Durability of polymer materials subjected to multi-weathering factors: the role of mechanical stress

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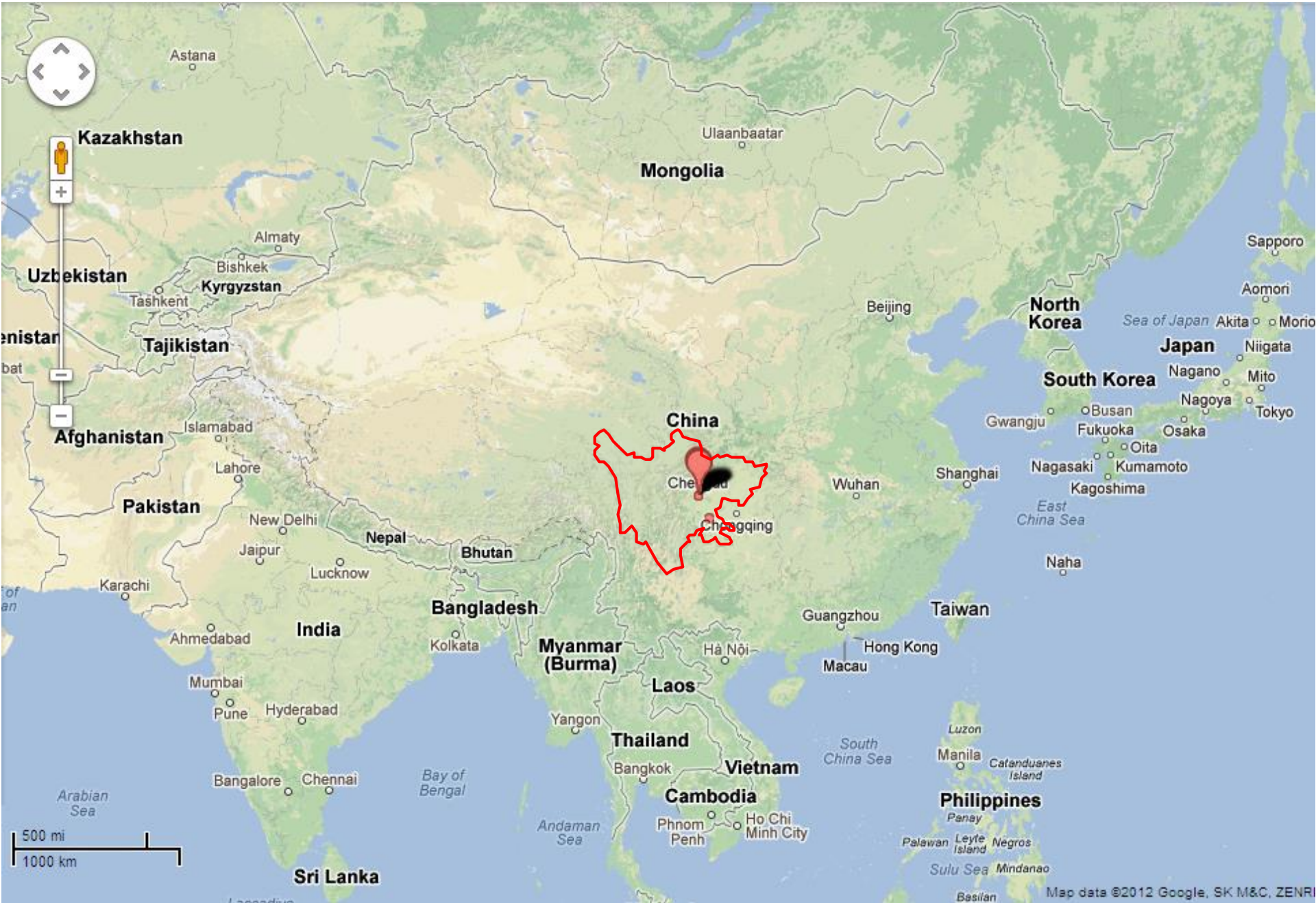
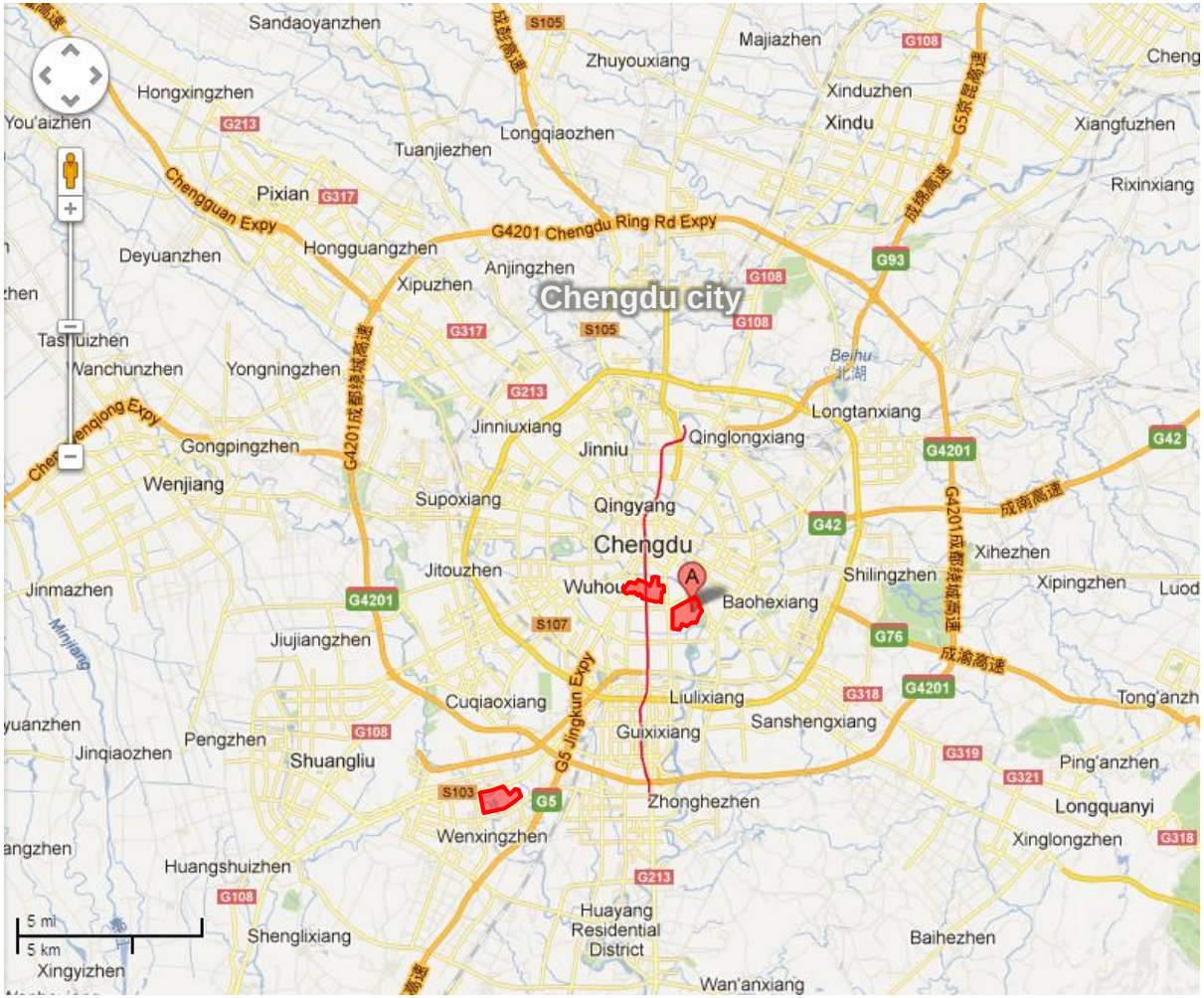
Location of Sichuan Province, China



Location of Sichuan University



Status of Polymer Discipline in SCU

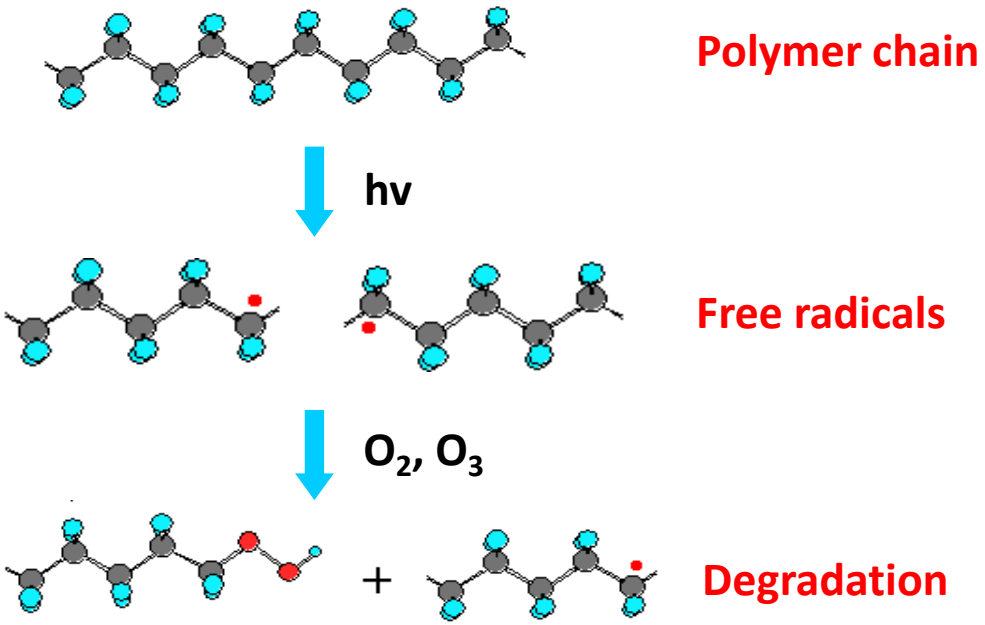
- **The earliest one in Chinese Universities, founded in 1953**
- **One of the largest bases of polymer material science and engineering in China (over 200 staff and faculty, over 2300 full-time students)**
- **SKLPME set at SCU in 1991, the first State Key Lab in polymer materials**

State Key Lab of Polym Mat Eng

Outline

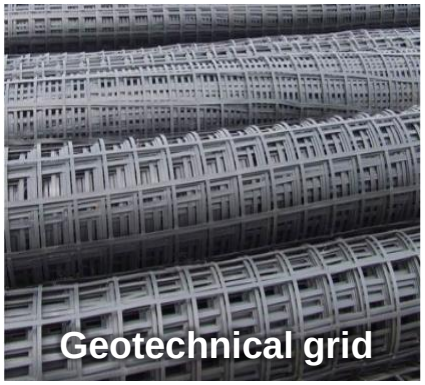
- Background
- Photo-oxidation of stressed PVC
- Creep failure behavior of PP
- Hydrothermal-oxidation of stressed PA6
- Conclusions

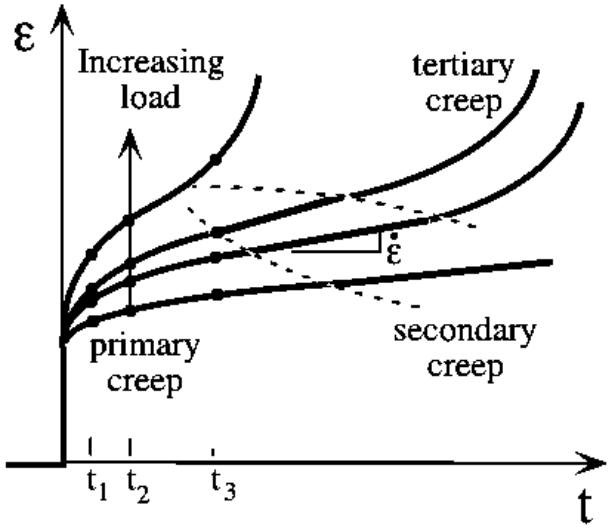
Chemical aging

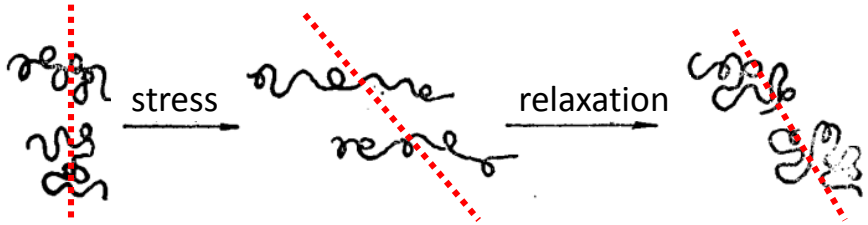


Failure or deterioration of materials due to the degradation or crosslinking of polymer chains in the presence of heat, oxygen, UV light, humidity, etc.

Physical aging







Failure or deterioration of polymers caused by the creep or relaxation of polymer chains in the presence of heat, stress, etc.

Polymer aging: diversity and complexity

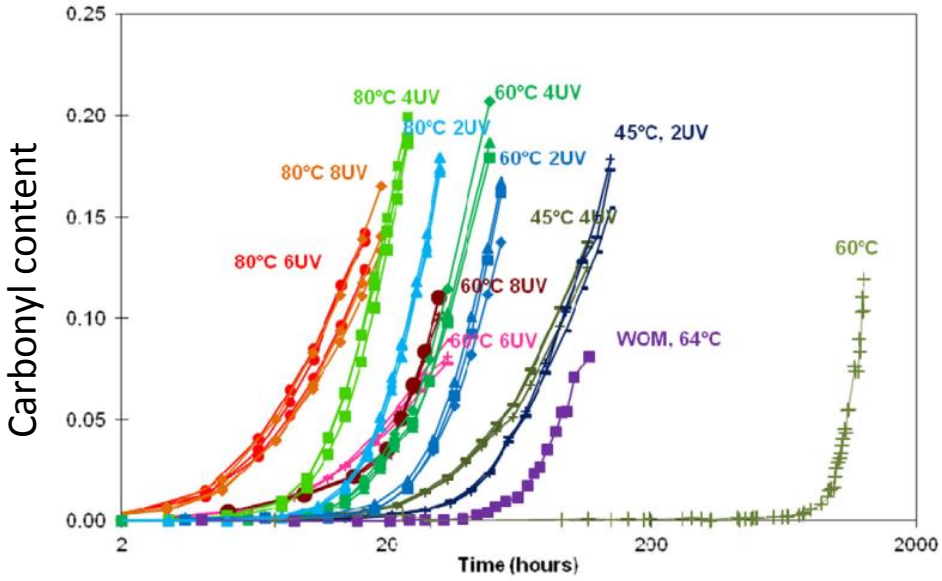
- **Complex impact factors**
  - Temperature
  - Irradiation
  - Oxygen
  - Humidity
  - Mechanical Stress

  } **Coupling & Competition**

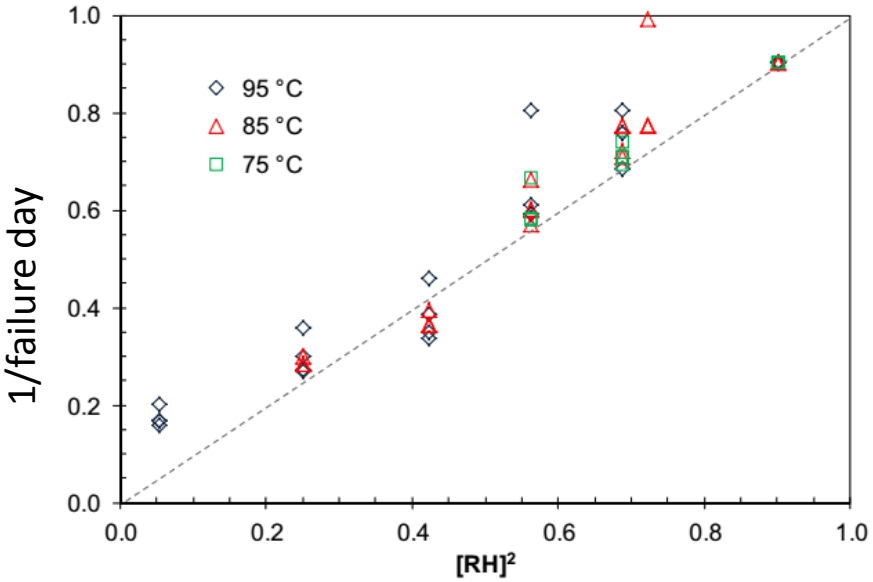
- **Complex materials**
  - Crystallization
  - multiphase structure
  - Fillers

  } **Multicomponent & Heterogeneous**

Lots of researches focused on the thermo-oxidation and photo-oxidation behavior of polymers caused by oxygen + temperature, oxygen + temperature + UV, etc



PP: Temperature + UV

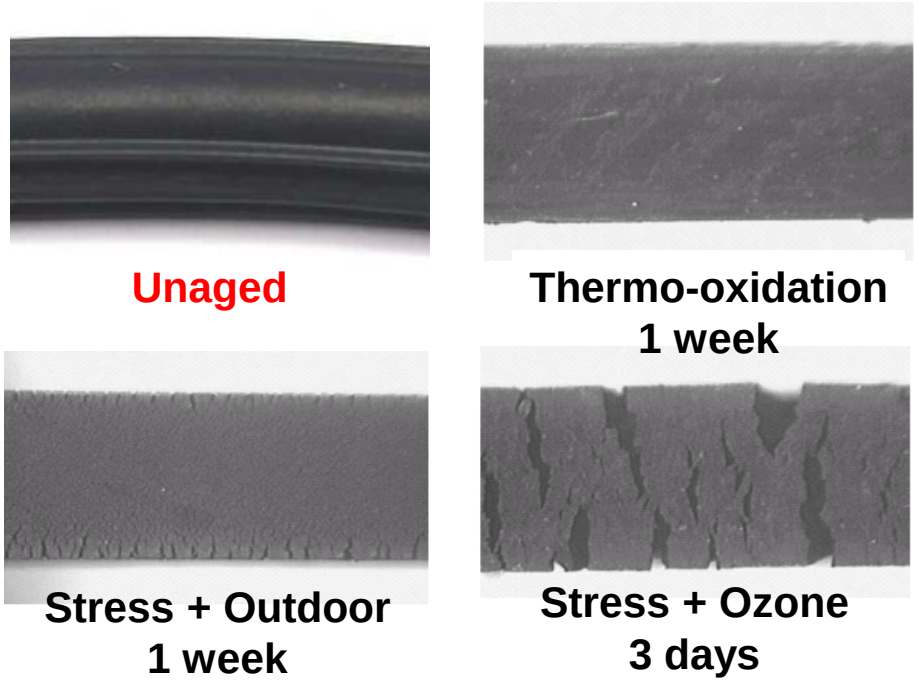


PET: Temperature + Humidity

François-Heude A, Polymer Degradation and Stability, 2014, 100, 10; Pickett, Polymer Degradation and Stability, 2013, 98, 1311

Aging of polymers in stressed conditions

Polymers are often used in conditions in which chemical and physical (especially mechanical stress) factors exist simultaneously



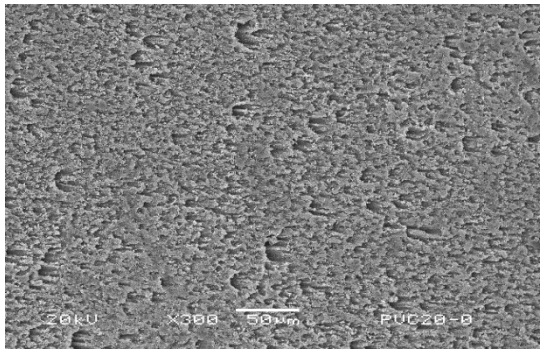
Mechanical stress accelerates the degradation of polymer materials

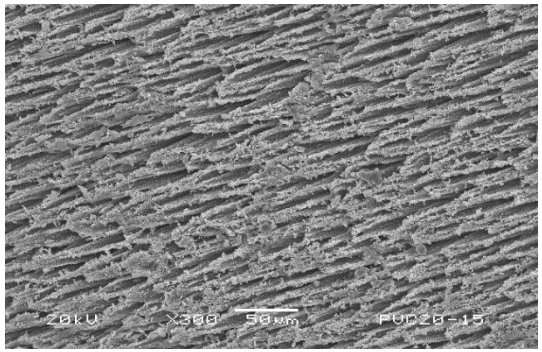
Case 1:
Photo-oxidation of stressed PVC

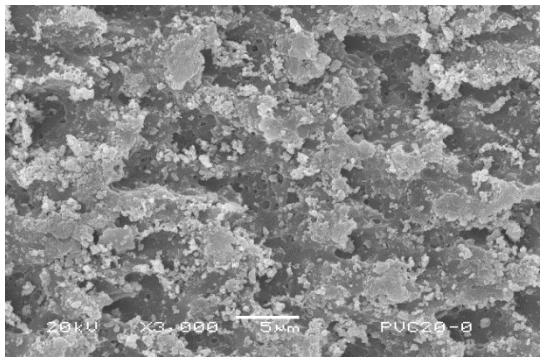
Surface morphology of sliced sample

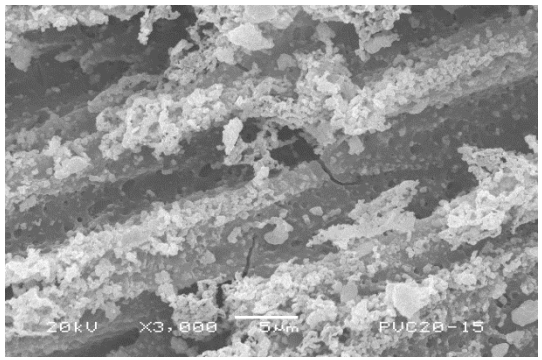
300x

3000x







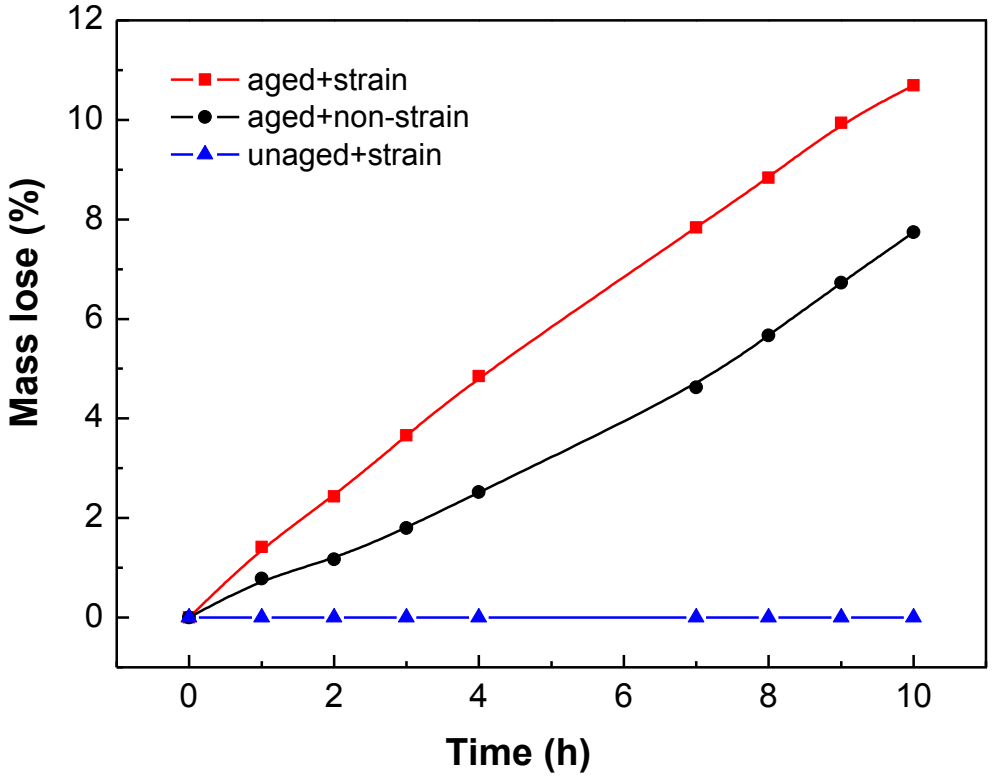


Without stress **With stress**

Strain=2%

- **Deeper microcracks and some of orientation are formed in stressed samples, facilitating the diffusion of oxygen**

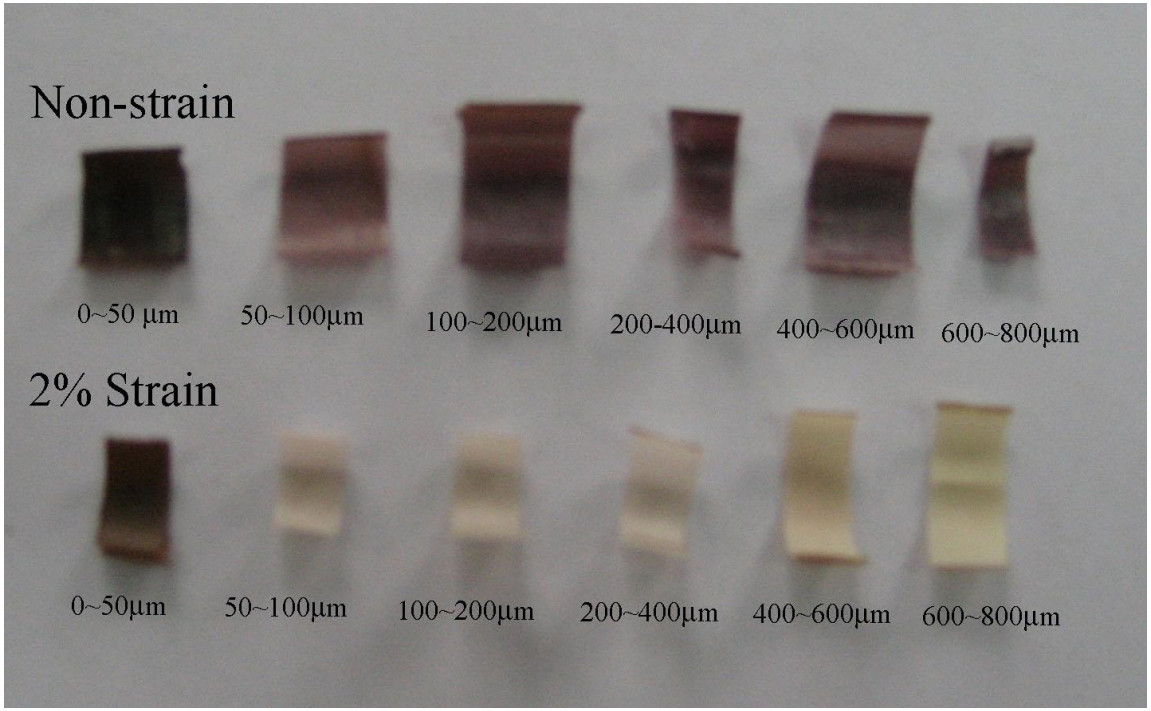
Mass loss of PVC samples



Stress increases mass loss (evaporation)

- **The simultaneous acting of stress and UV leads to more rapid mass loss than the case which only UV is involved**
- **Without UV irradiation, there is no mass loss in stressed sample**

Appearance of sliced samples

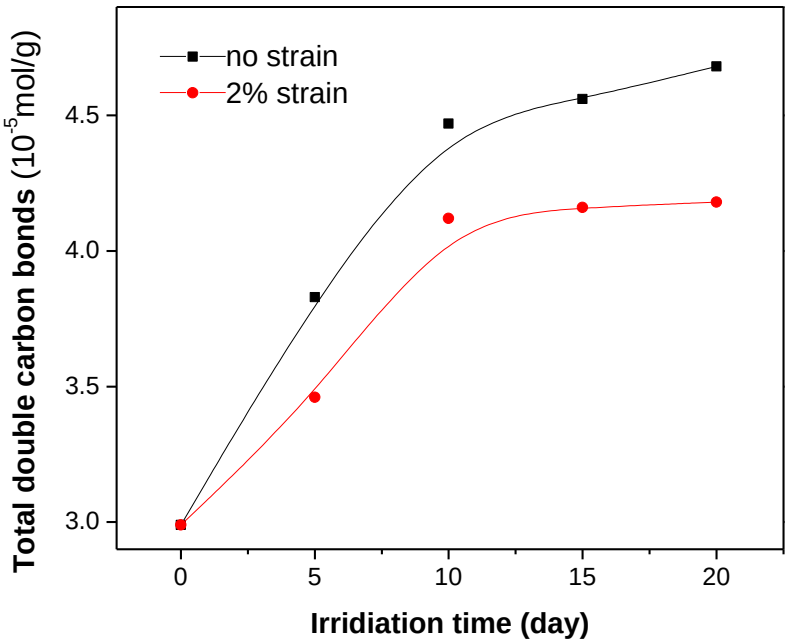


Color of sliced sample at different depths (irradiated for 20 days)

- **The color change caused by chromophore is depth dependent**
- **The stressed sample shows a photo bleaching effect: darkening color happened only in the surface layer**

Changes in chromophore groups

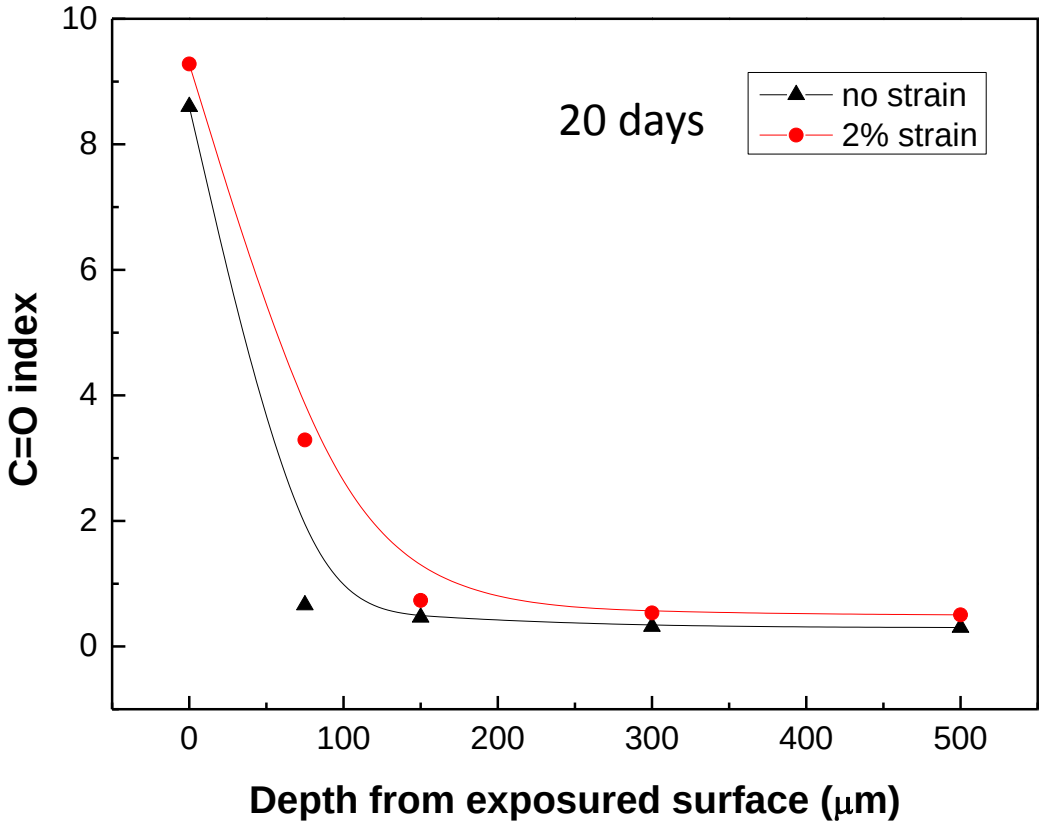
➢ Total C=C bonds (n=3~8) by UV-Vis analysis



- **The stressed PVC had less C=C bonds compared with no-strain ones**
- **Stress should promote the oxidation of C=C bonds and lowers the concentration of double bonds**

Changes in molecular structure

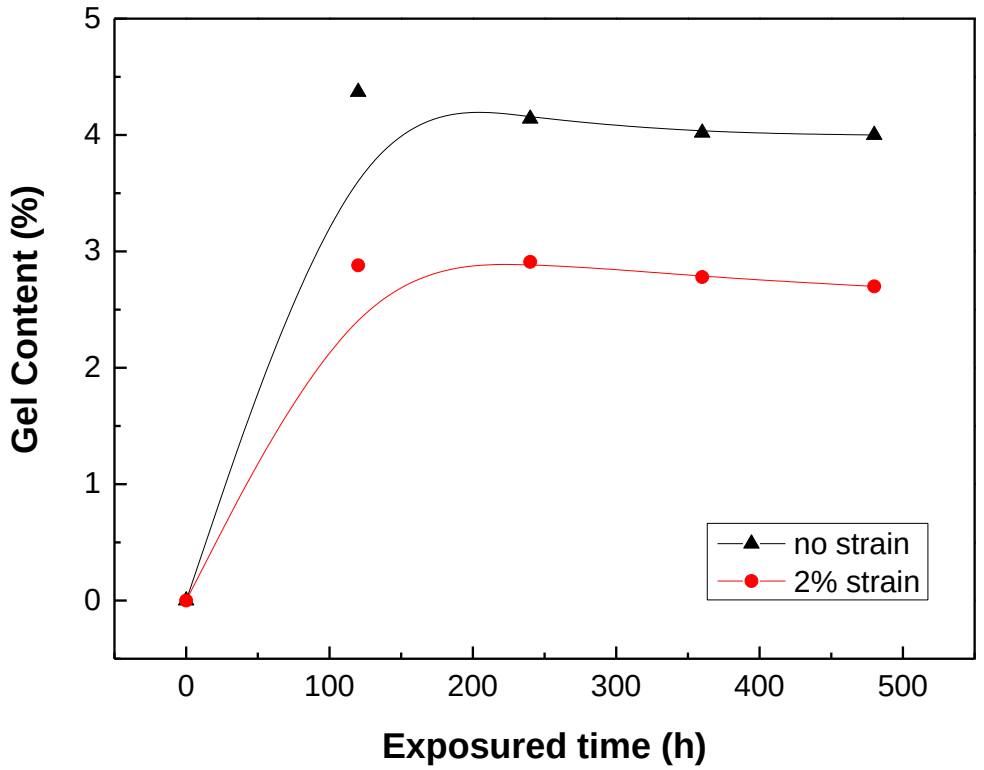
➢ C=O index by FTIR



The carbanyl group increased after imposed stress

Changes in molecular structure

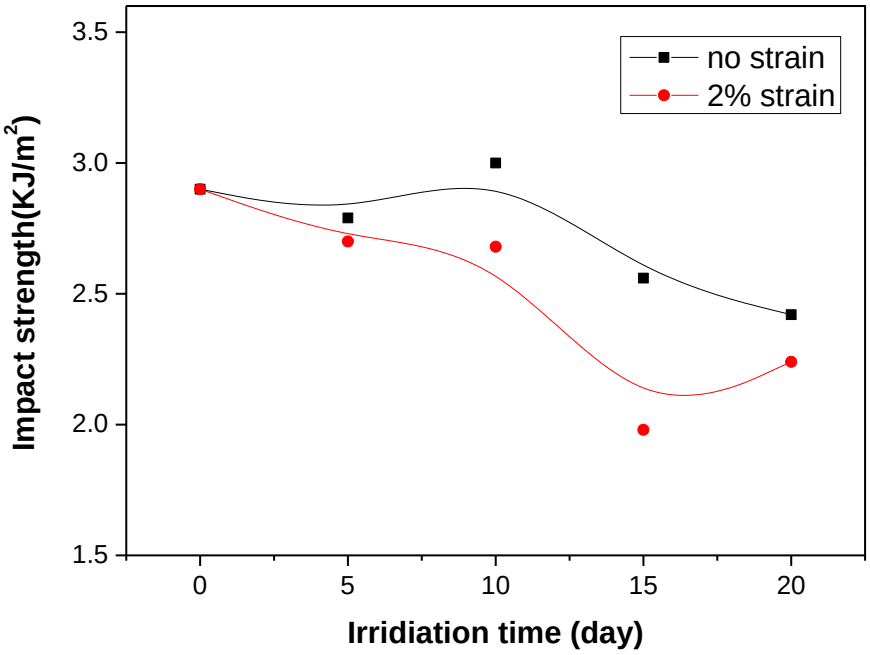
➢ Gel content



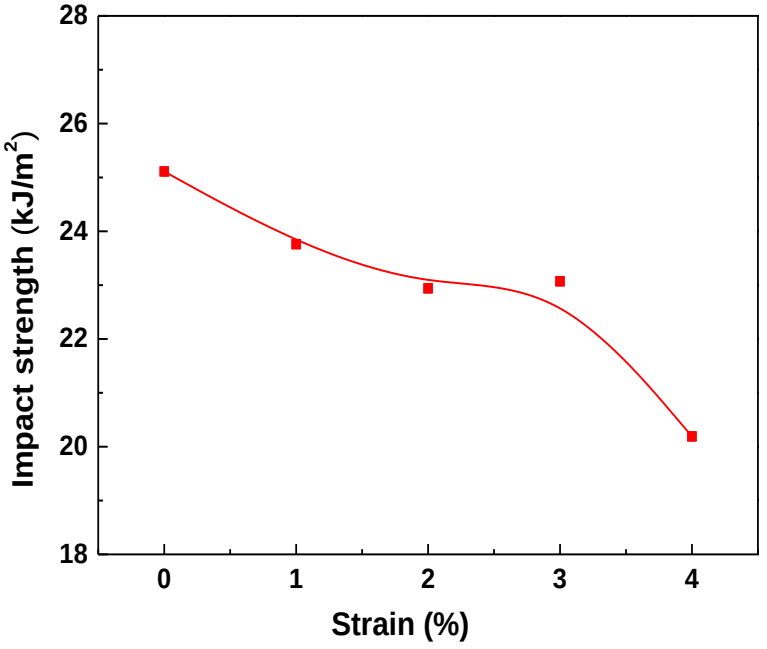
- **The gel content decreased after imposed mechanical stress as it may suppress crosslinking reaction**

Deterioration in mechanical properties

➢ Impact strength



Changes of notched impact strength with time

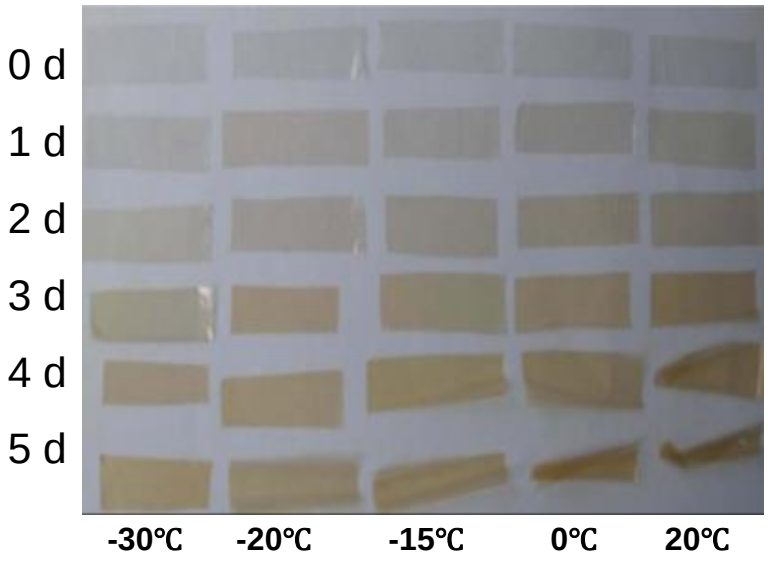


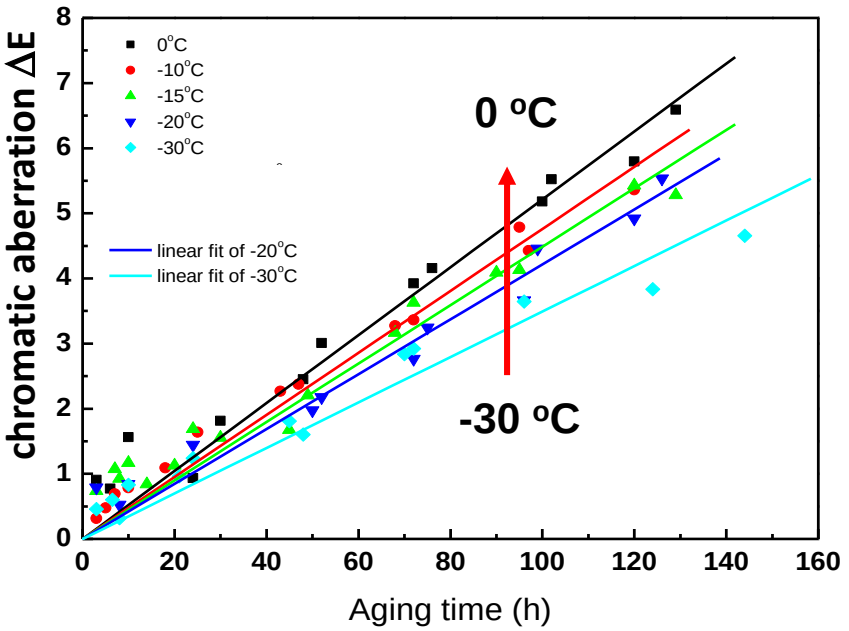
Unnotched impact strength after 20 days

- **Increasing the stress induced more microcracks, as well as oxidation-induced degradation, resulting in lower impact strength**

Low-temperature ultraviolet radiation method for aging mechanism of PVC

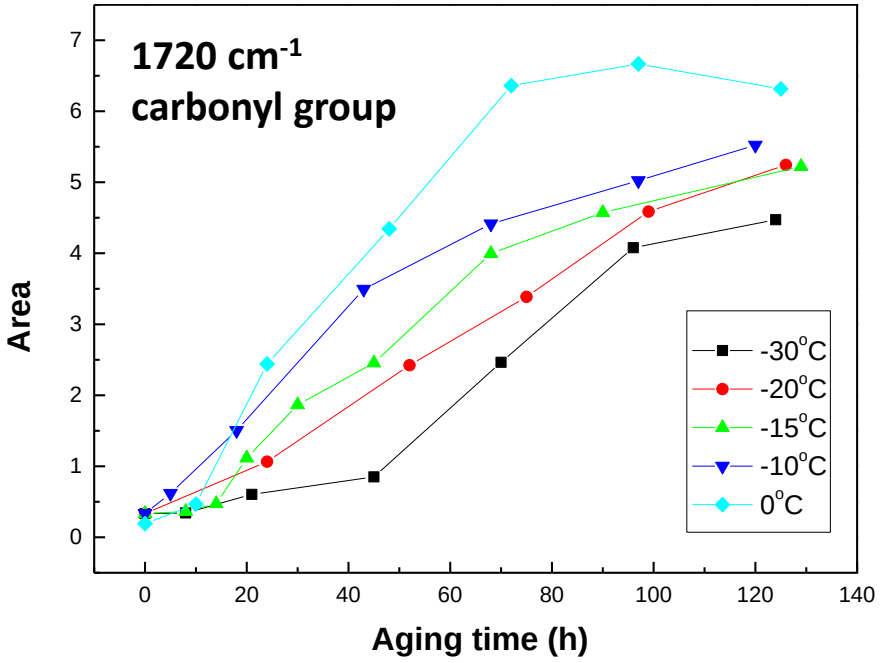
- **Photo-oxidation mechanism at low Temp (-30~0 ºC) and strong UV radiation conditions is unclear**

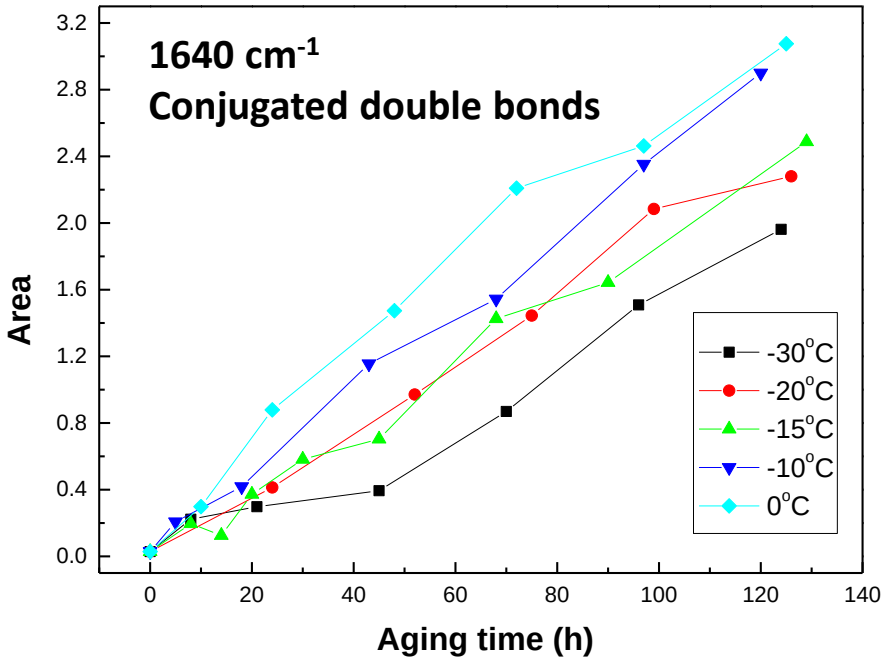




- **Temperature significant affected yellowing of PVC during photo-oxidation**
- **The slow aging rate enables the study of photo-oxidation mechanism easily**

➢ Functional group content analysis by FTIR

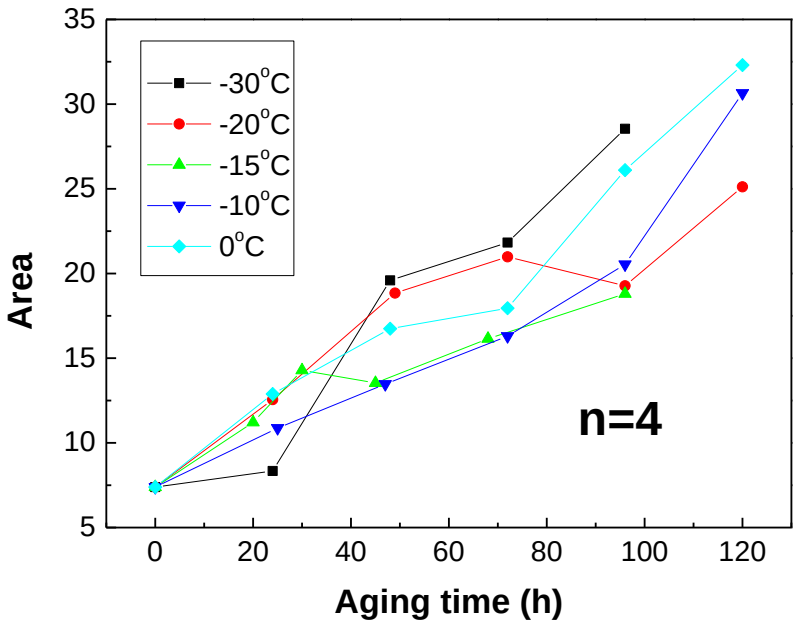


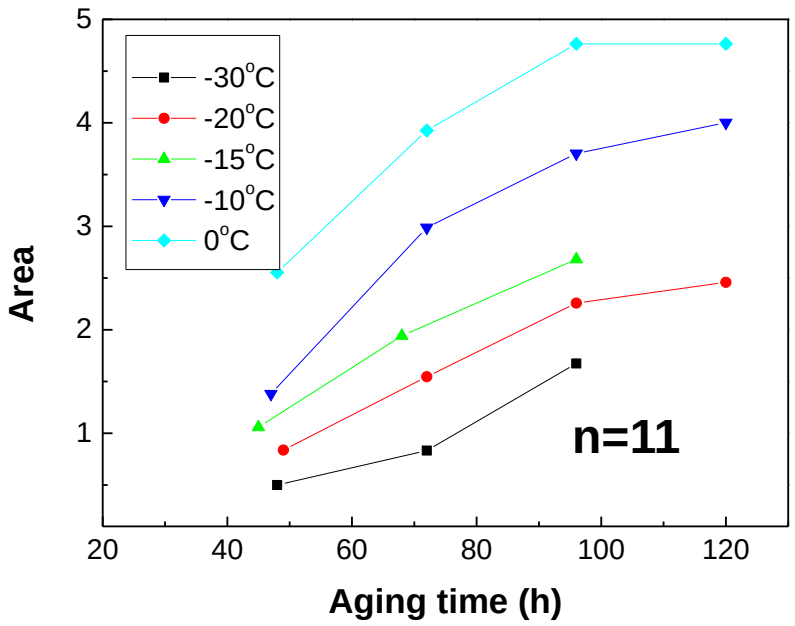


- **With elevating temperature, the absorption intensities of carbonyl group and conjugated double bonds increased similar to that happened at high temperature**

➢ Analysis of conjugated C=C double bonds

By fitting the UV-vis absorption peaks, the contents of conjugated double bonds with different lengths (n) are obtained





Short double bonds：change little with temperature

Long double bonds：**increase with temperature**

- **Long conjugated double bonds should be the main reason for the color change (as the sample appeared darker/yellowing at higher temperature)**

Mechanism for stress-accelerated photo-oxidation of PVC

Stress

- **Microcracks**
- **Orientation (at higher stress)**
- **Increased molecular mobility**

Change the photo-oxidation process:

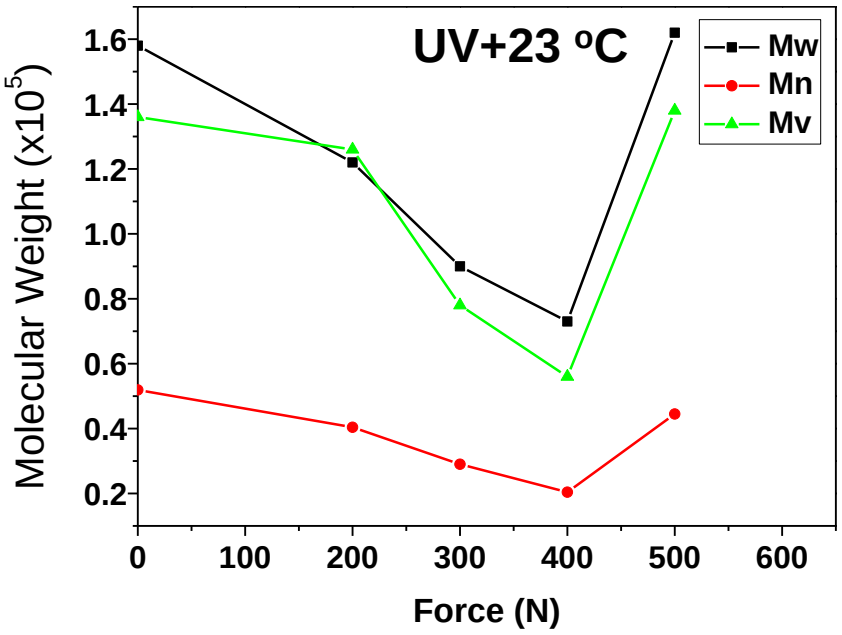
- **Promote oxidation reaction**
- **Decrease double bonds and crosslinking**
- **Promote the formation of carbonyl group**

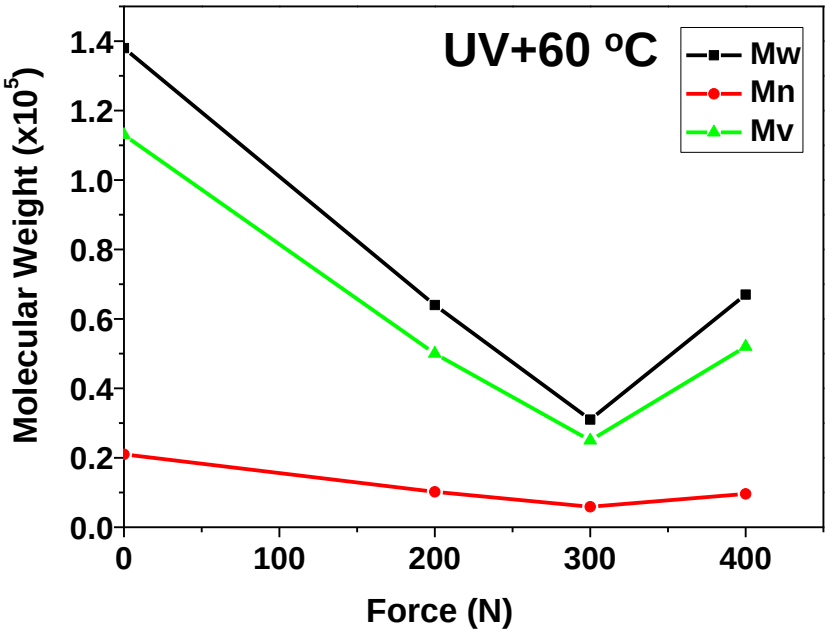
CASE 2

Creep failure behavior of PP

(Semicrystaline polymer)

Stress promoted chem-aging of iPP: degradation of MW

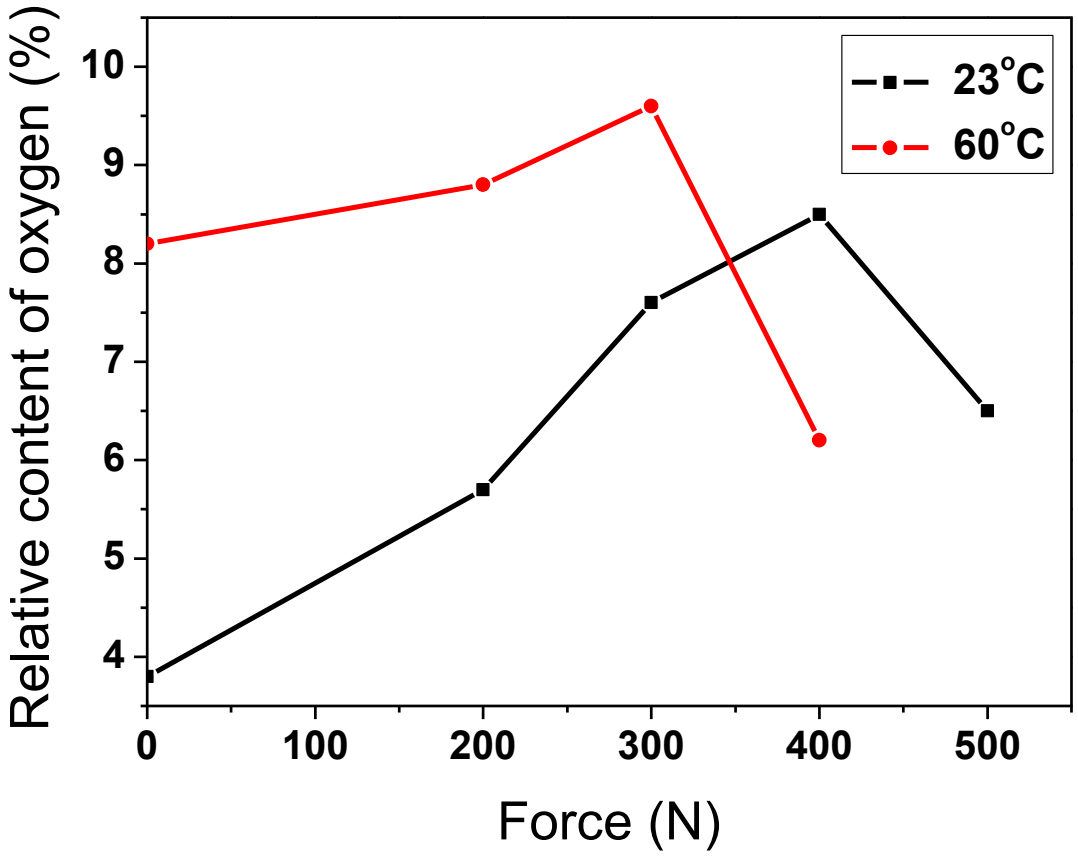




Molecular weight of iPP subjected to different stress levels after photo-oxidation for 12h

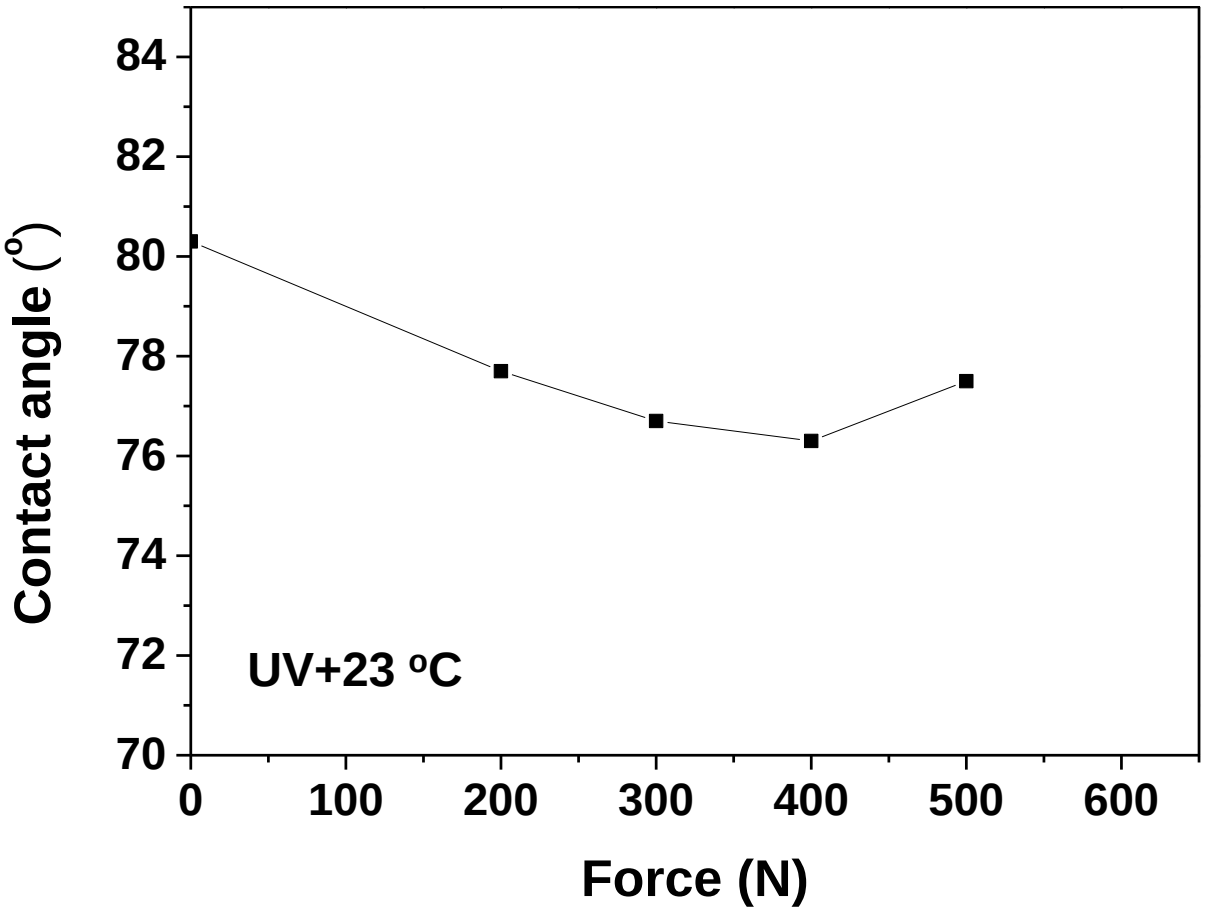
With increasing mechanical stress level, the molecular weight decreases at first and then arise at higher stresses

Stress promoted chem-aging of iPP: oxidation of surface



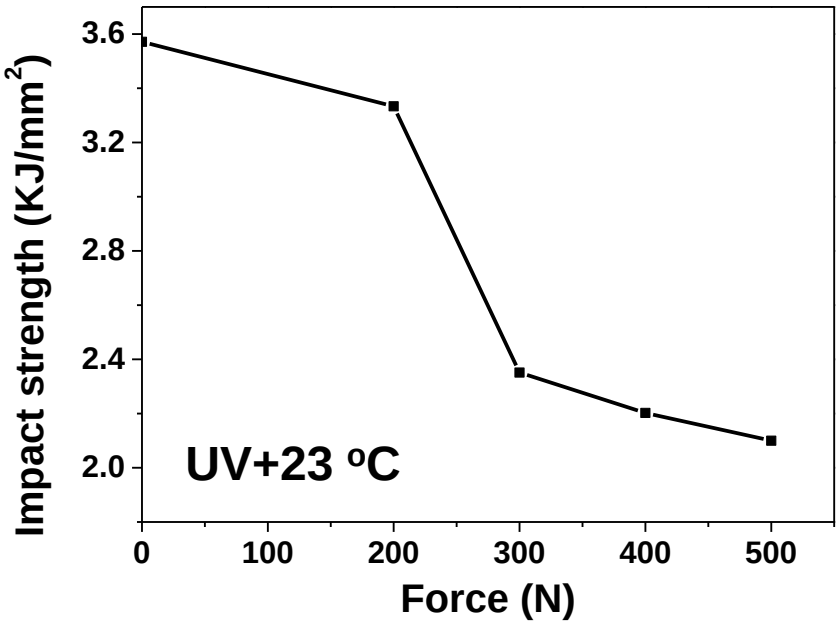
With increasing stress level, the photo-oxidation degree increased at first and then decreases at higher stresses (XPS)

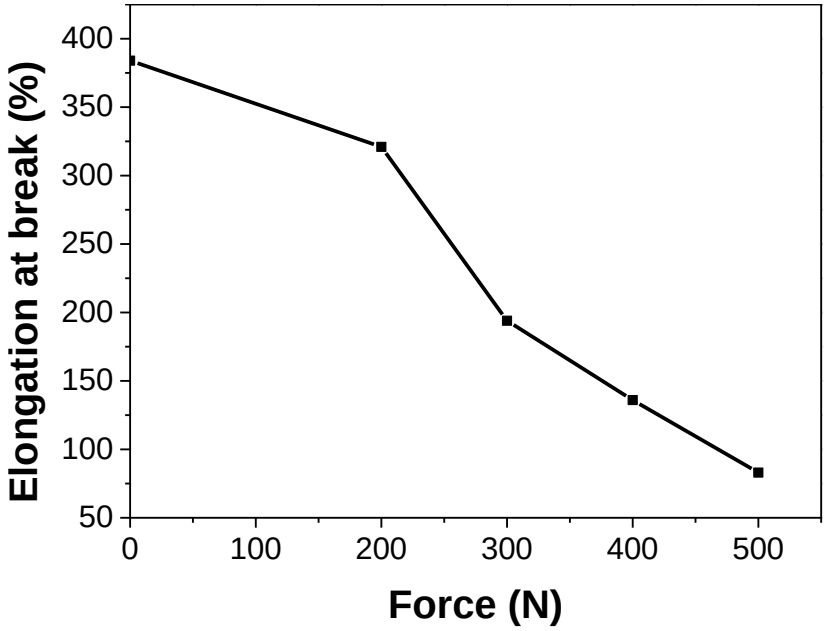
Stress increased the contact angle of iPP



With increasing stress level, the contact angle decreased at first and then increases at higher stresses

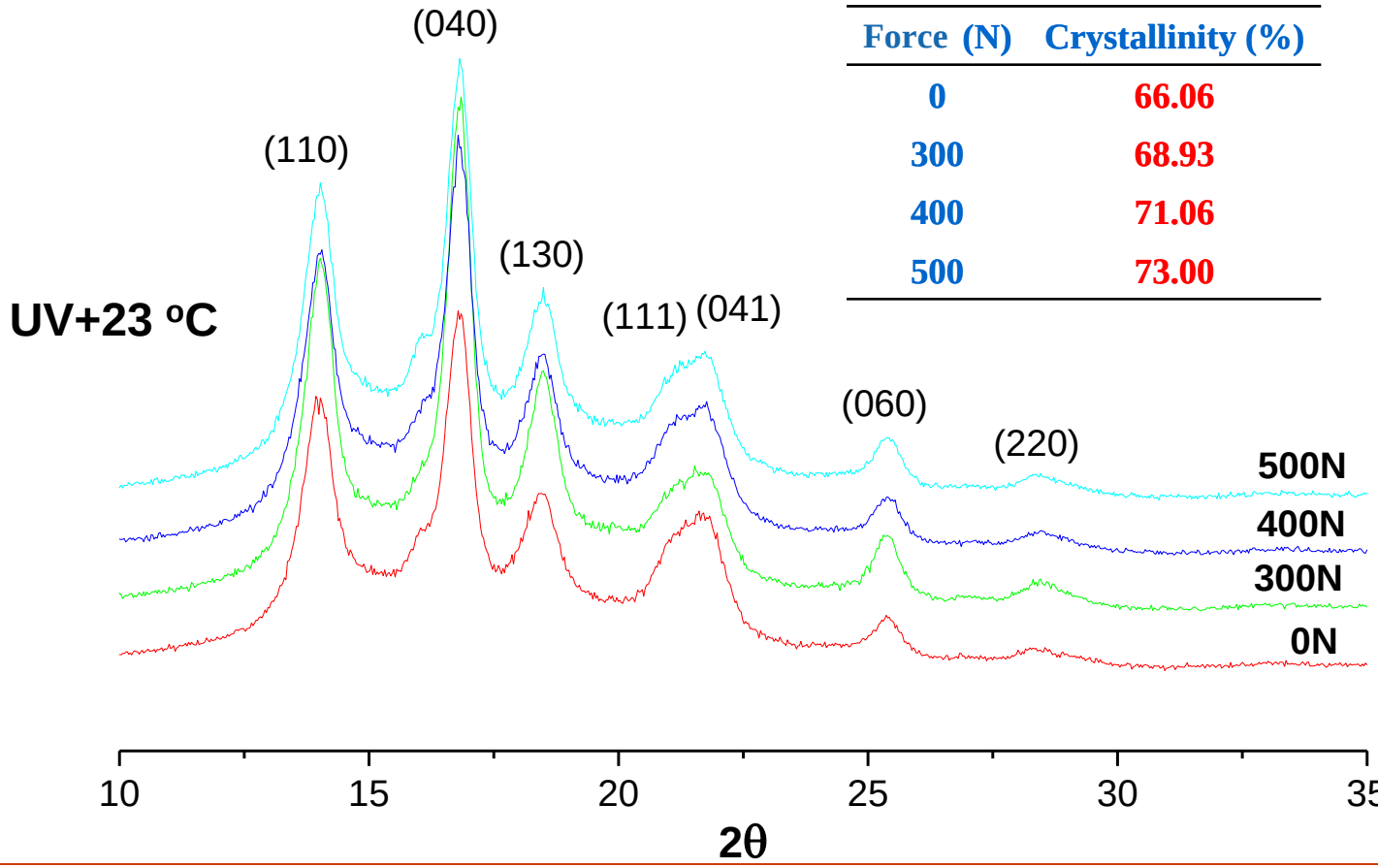
Deterioration of mechanical properties





Stress promoted chemical degradation and mechanical deterioration

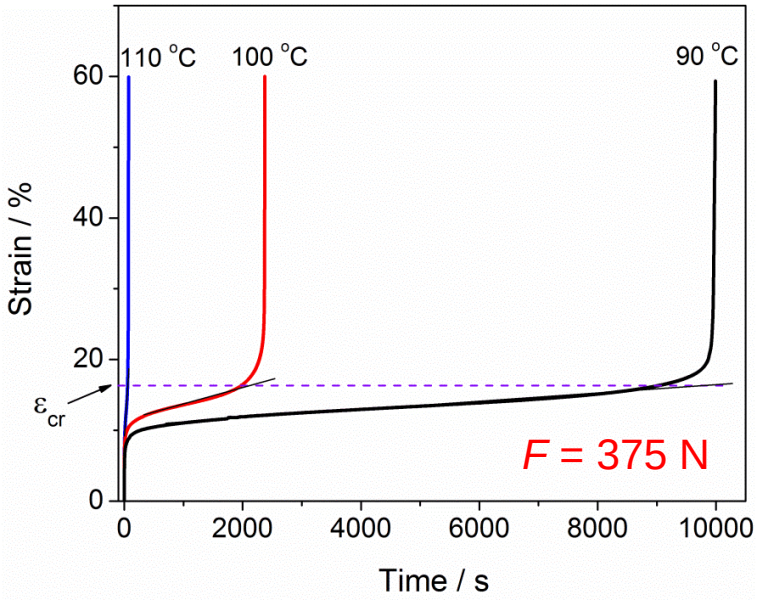
Orientation and crystallization of iPP under stress



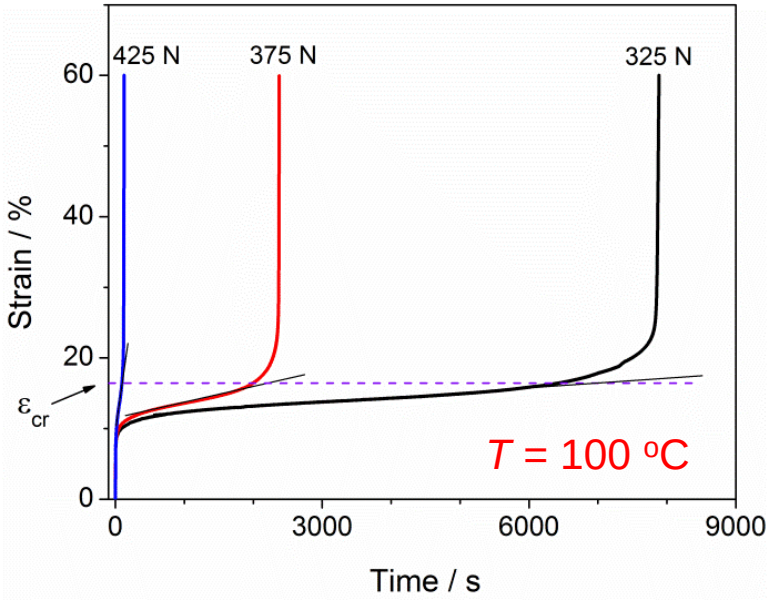
Force (N)	Crystallinity (%)
0	66.06
300	68.93
400	71.06
500	73.00

Higher stress increased the crystalinity and orientation, reducing the oxidation degradation (diffusion of oxygen) of iPP

Temperature and stress promoted the creep of iPP



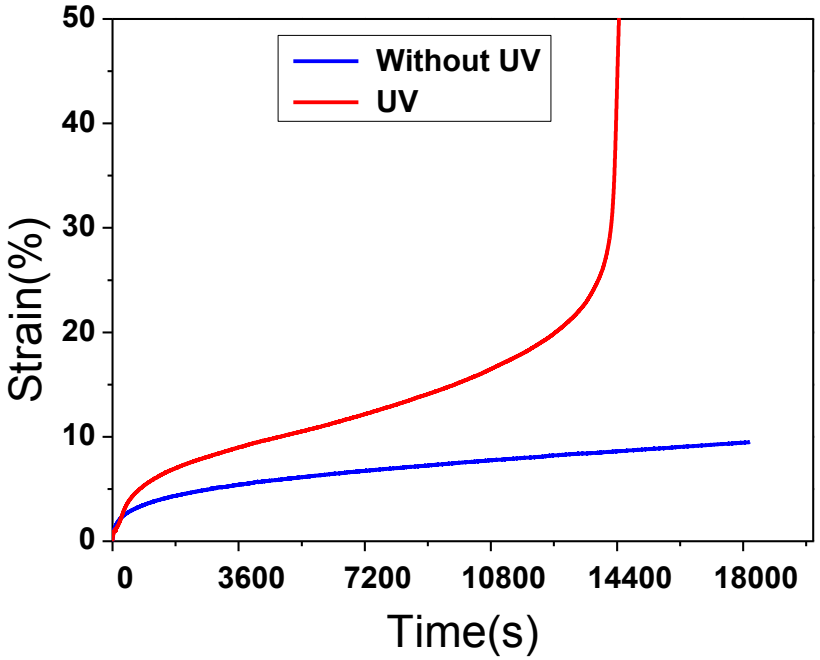
(a) temperature



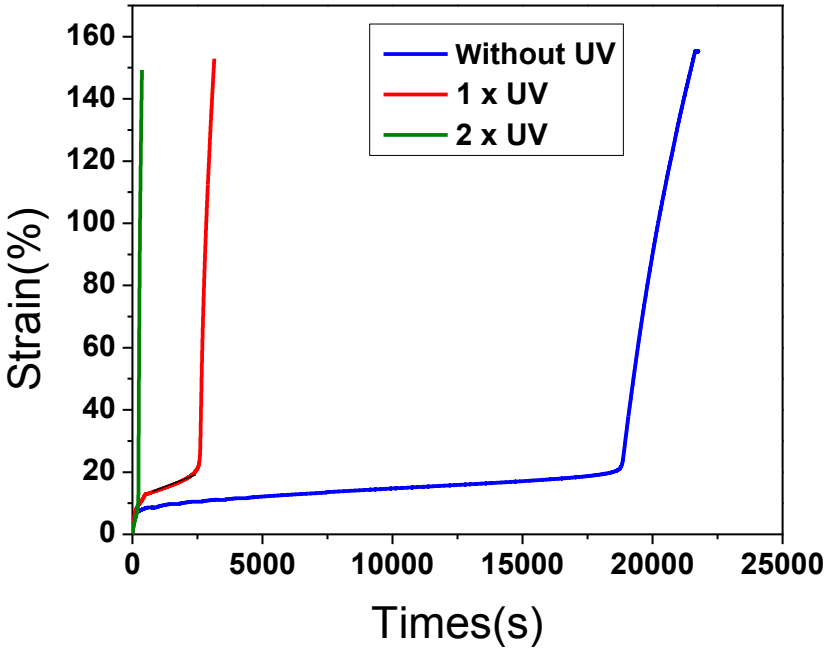
(b) stress

- The elevation in temperature or stress leads to a faster creep failure (higher molecular mobility and lower activation energy)
- There is a constant critical failure strain (ε_{crit}) for all cases

UV promoted the creep of iPP



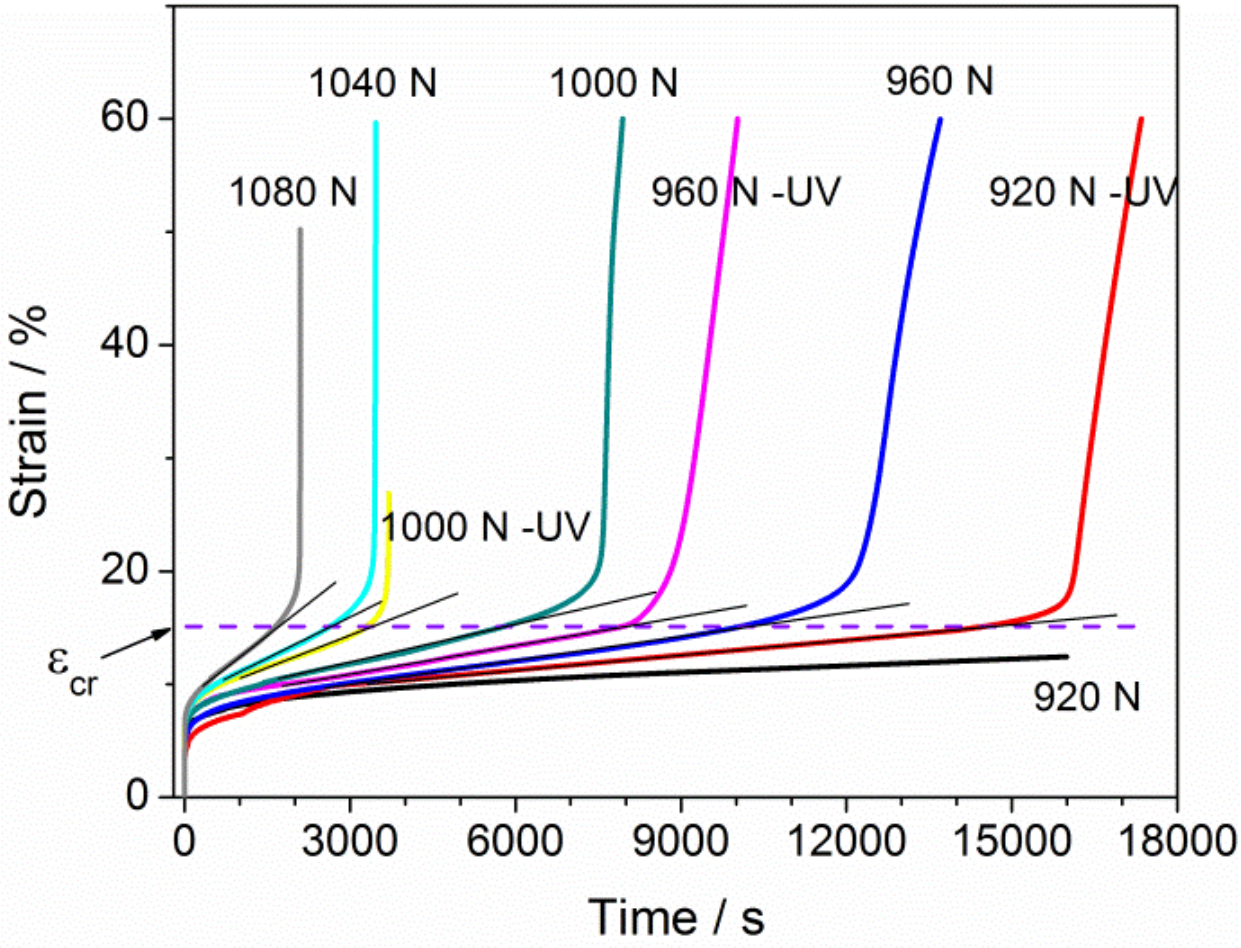
(a) 800N and 23°C;



(b) 500N and 60°C

The incorporation of UV light accelerated the failure of iPP (degradation + activation of chains) but did not change the level of the critical failure strain (ε_{crit} ≈17%)

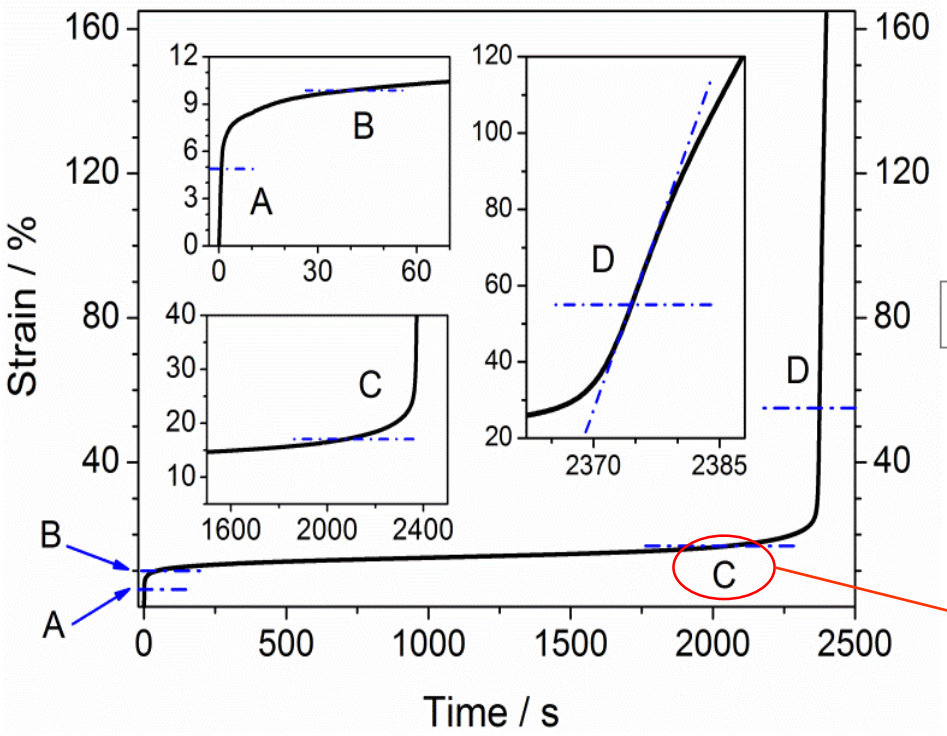
UV promotes the creep of iPP



The critical failure strain does not change with stress level and UV

The mechanism of critical failure strain

F = 375 N, T = 100 °C



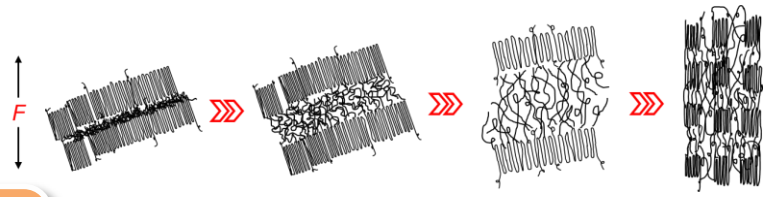
Four intervals

- **0~A, primary creep**
- **A~B, transition region**
- **B~C, secondary creep**
- **C~, tertiary creep**

The strain increased sharply after point C, which was defined as the point of critical failure strain (ε_{cr}).

Jia, Liao, Li, *et al*. *Polymer,* 2015, *67:* 92-100.

The mechanism of critical failure strain (multiscale structures)



Crystalline region

Crystalline blocks

Nano-scale lamellae

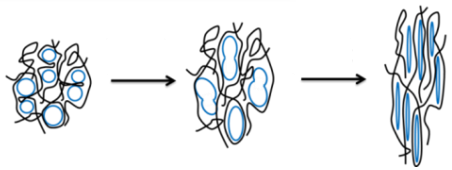
Micron-scale spherulites

Hierarchical microstructure changes

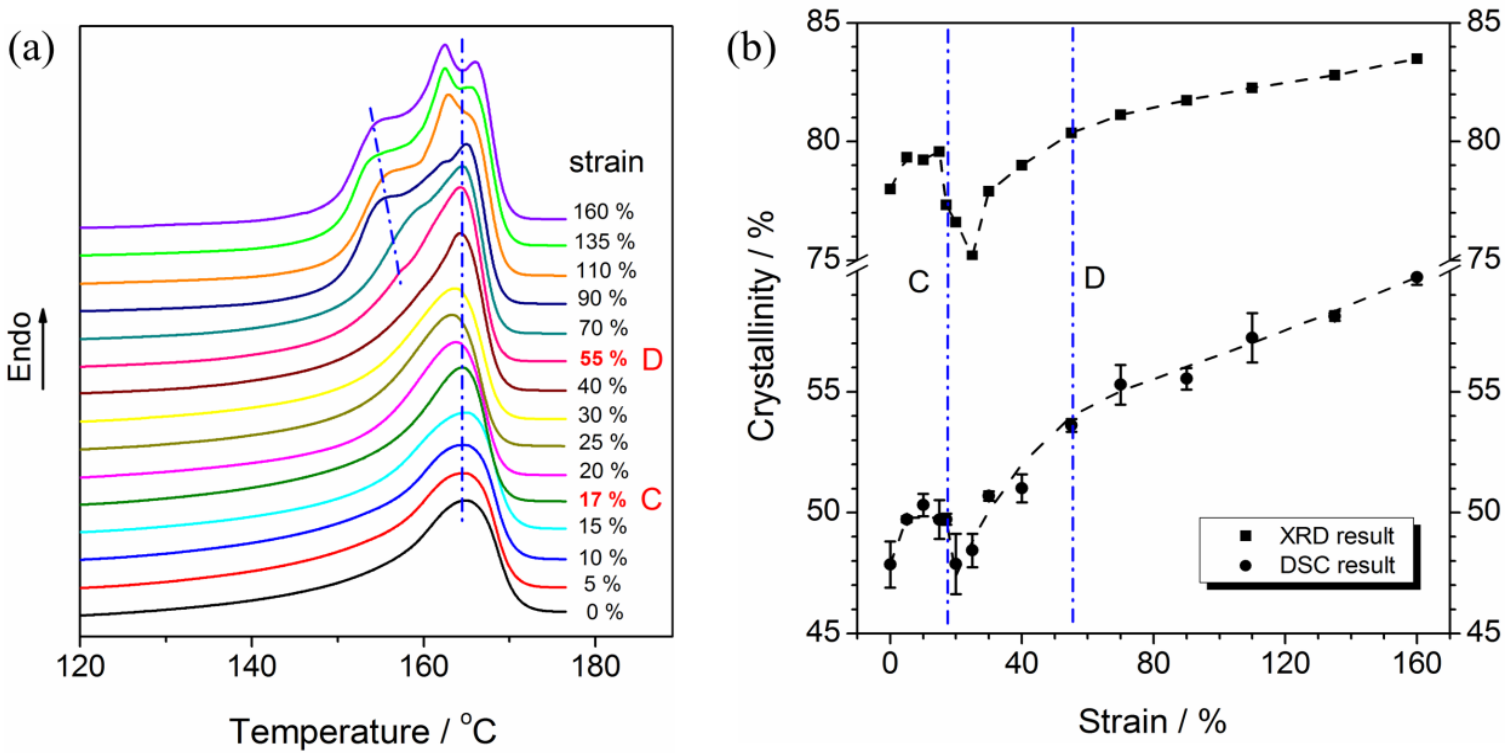
Crystalline-amorphous interfacial phase

Amorphous region

Subnanoscale free volume



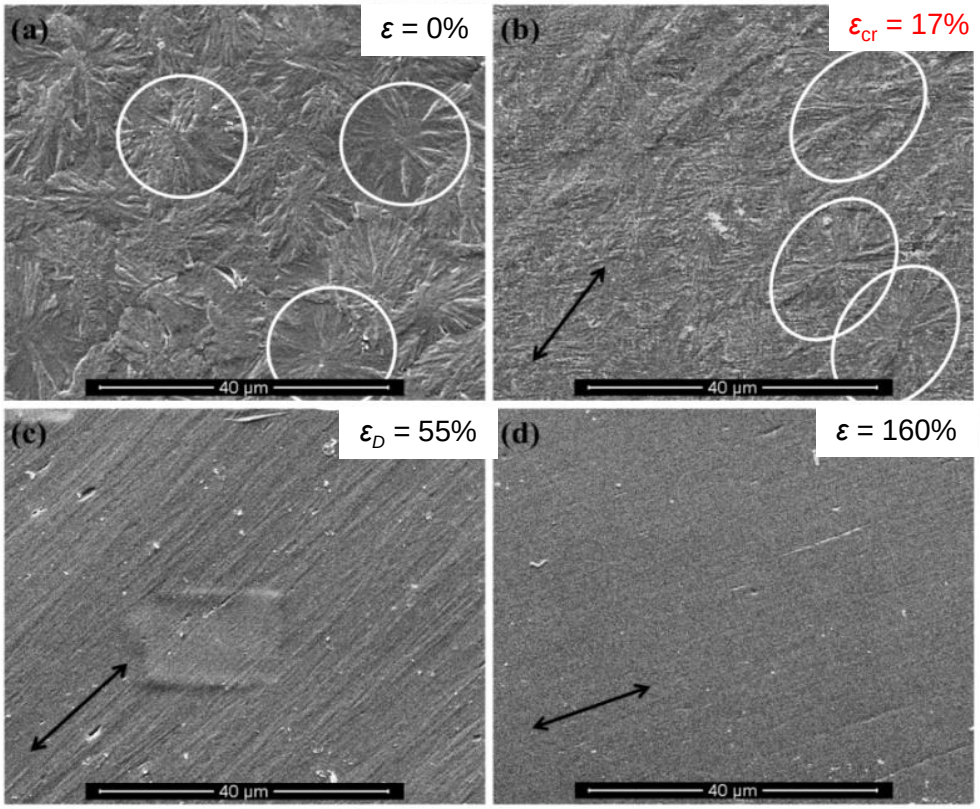
DSC curves and crystallinity



The stress induced the process of crystalline block disaggregation-recrystallization.

Crystalline morphology evolution

Spherulites



Deformation of spherulites

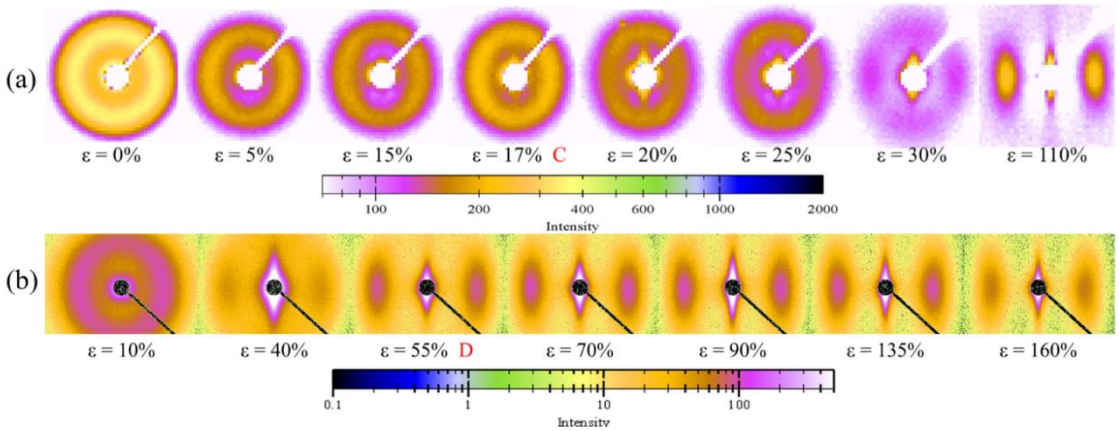
Fibrous crystal

Highly aligned fibrous crystal

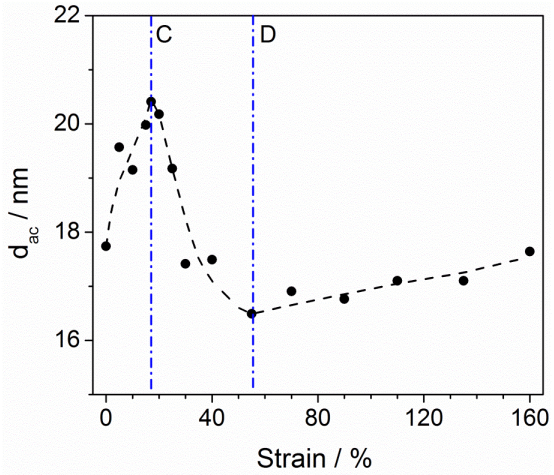
SEM photographs

The spherulites transformed into fibrous crystal with increasing strain

Nano-scale lamellar structure



2D-SAXS patterns

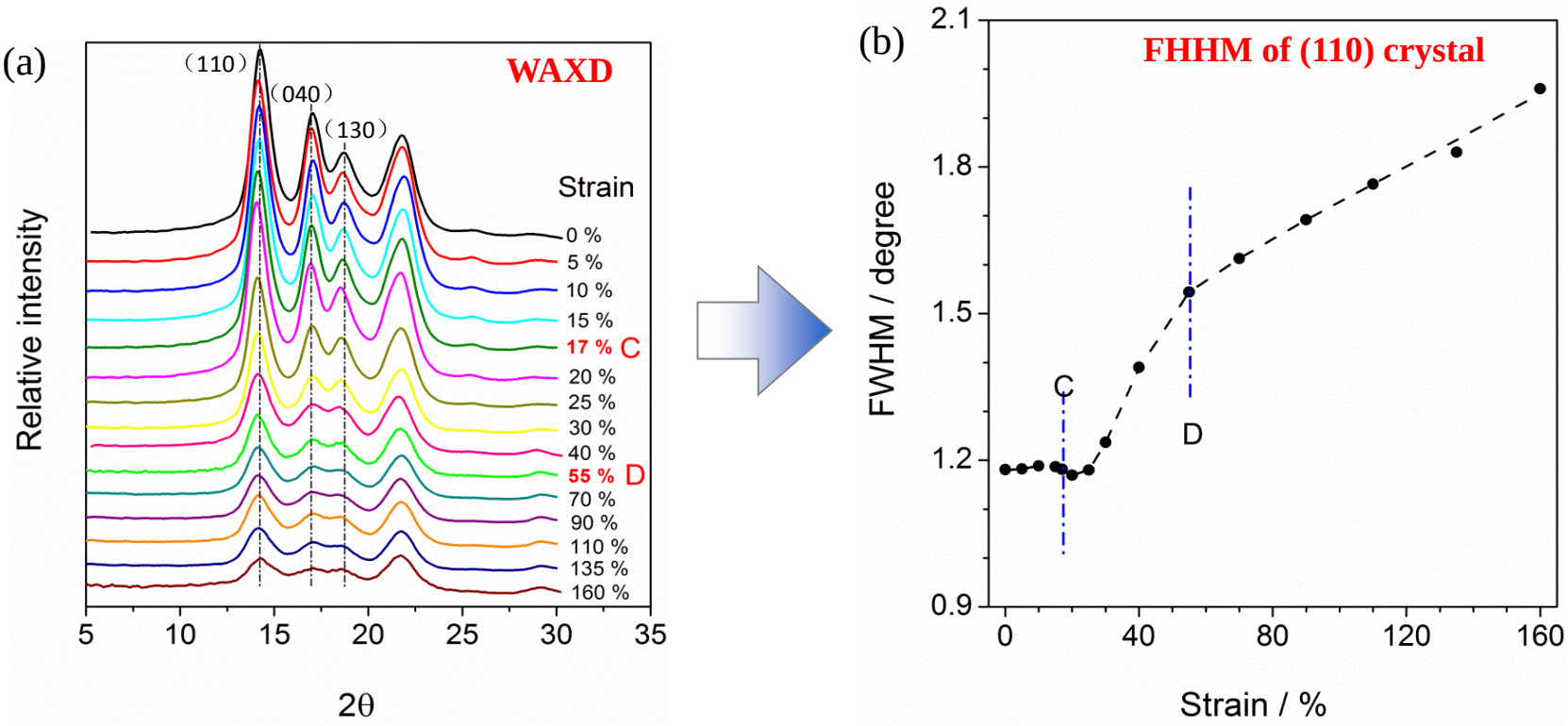


Long period d_{ac}

Anisotropic scattering pattern	Slightly anisotropic scattering pattern	Four-point scattering pattern	Two-point scattering pattern
No deformation	Less deformation (before point C)	Moderate deformation (between point C to D)	High deformation (after point D)

- **The d_{ac} increased before point C and then decreased between point C and D;**
- **The lamellar crystals slipped, disaggregated and recrystallized with strain, and then the highly oriented lamellar structure formed.**

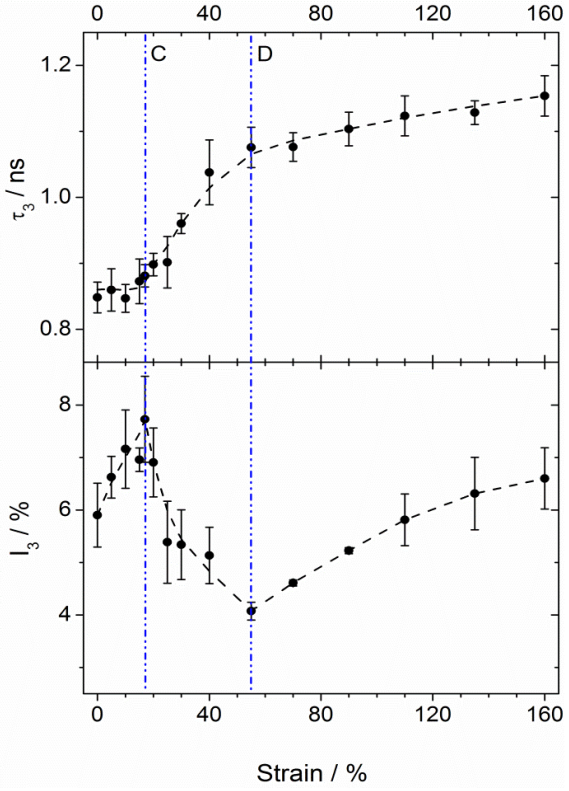
Crystalline blocks



The FHWM of (110) crystal increased with strain, reflecting that the structural perfection of crystalline blocks in lamellae were reduced.

Subnanoscale free volume measured by Positron Annihilation Lifetime Spectroscopy (PALS)

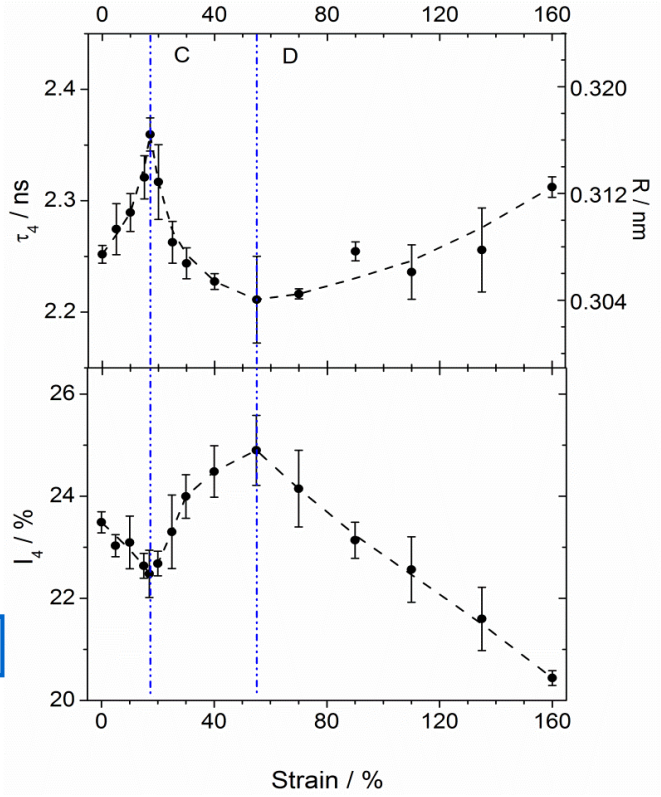
Defects in crystalline phase



Lifetime → Size

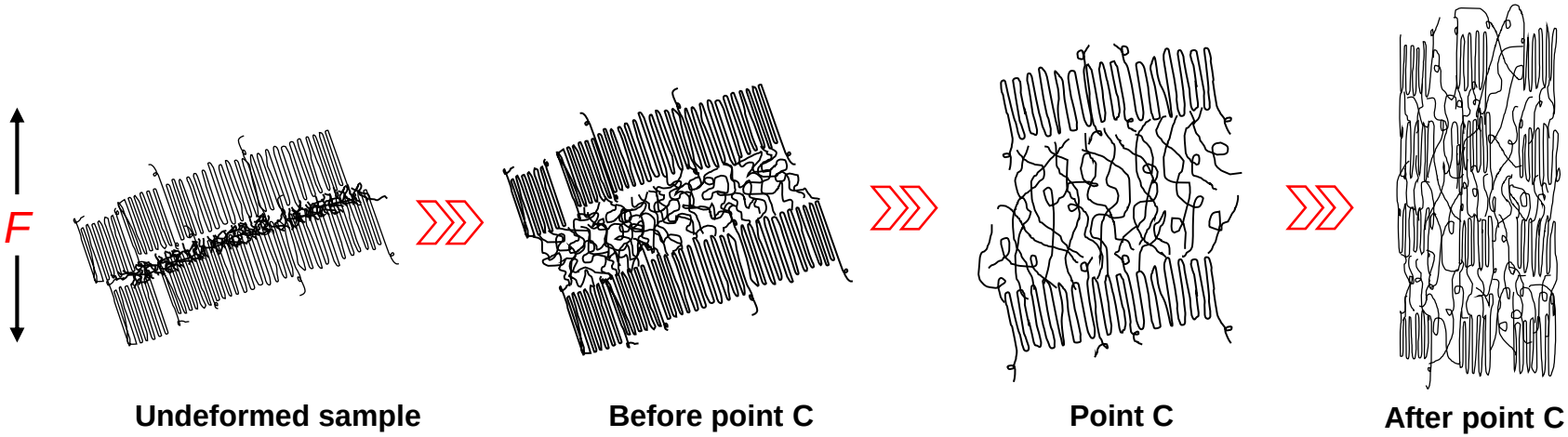
Intensity → Concentration

Free volume in amorphous region



- Before point C, the **defects** in crystalline phase and the **free volume size** of sample **increased**; but the total **concentration of free volume holes decreased**.
- Between point C and D, the **concentration of defects** in crystalline phase and **free volume size** decreased; but the concentration of free volume increased.

Mechanism of critical creep failure

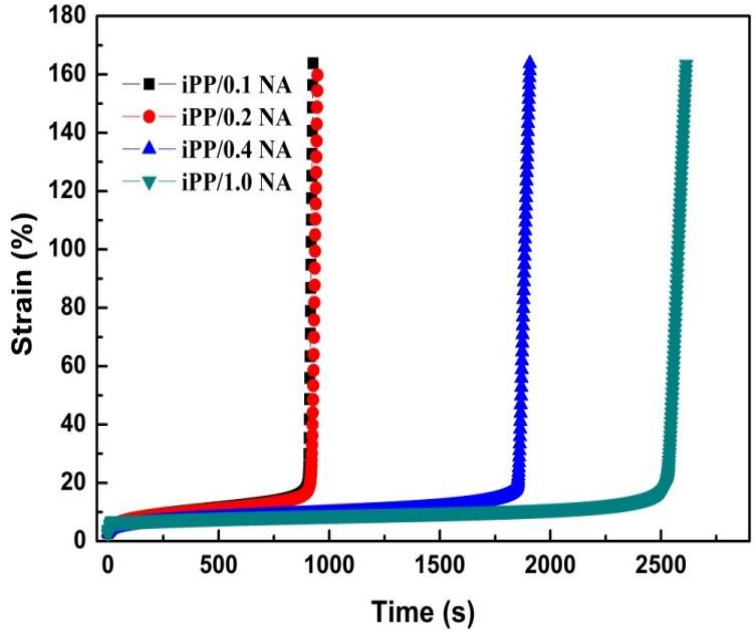


Less deformation (before point C): the entangled molecular chains in the amorphous region were stretched by the force (Long period d_{ac} **rise)**

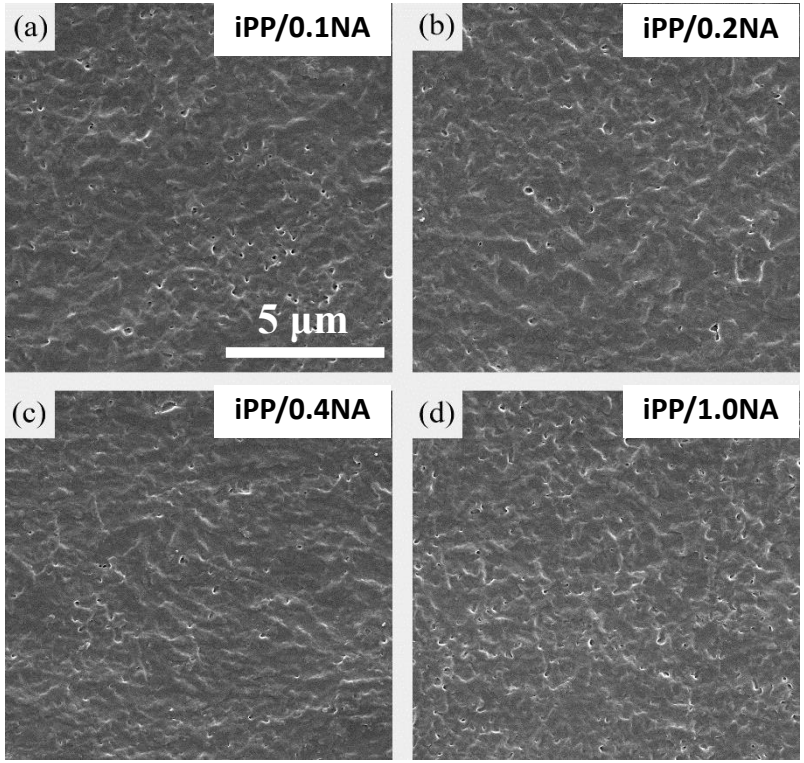
- **Creep failure (point C)：the molecular chains in the amorphous region were elongated further, and the folded-chains in the crystalline region were pulled out (defects and holes increased) , and then the material was failed ;**
- **Large deformation (after point C)：the disaggregated lamellar crystals recrystallized, and then the fibrous crystal formed along the creep direction.**

Effect of crystalline modification

➢ α-polypropylene



α-phase nucleating agent	0.1	0.2	0.4	1.0
ε_{cr} (%)	17	17	17	17

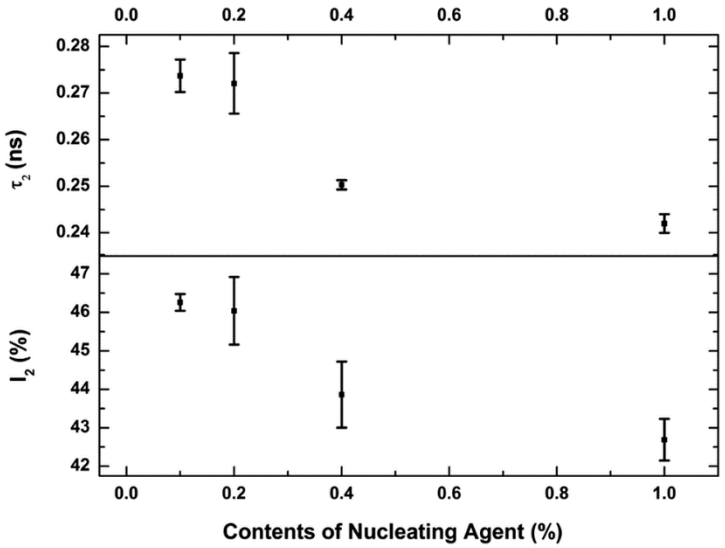


- The critical failure strain does not change
- The creep resistance increases with the content of nucleating agent because of the increased concentration of fibrillar crystals.

Chenfei Jia, Xia Liao, Guangxian Li, *et al*. *RSC Adv., 2016, 6: 84801-84809*.

Positron annihilation lifetime spectroscopy (PALS)

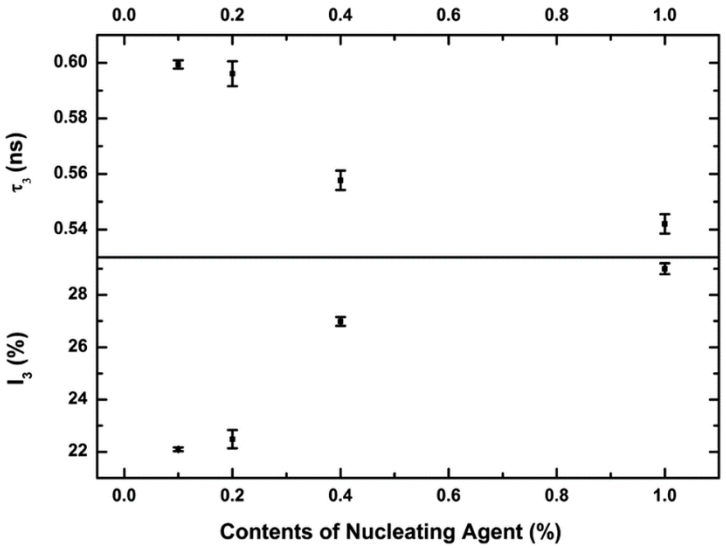
Defects in crystalline interface



Lifetime → Size

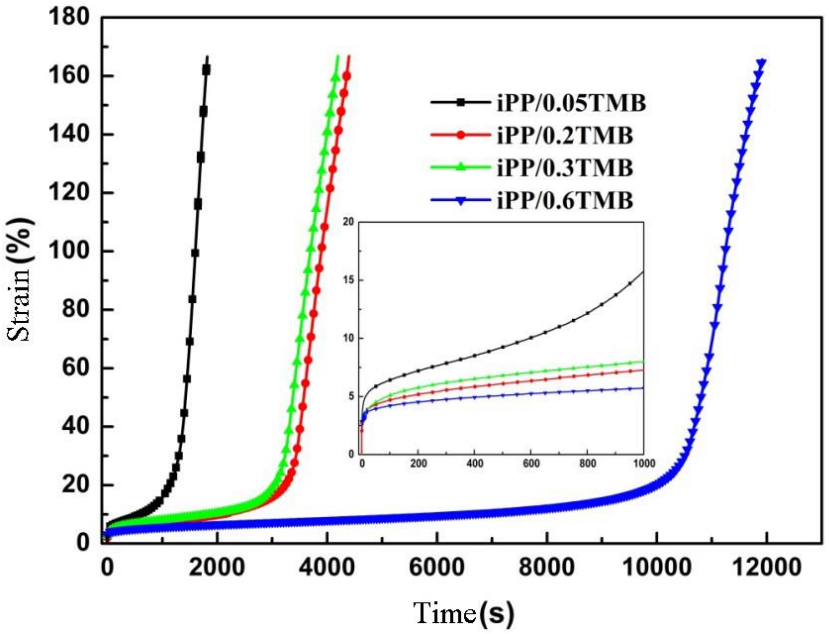
Intensity → Concentration

Defects in crystalline phase



The defects inside the material decreased with increasing content of nucleating agent, which are in favor of the improvement in creep resistance.

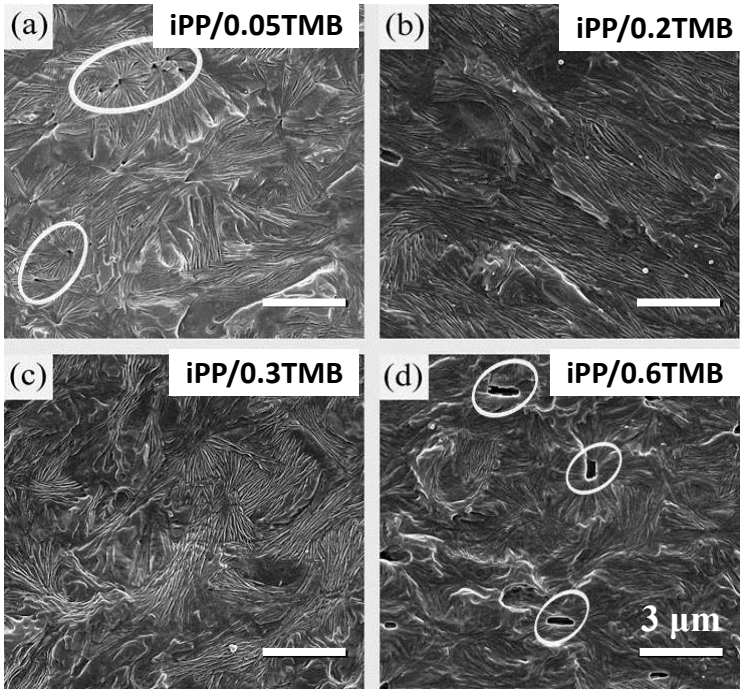
➢ β-PP (obtained by adding TMB nucleating agent)



β-phase nucleating agent	0.05	0.2	0.3	0.6
ε_{cr} (%)	11	11	11	11

Spherulites

Bundle-like morphology



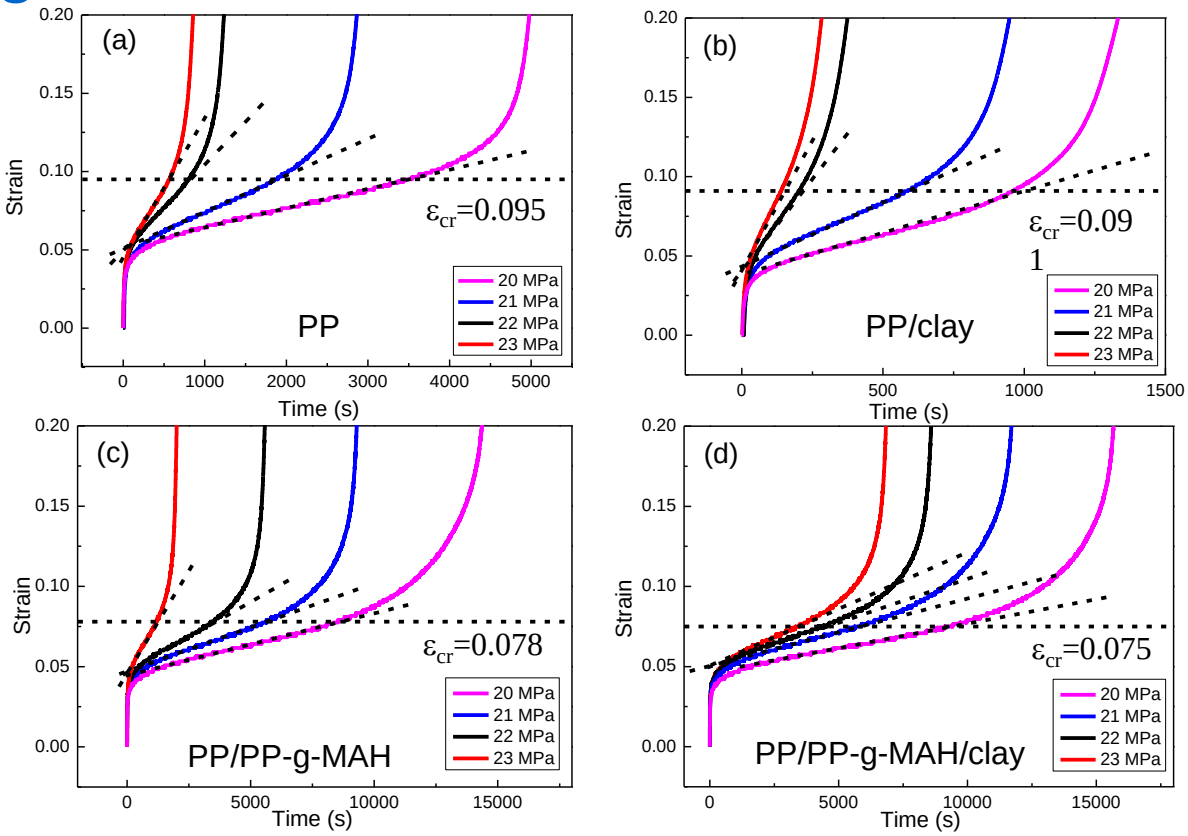
bundle-like morphology

needle-like crystals

- The time to reach the ε_{crit} increases with the content of nucleating agent but the ε_{crit} value does not change
- The ε_{crit} of β-PP is lower than that of α-PP (β-PP has more loose structure)

Chenfei Jia, Xia Liao, Guangxian Li, *et al*. *RSC Adv., 2016, 6:* 30986-30997.

Application of ε_{crit} in predicting service lifetime of polymers at low stress



- All materials display a constant critical failure strain (ε_{cr}) which does not depend on the stress
- A small change in stress leads to a large prolongation in creep failure time

Composites Science and Technology, 2014, 96: 71

Application of ε_{crit} in predicting creep failure lifetime

- **The key to predict lifetime: (a) aging equation; (b) failure criterion**

Kolarik's Stress Acceleration Method

(Basic idea: the creep of materials is a non-equal free volume process)

$$f\left(T,\varepsilon(t)\right) = f_g + \alpha_T\left(T - T_g\right) + (1-2v)\varepsilon(t)$$

$$\log t^* = \log t - \log a_\varepsilon(t)$$

$$= \log t + (B/2.303)\frac{\left[(1-2v)M\varepsilon(t)/\left(f_g + \alpha_T\left(T-T_g\right)\right)\right]}{\left[(1-2v)M\varepsilon(t) + \left(f_g + \alpha_T\left(T-T_g\right)\right)\right]}$$

ε_t – strain f – free volume

T – temperature f_g – free volume at glass state

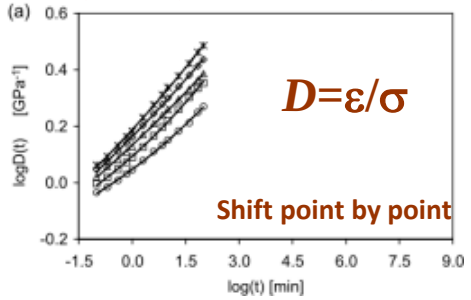
v– Poisson's ratio a_T– coefficient of thermal expansion

B – Material constant M – strain amplification factor

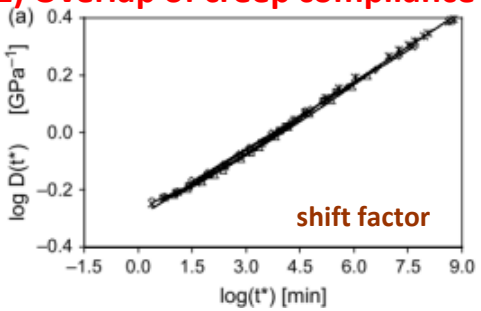
t^* – Internal time a_ε –shift factor

Lv, Huang, Li. Composites Science and Technology, 2014, 96, 71; CN Patent ZL 201310237622.1

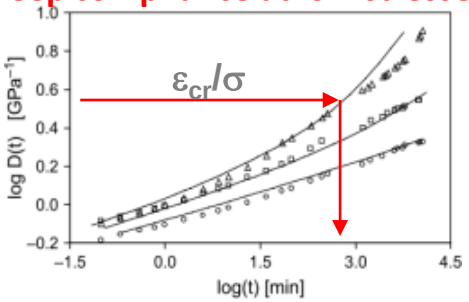
(1) Creep compliance at high stresses



(2) Overlap of creep compliance curves

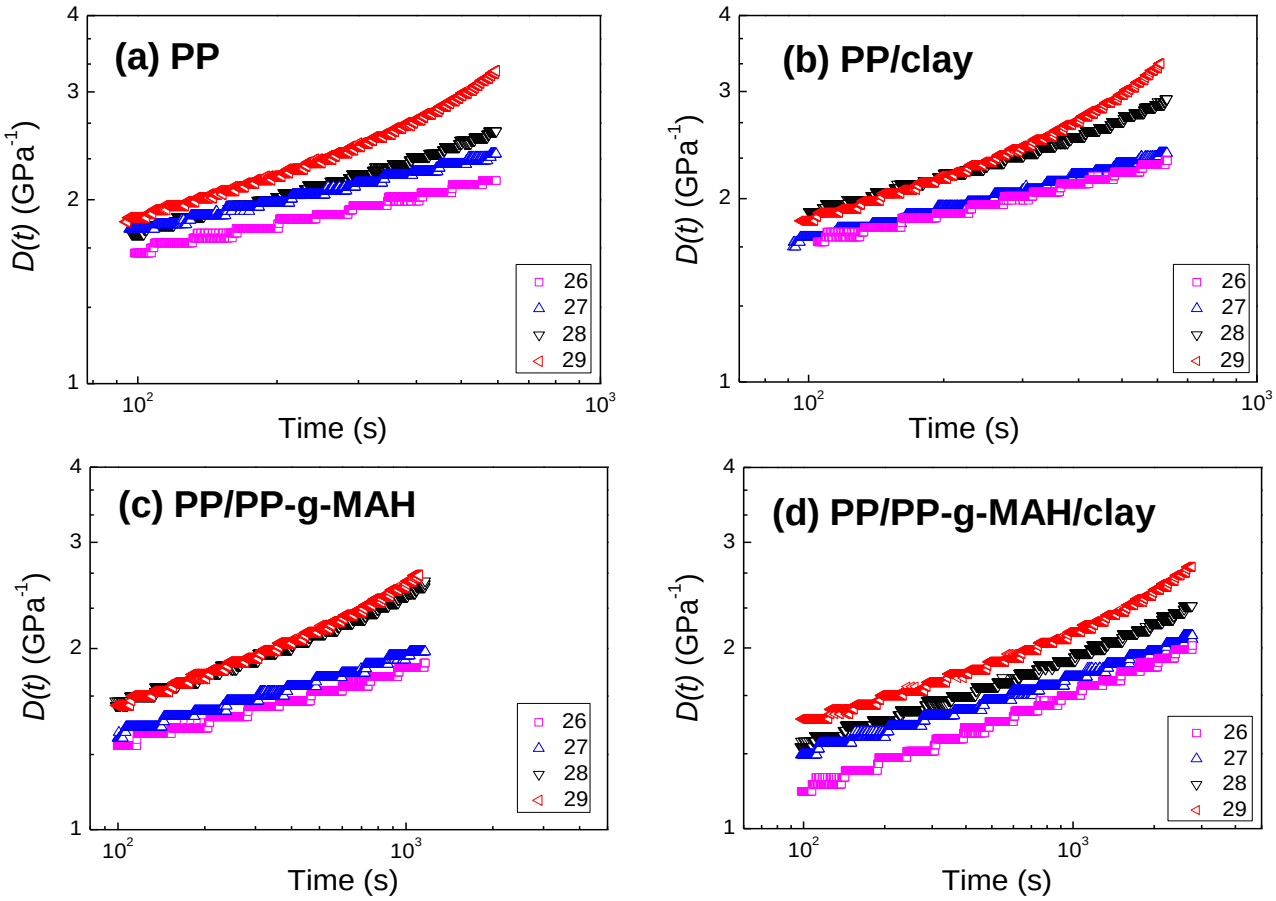


(3) Creep compliance at low stresses obtained



- Obtain the compliance ($D=\varepsilon/\sigma$) of samples at different times for each high mechanical stress (acceleration) according to the Kolarik's method
- Obtain a compliance master curve by shifting and overlapping the compliance curves (the shift factor for each stress is obtained at the same time
- Obtain the compliance curve at low stress by shifting the master curve according to the shift factor of low stress
- Obtain the **compliance at creep failure** ($D_{low}=\varepsilon_{crit}/\sigma_{low}$) and find the failure time on the compliance curve at low service stress

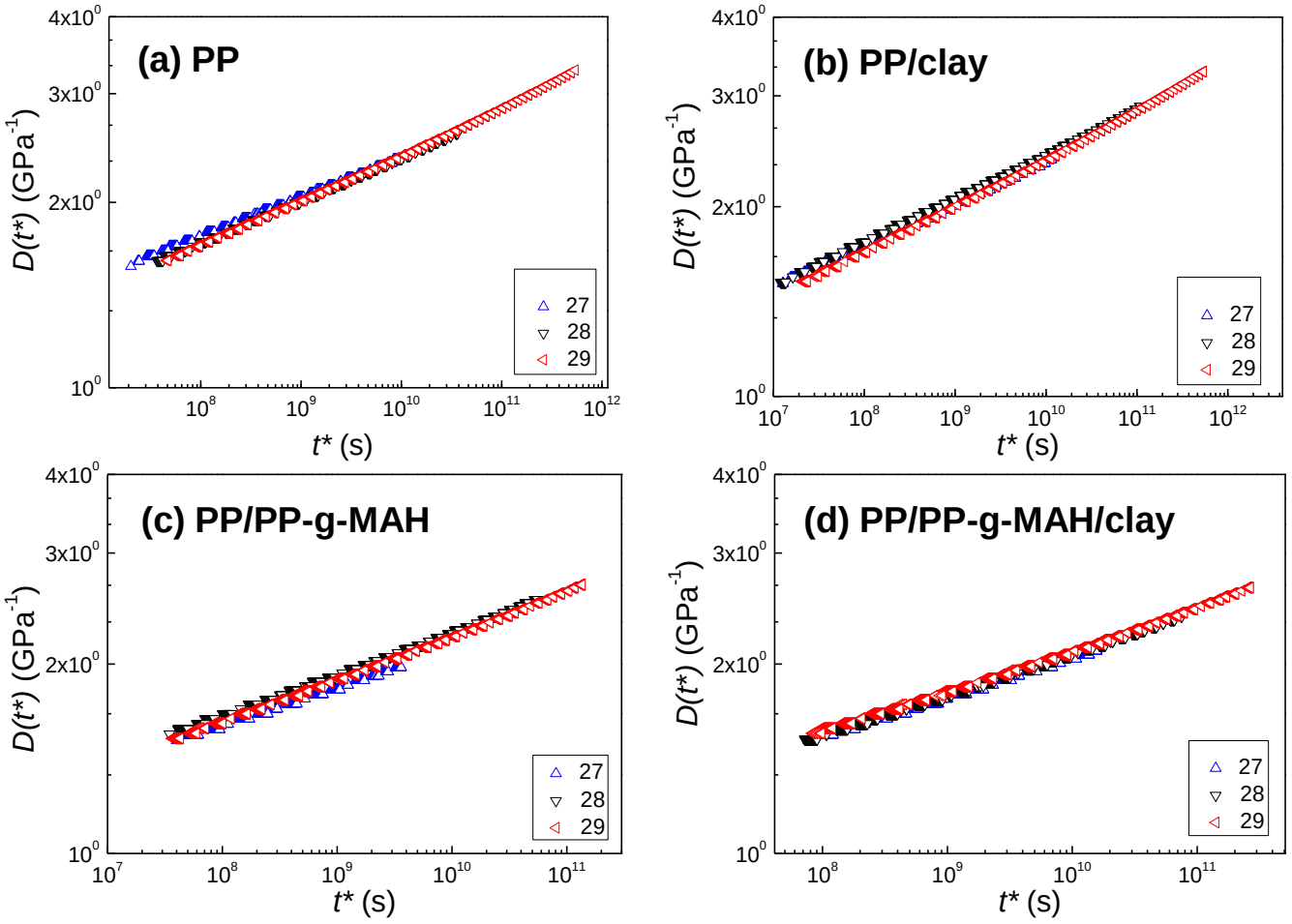
Creep compliance curves of iPP and its composites at 60°C



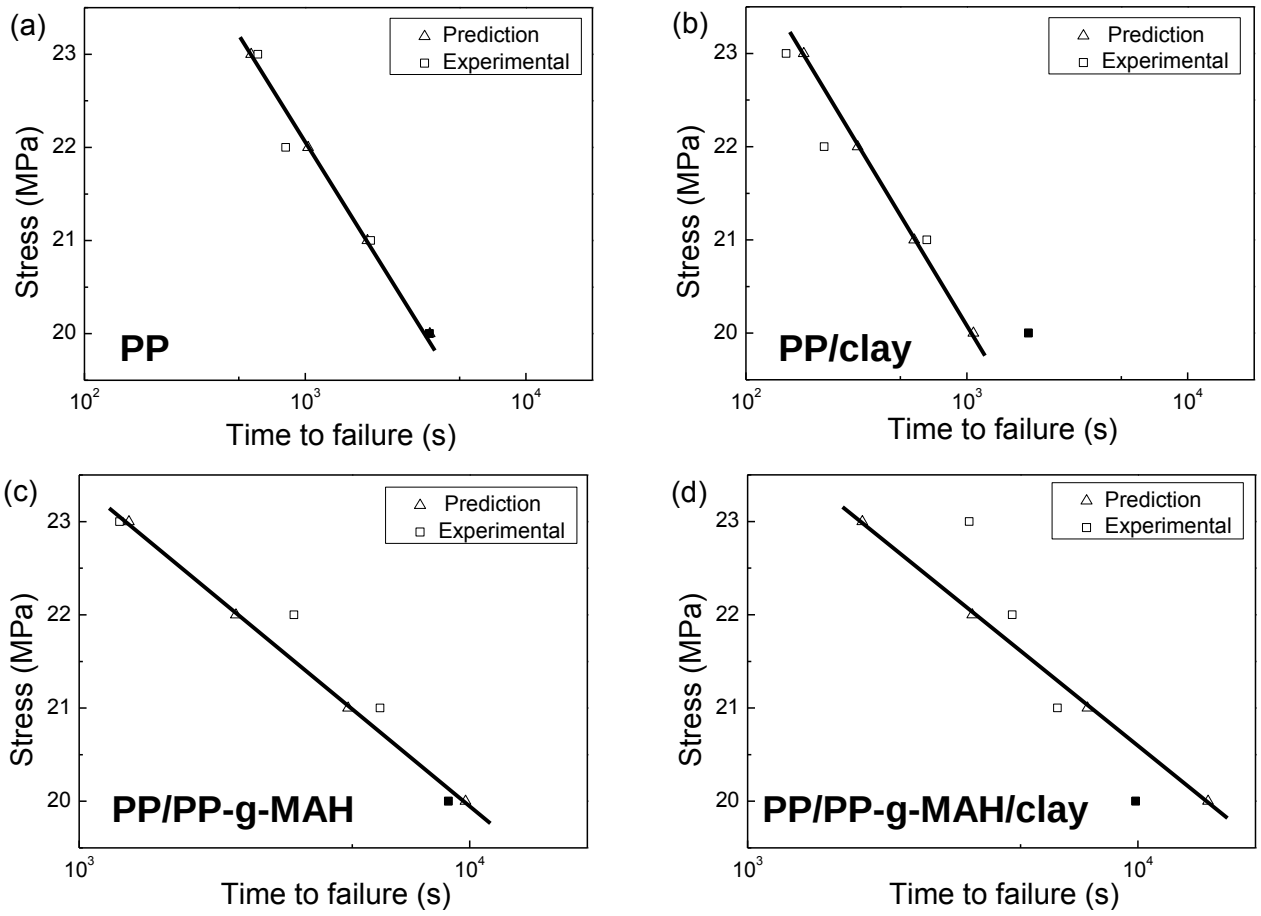
- **The creep compliance increases with stress and declines significantly upon the addition of clay and compatibilizers**

Lv, Huang, Li. Composites Science and Technology, 2014, 96, 71

Master curves of creep compliance



➢ Predicted lifetime for creep failure at lower service stress



- **By using the critical strain criterion and the time-strain superposition method, the failure lifetime of iPP materials can be predicted satisfactorily**

Mechanism for stress-accelerated aging of iPP

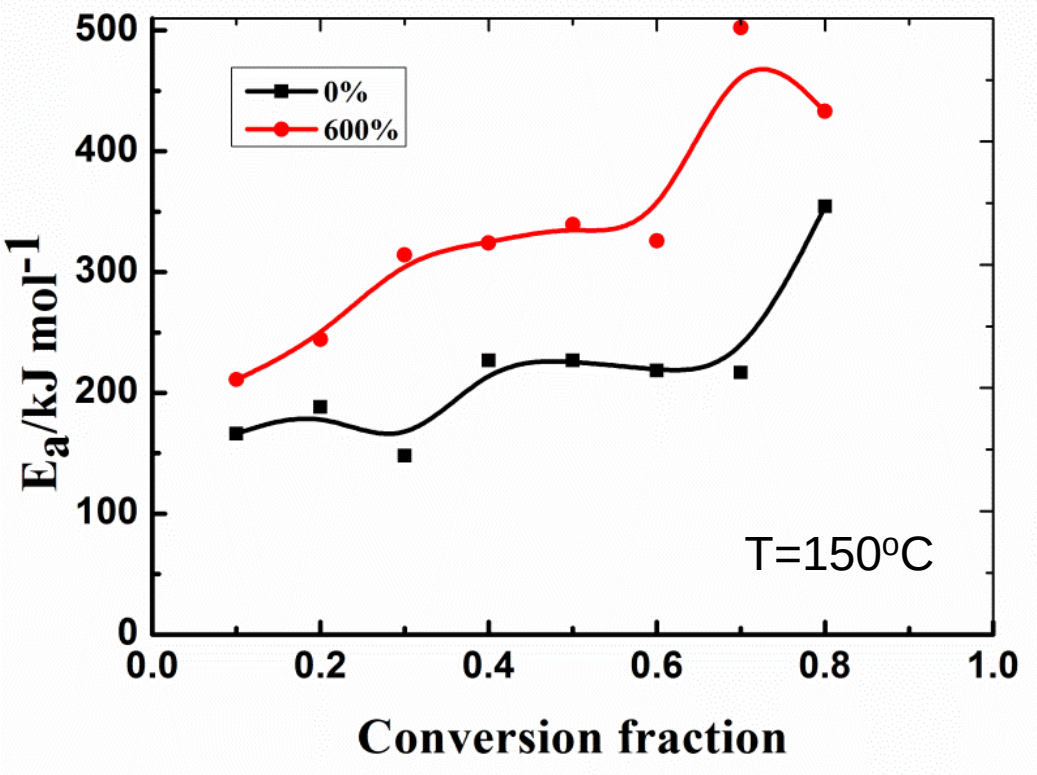
- The coupling of physical and chemical factors lead to the rapid degradation and creep failure of iPP

- The stretching of molecular chains in the amorphous region and the pull-out of the folded chains in the crystalline region lead to an unique critical failure strain which does not depend on temperature, stress or UV

- The critical failure strain can be used to predict the service lifetime of iPP under stress by combining with the time-strain superposition

Case 3:
Hydrothermal oxidation of stressed PA6 (under much higher mechanical stress)

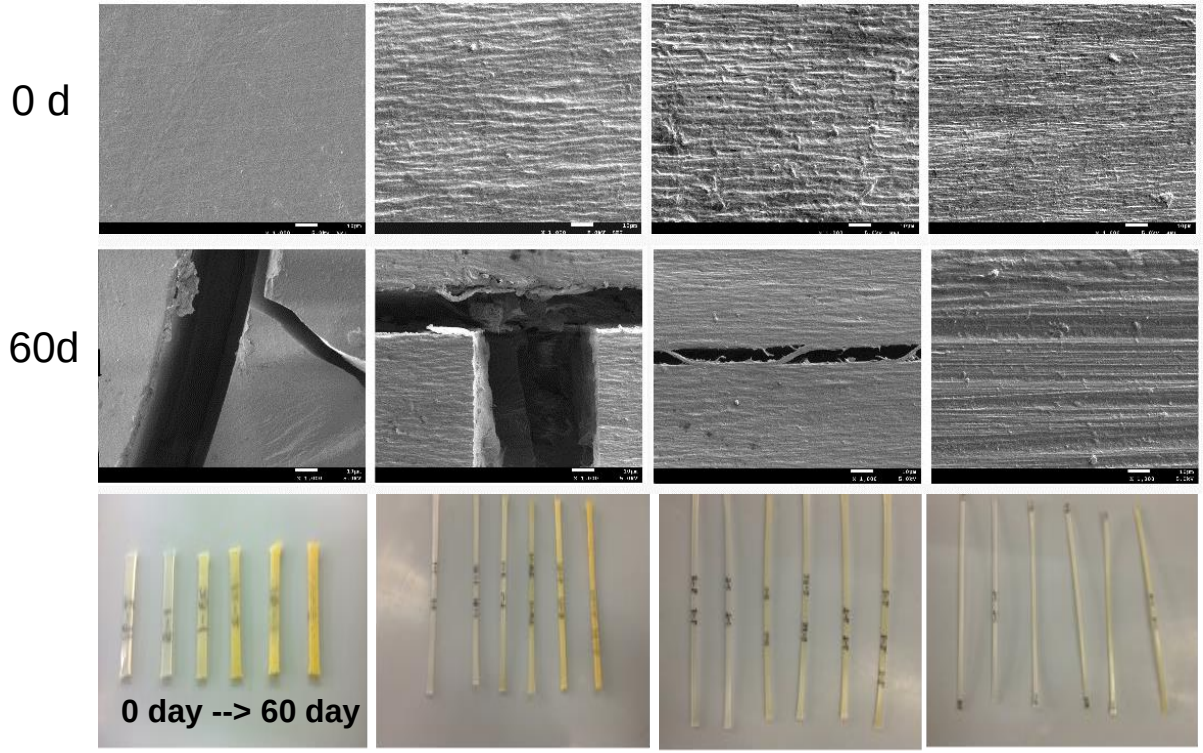
Effect of mechanical drawing on activation energy



- **Polymer chain orientation （under 600% strain）increases the activation energy of PA6 during thermo-oxidation**

Shi K, Ye L, Li G. Journal of Thermal Analysis and Calorimetry, 2016, 126, 795

Effect of mechanical drawing on microstructure

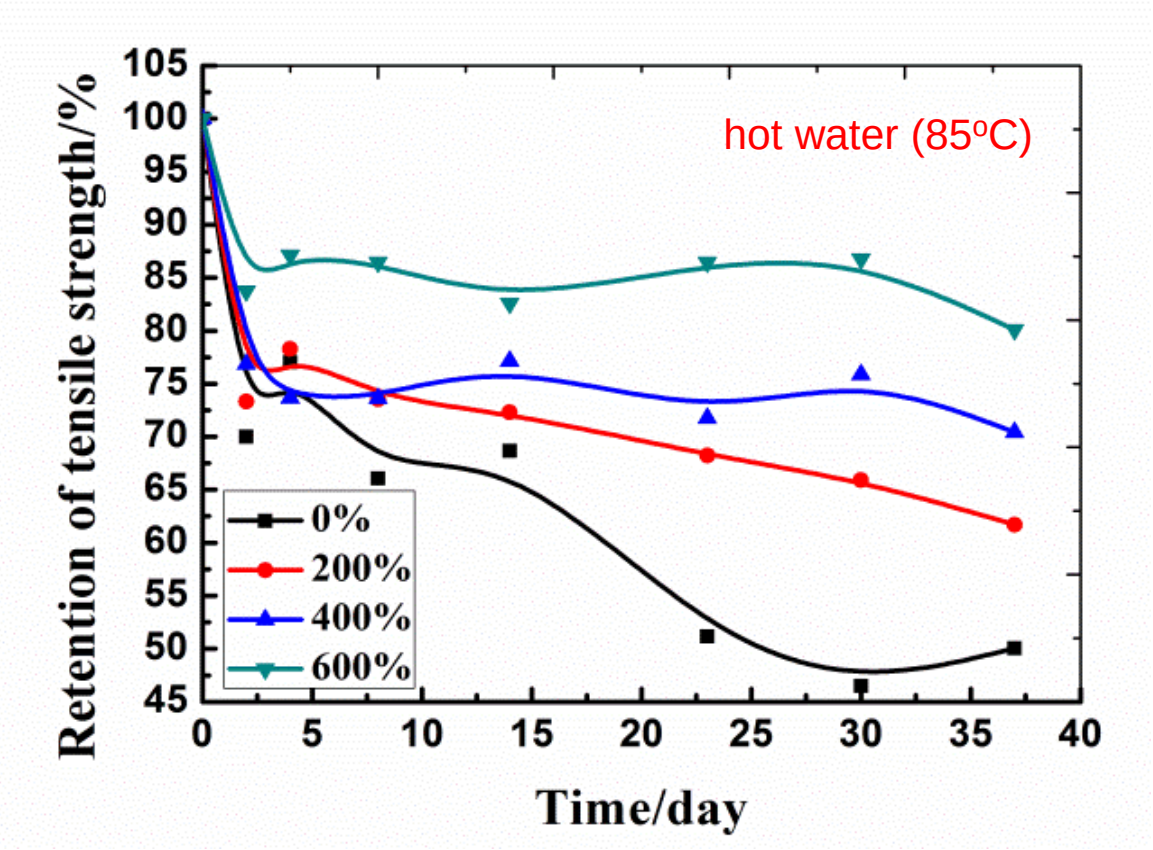


SEM and photographs of PA6 samples after been immersed in hot water (85°C) for 60 days

- **Polymer chain orientation suppressed the cracking and yellowing of PA6 during hydrothermal oxidation**

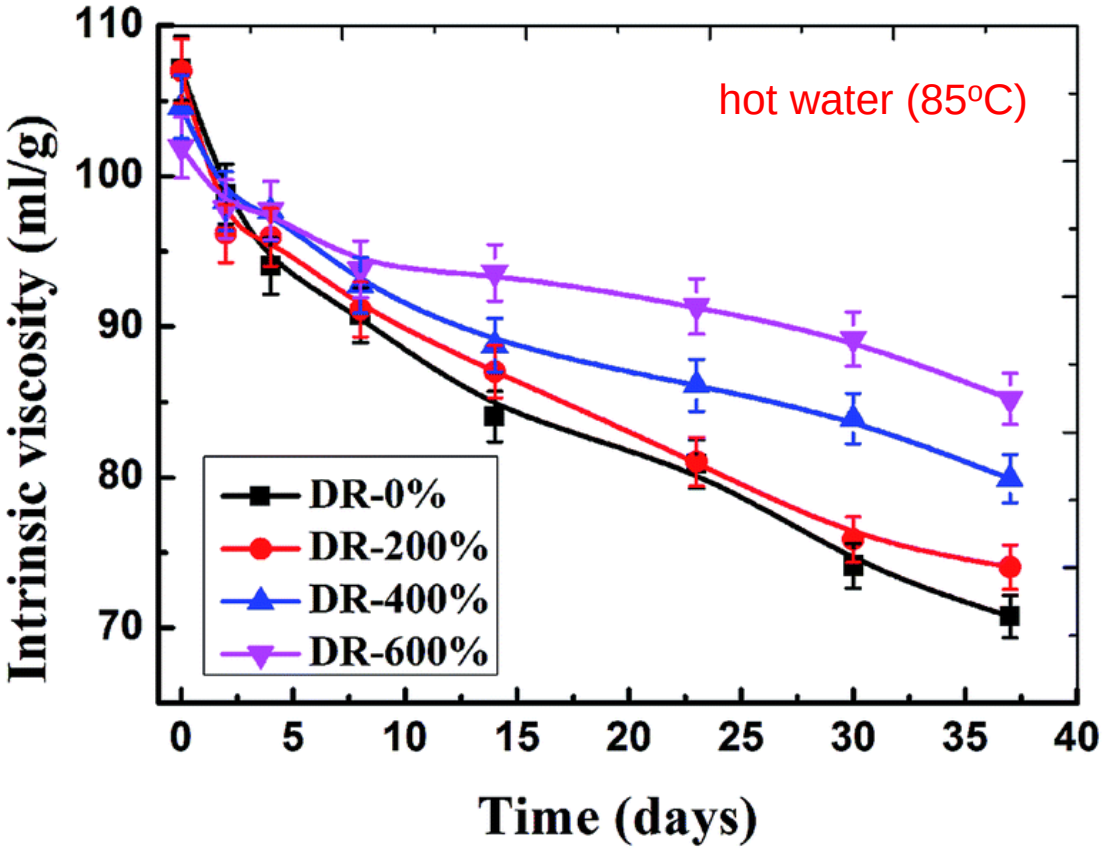
Shi K, Ye L, Li G. *RSC Advances,* 2015, 5, 30160

Effect of drawing orientation on tensile strength



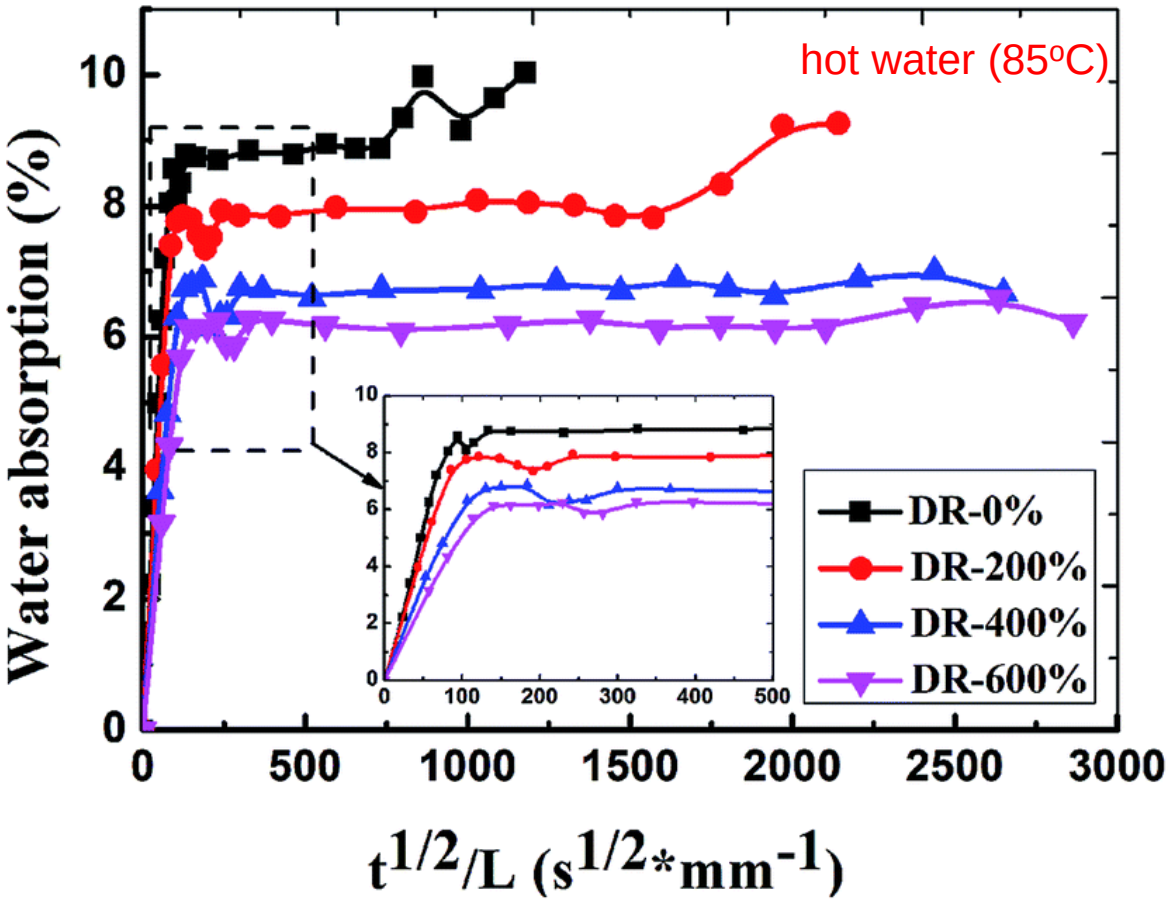
- **The orientation increases the retention of mechanical properties during hydrothermal oxidation**

Effect of drawing orientation on molecular weight



- Polymer chain orientation **suppressed the decline of molecular weight** during hydrothermal oxidation

Effect of drawing orientation on water absorption



DR	Xc %	*f*
0	39.2	-
200	45.0	0.17
400	45.4	0.18
600	53.6	0.21

- **Polymer chain orientation increases the crystallinity and orientation degree of PA6, leading to lower water absorption**

Conclusions

- The mechanical stress plays an important role in the thermo- or photo-oxidation of polymers

- The mechanical stress produces polymer chain activation and orientation, even microcracks, which affect the diffusion of aging factors (O_2, UV light and H_2O etc) and change the thermo-, photo- and hydrothermal oxidation process

- For amorphous polymers, increasing the mechanical stress will promote photo-oxidation of materials

- For semicrystalline polymers, additionally, the application of stress will also accelerate physical aging (creep) of materials

- For much stronger strain (stress), the resulted chain orientation may improve the thermo-oxidative and hydrothermal stability of polymers

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Thanks for your attention !