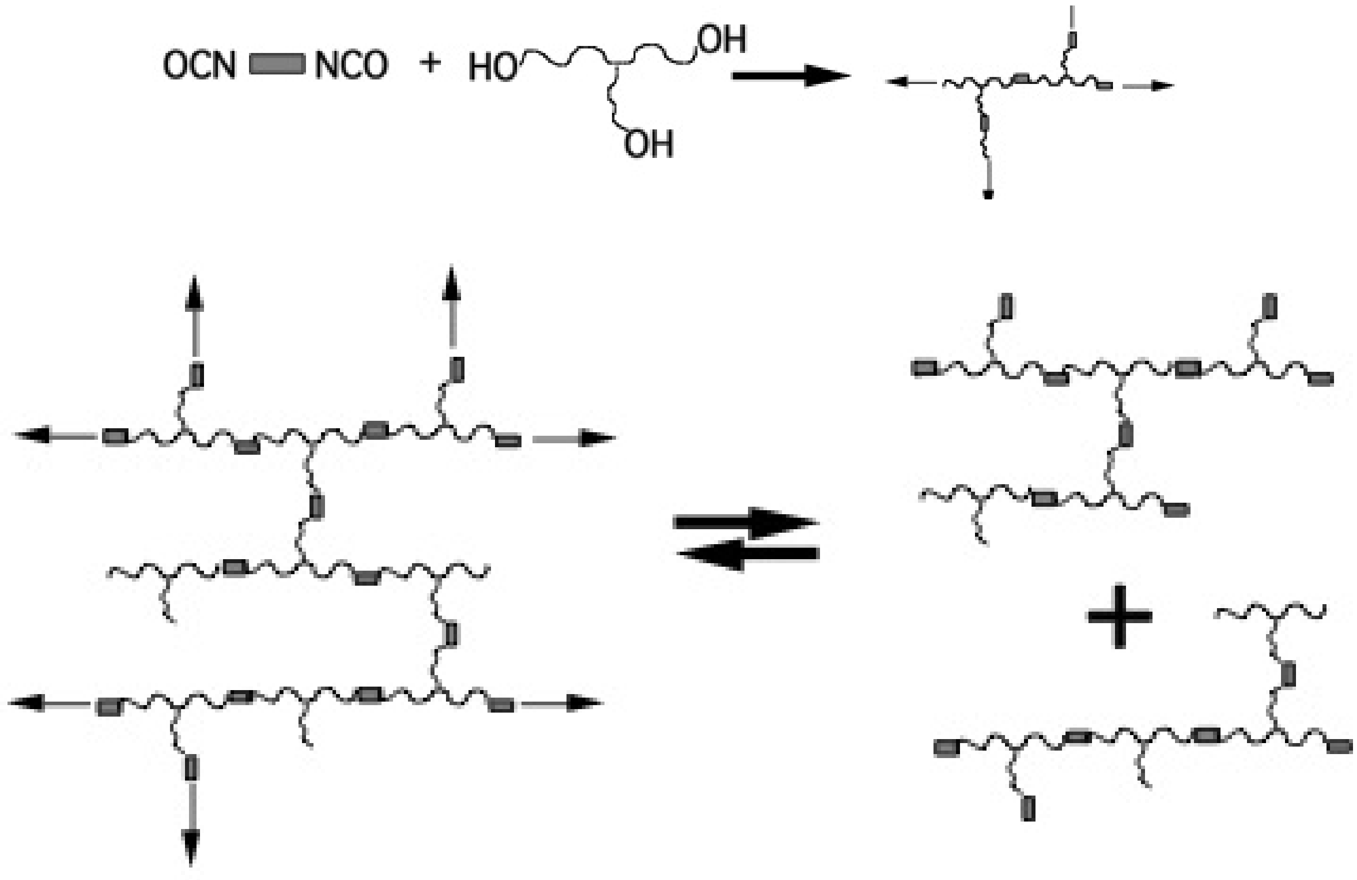


- Chief concern: urethane bond stability during processing of polyurethanes.
- Key variable in modeling processing operations: melt viscosity.
- Degradation of polyurethanes in the melt state is unavoidable.
- Melting occurs at temperatures higher than the stability temperature of urethanes.

Moses, P. J. *ANTEC* **1989**, 860-865.
Chen, A. T.; Ehrlich, B. S.; Moses, P. J. *Proc. SPI Annu. Tech./Mark. Conf.* **1990**, *33*, 225-230

THERMAL DEGRADATION

Urethanes can undergo reversible degradation.



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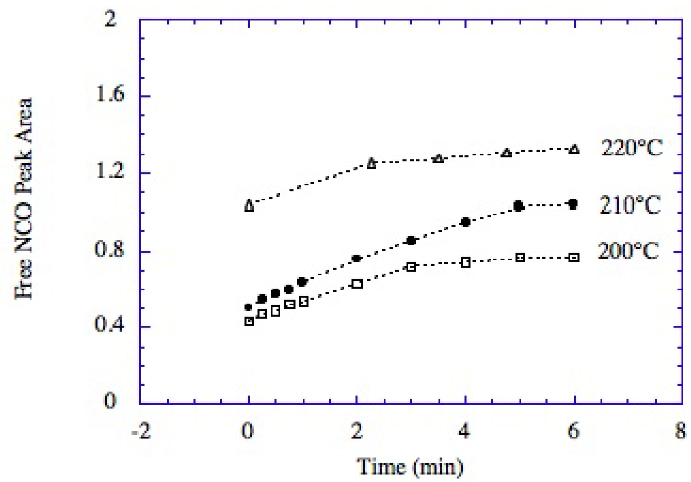
POLYMER PROCESSING PARAMETERS

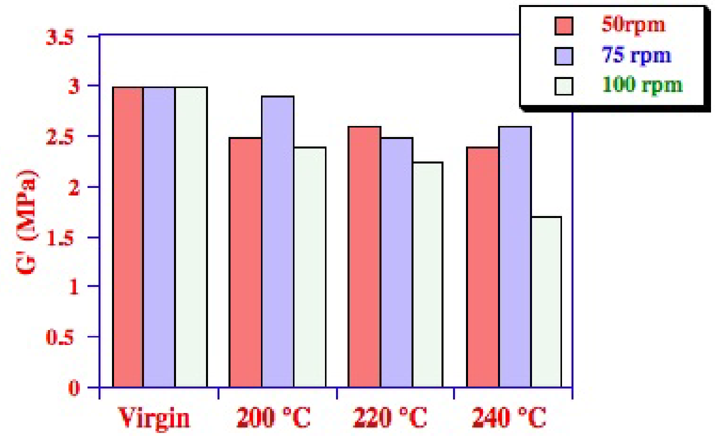
During melting:

- Teq = Tstab - 50 ºC
- several degradation mechanisms
- thermal degradation affects
    1. rheological behavior
    2. processing conditions
    3. material properties



During processing:

- sharp increase in flow
- greater than expected due to thermal effects only.



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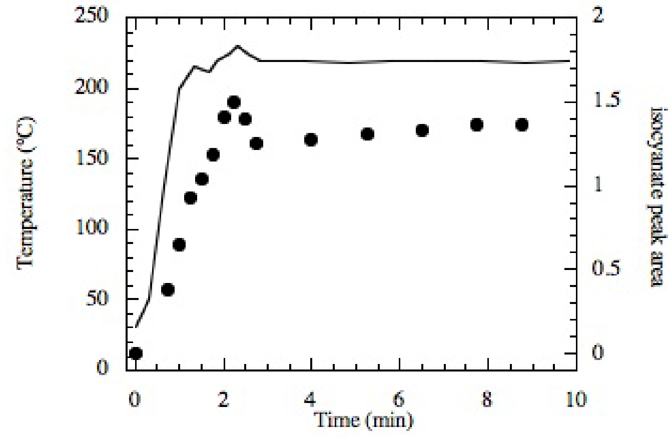
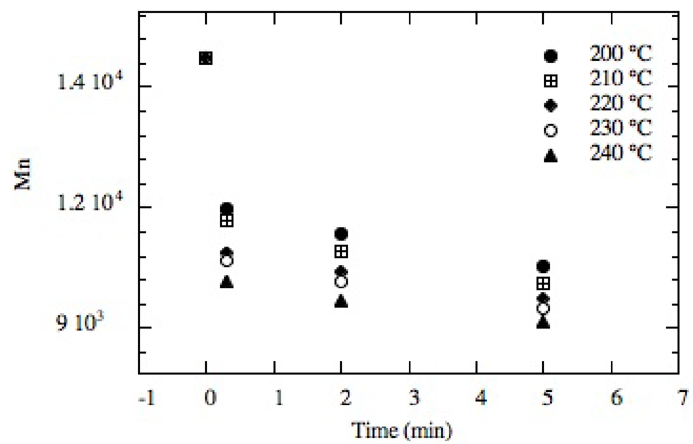
POLYMER PROCESSING PARAMETERS

To explain this unusual processing behavior, it is important to understand and predict the rheological properties of TPU under processing conditions.

Care must be taken when working with traditional rheological models that deal with temperature and molecular weight separately. ‘

Since the degree of thermal degradation is changing with temperature, molecular weight also becomes temperature-dependent.





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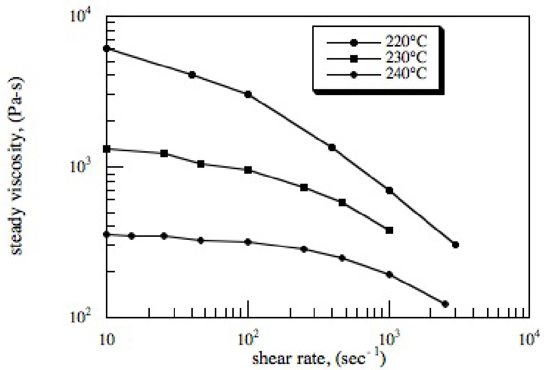
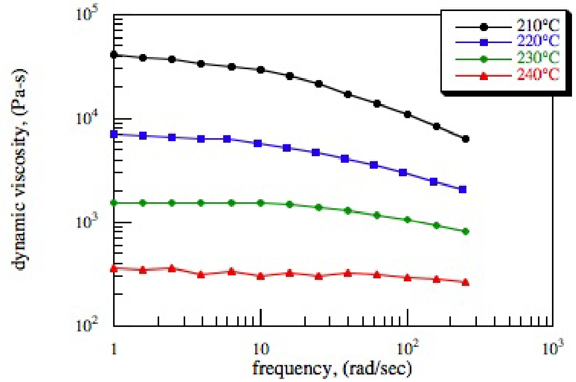
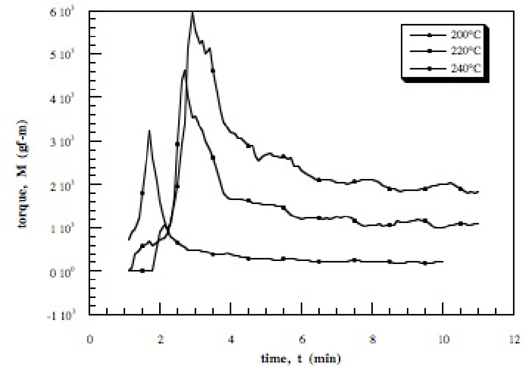
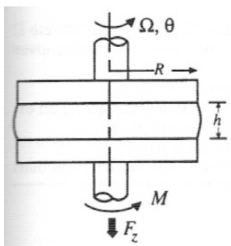
RHEOMETRY







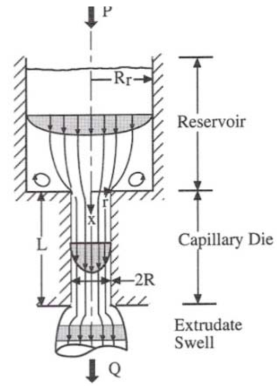


Shear rate at $r = R$

$$\dot{\gamma}_R = \frac{R\Omega}{h}$$

Shear stress

$$\tau_{12} = \tau_{\theta z} = \frac{M}{2\pi R^3}\left[3 + \frac{d\ln M}{d\ln \dot{\gamma}_R}\right]$$

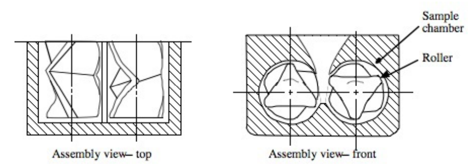


Wall shear stress

$$\tau_w = \frac{R}{2}\,\frac{p_c}{L}$$

Wall shear rate

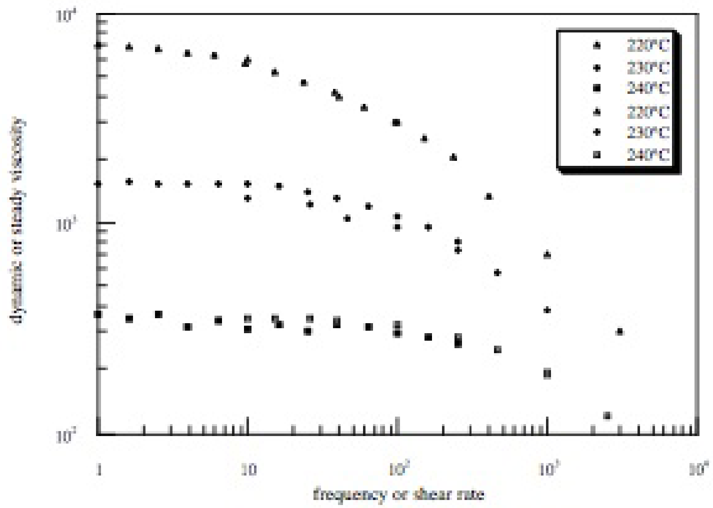
$$\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3}$$

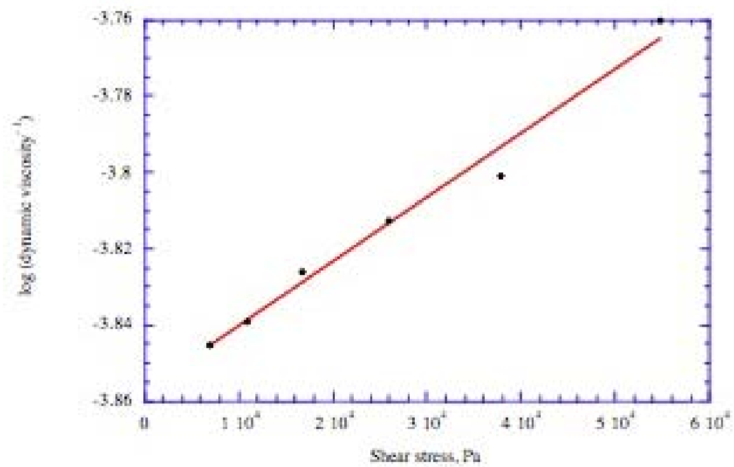


$$\dot{\gamma} = \frac{0.075N}{n(1 - 0.924^{2/n})}$$

$$\eta = \frac{800Mn(1 - 0.924^{2/n})}{N}$$

RHEOMETRY





$$\eta_{app}(\dot{\gamma}) = \eta^*(\omega)\big|_{\omega=\dot{\gamma}}$$

$$\eta \cong \frac{\eta_o}{K^{1-n}}\,\dot{\gamma}^{\,n-1}$$

T °C	η_o Pa-s	ω_{onset} sec^{-1}	K_η $Pa\text{-}s^{2-n}$	n
210	42600	160	92316	0.54
220	7200	70	12025	0.70
230	1540	37	2507	0.82
240	355	6	354	0.97

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VISCOSITY MODEL

✓Relationship
- molecular weight
- thermal dissociation
- shear thining

$$\eta = \eta_0(M_w, T)g(\dot{\gamma})$$

$$\eta = A_\eta \, exp\left(-\frac{E_\eta}{RT}\right)$$

$$\eta \cong \frac{\eta_0}{K^{1-n}} \dot{\gamma}^{n-1}$$

✓Viscosity Correlation
- overall activation energy
- deltaH of degradation reaction.

$$\text{reaction rate} \propto e^{-E_{dep}} \propto ln \frac{[U]|_{t=t'}}{[U]|_{t=0}} \propto \frac{1}{Mn} \propto \frac{1}{Mw}$$

$$K \propto -\Delta H_{deg} \propto -E_{dep}$$

✓Master Curve Concept
- Rheo Data Agreement
- Dinamic, Steady & Torque

$$log\, \eta(T) = log\, \eta(T_r) - \frac{C_1(T - T_r)}{C_2 + (T - T_r)}$$

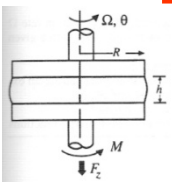
$$\eta_{app}(\dot{\gamma}) = \eta^*(\omega)|_{\omega=\dot{\gamma}}$$

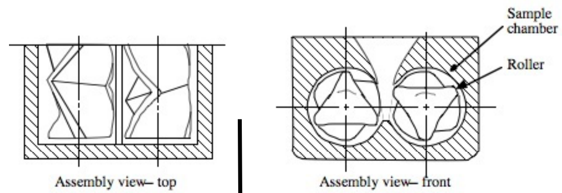
✓Flow Activation Energy Model

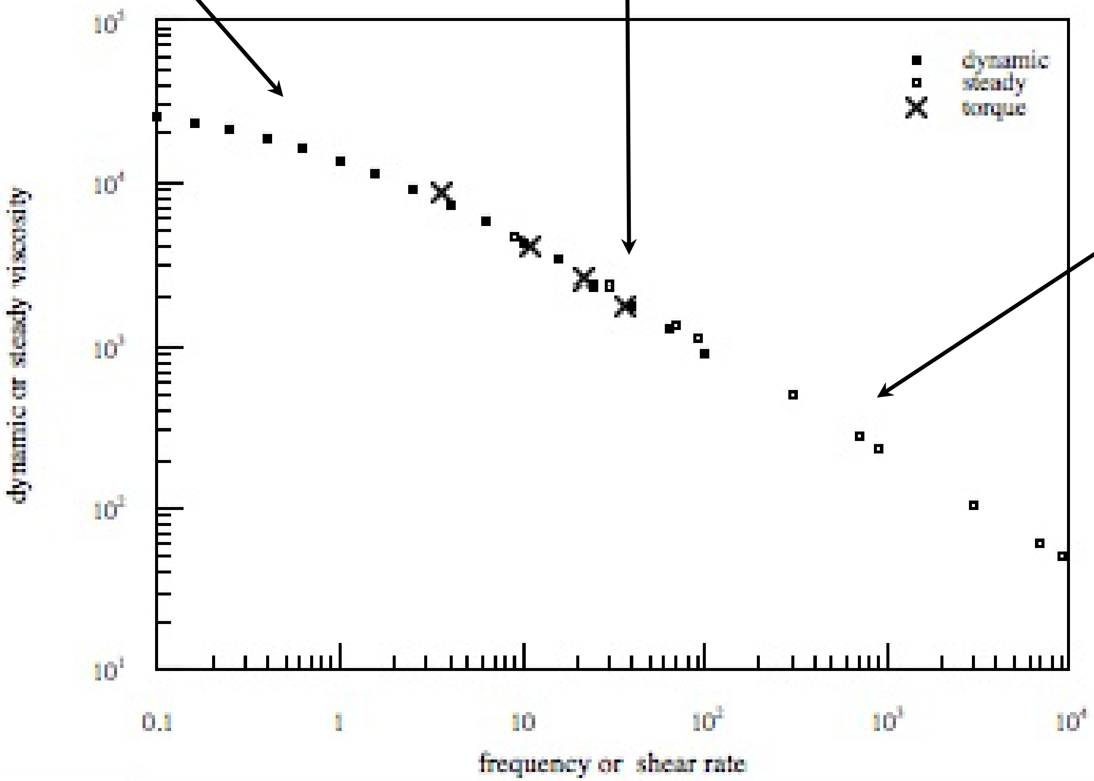
$$E_a = E_\eta + 3.4\, E_{dep}$$

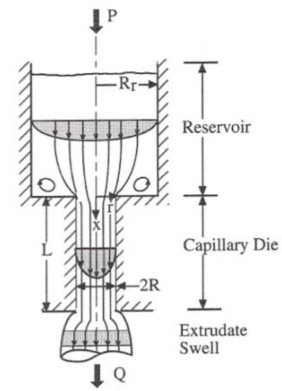
Q. Lu, M. Hernandez-Hernandez, C. Macosko, Explaining the abnormally high flow activation energy of thermoplastic polyurethanes, Polymer 44, 2003, 3309–3318

VISCOSITY MODEL









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CONCLUSIONS

Thermoplastic urethanes (TPU) exhibit unusual high flow activaton energy.

Care must be taken when working with traditional rheological models that deal with temperature and molecular weight separately since both phenomena are important for TPU

Apparent Activation energy shows two components: thermal degradation and rate processes flow.

Thermal degradation is the chief phenomena and can be evaluated under flowing as well as quiescent conditions.

TPU viscosity follows a master curve for different types and levels of regimes: oscillatory, steady laminar and complex shear-extensional flows; shear rate range including 3 decades.

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