Functionalization of Polypropylene With Sulfonyl Azide Through Reactive Blending

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Overview

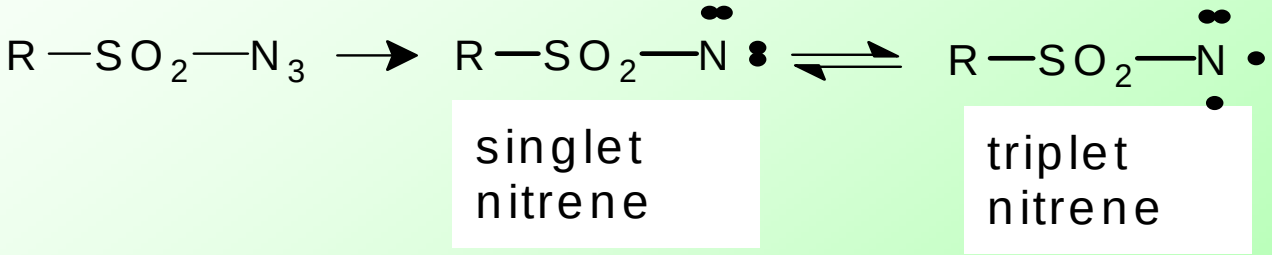
- Introduction
  - Functionalization of PP
  - Sulfonyl Azide and Nitrene
  - Research Activities and Applications
- Objectives
- Experimental
- Results and Discussion
- Conclusions

Introduction

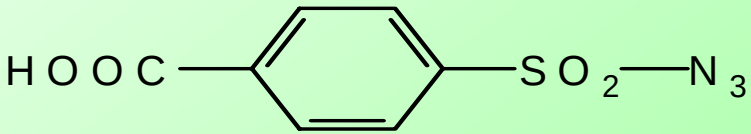
- Functionalization of PP
  - **Purpose**
    - Excellent properties of PP
    - Introduction of polar groups
    - Improvement of adhesion and compatibility
    - Modifying the surface energy
  - **Functionalization by reactive blending and extrusion**
    - Maleic Anhydride (MAH)
      - Peroxide
      - Chain scissions
      - Side reactions
    - Sulfonyl azide – an alternative route

Introduction

- Sulfonyl Azide and Nitrene
  - Chemistry



  - Mono(sulfonyl azide)
    - 4-carboxybenzenesulfonazide (CBSA)

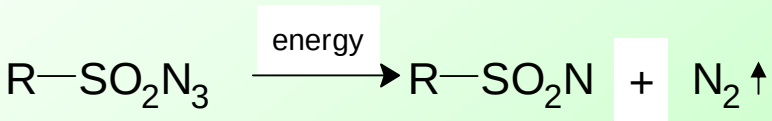


  - Poly(sulfonyl azide)
    - oxy-bis(4-sulfonylazidobenzene)

Introduction

Research Activities

- Mechanism Study (**R.A. Abramovitch et al. in 1960s**)

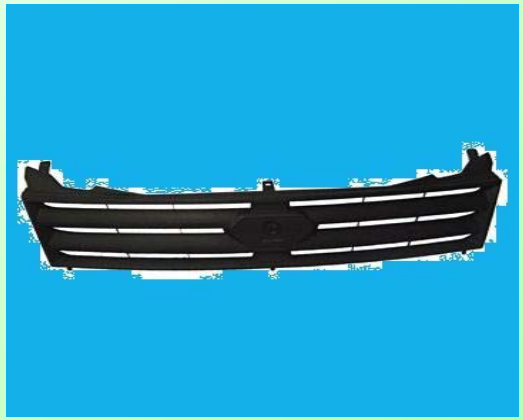


- Poly-/Mono-(sulfonyl azide)
  - As coupling agent or modifying agent
  - Rheology modification
  - Treatment of sulfonyl azides

Introduction

Main Applications

- Automotive Industries
  - TPO blends for car bumper et al
  - Paintability improvement
  - Mechanical properties
- Packaging Industries
  - Film manufacturing
  - Melt strength increase



Pictures from ExxonMobil Chemical and auto websites

Objectives

- To investigate an alternate route for the functionalization of polypropylene

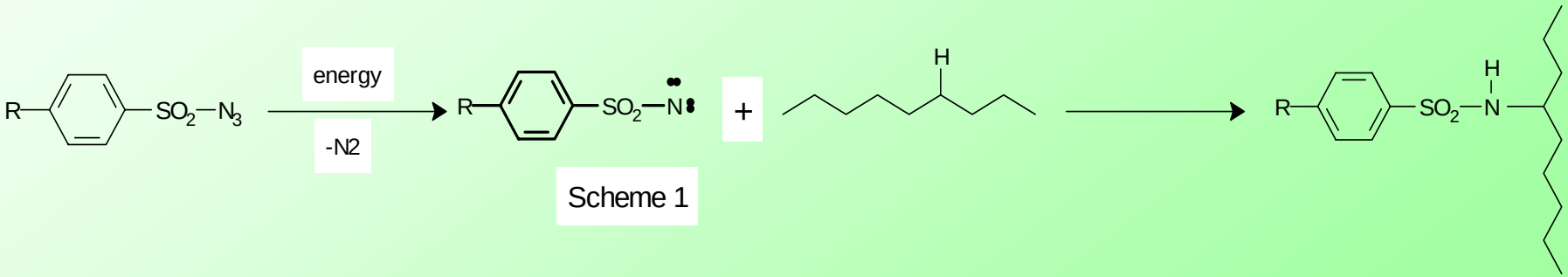
Experimental/Characterization

- Materials
  - PP: PDC1301 (homopolymer, 3.5MFI), Basell
  - Sulfonyl azide: 4-carboxybenzenesulfonazide(CBSA), Sigma-Aldrich
- Equipment
  - Haake batch mixer: Rheomix 3000
- Reactive Blending/Purification
- Characterization
  - Grafting degree: FTIR, ^{1}H-NMR
  - Rheology: Rotational Rheometer
  - Mechanical Properties: Instron tester

Results and Discussion

Reaction Mechanism

- singlet nitrene reaction (scheme 1)
  - decomposition into singlet nitrene
  - singlet nitrene insertion into PP C-H bond

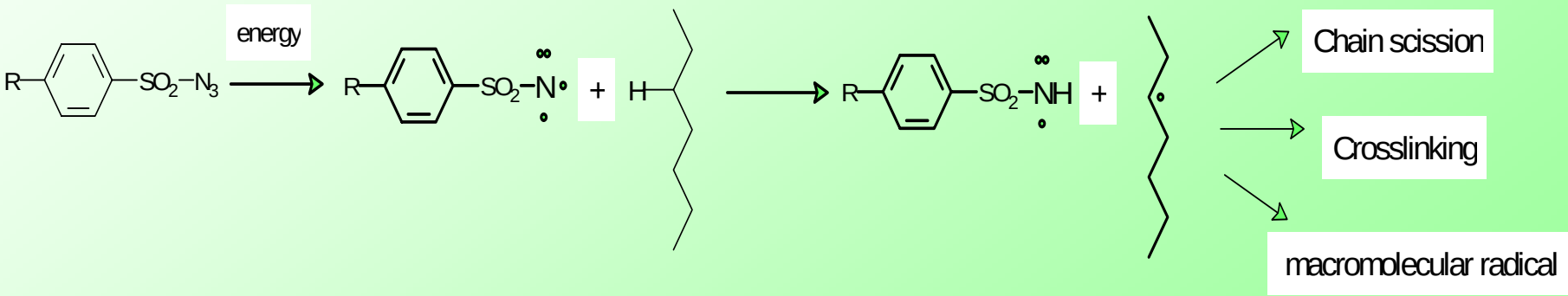


Scheme 1

Results and Discussion

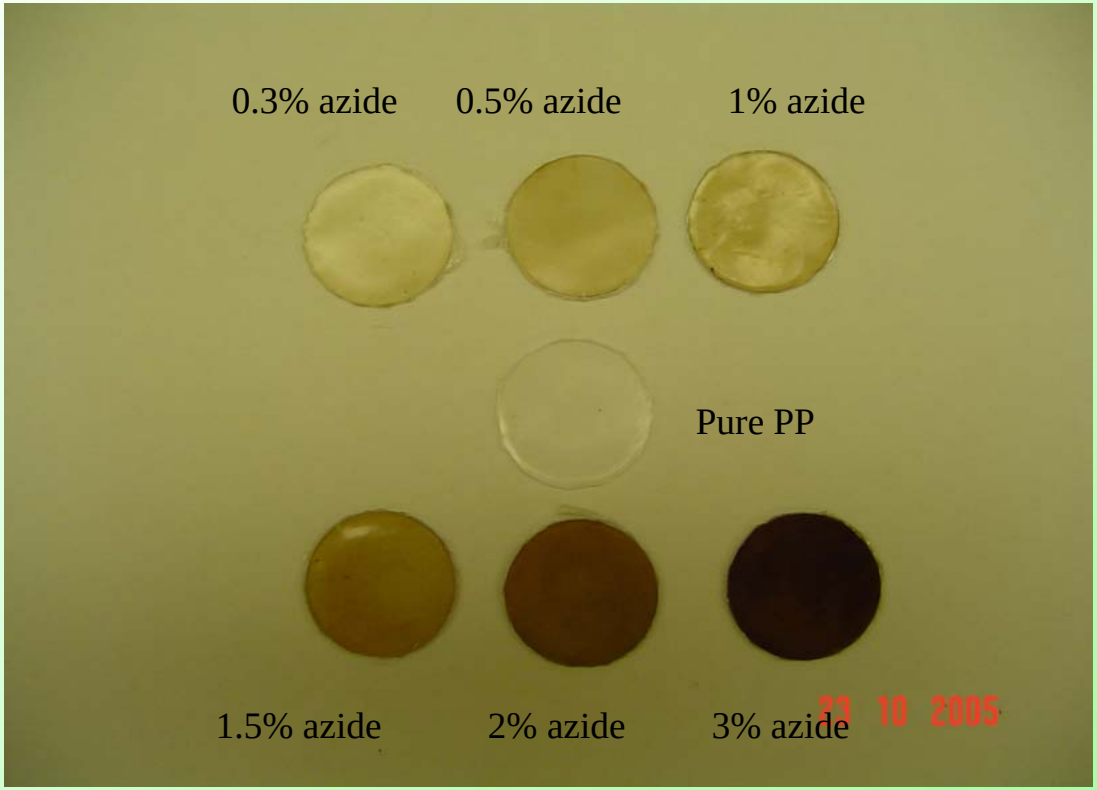
Reaction Mechanism

- triplet nitrene reaction (scheme 2)
  - singlet nitrene conversion to triplet nitrene
  - H-abstraction reaction
  - further reactions



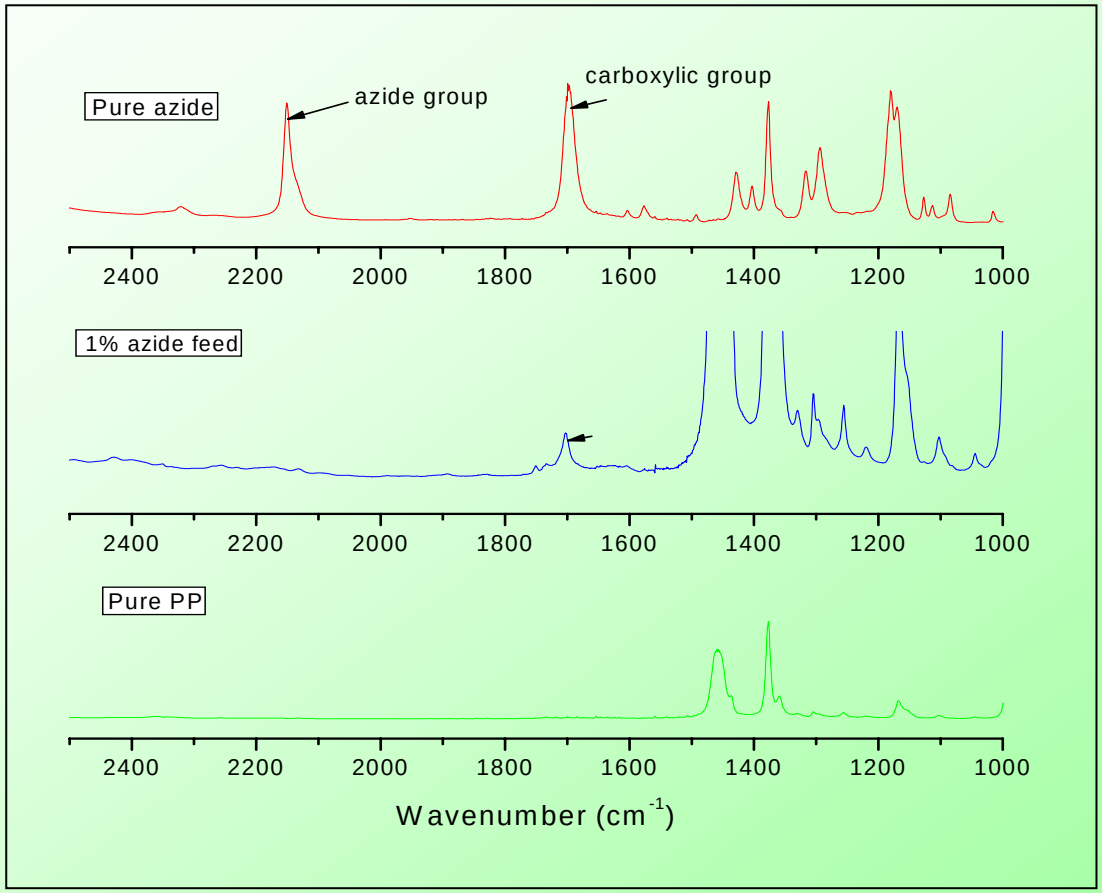
Results and Discussion

- Comparison of different purified grafted PP samples



Results and Discussion

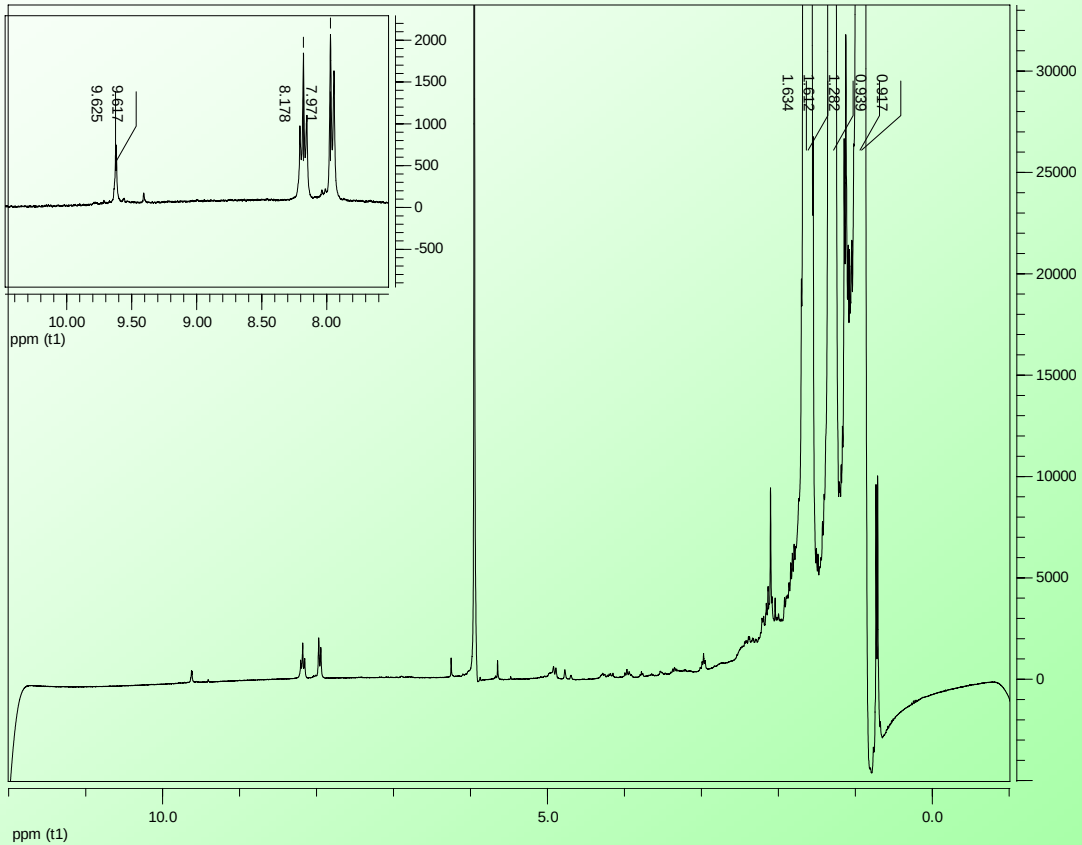
- Comparison of IR results of PP, pure azide and azide grafted PP

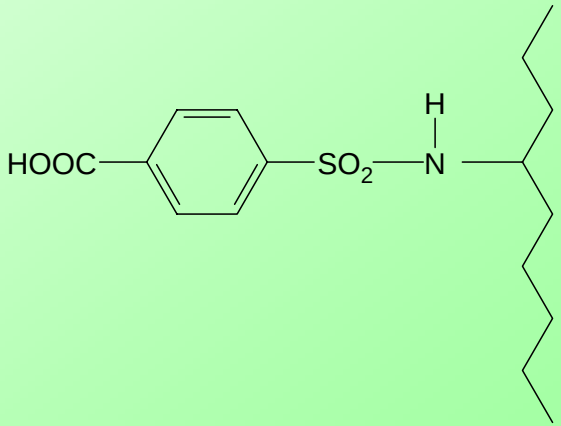


Azide group: 2150cm^{-1}
Carbonyl group: 1701cm^{-1}

Results and Discussion

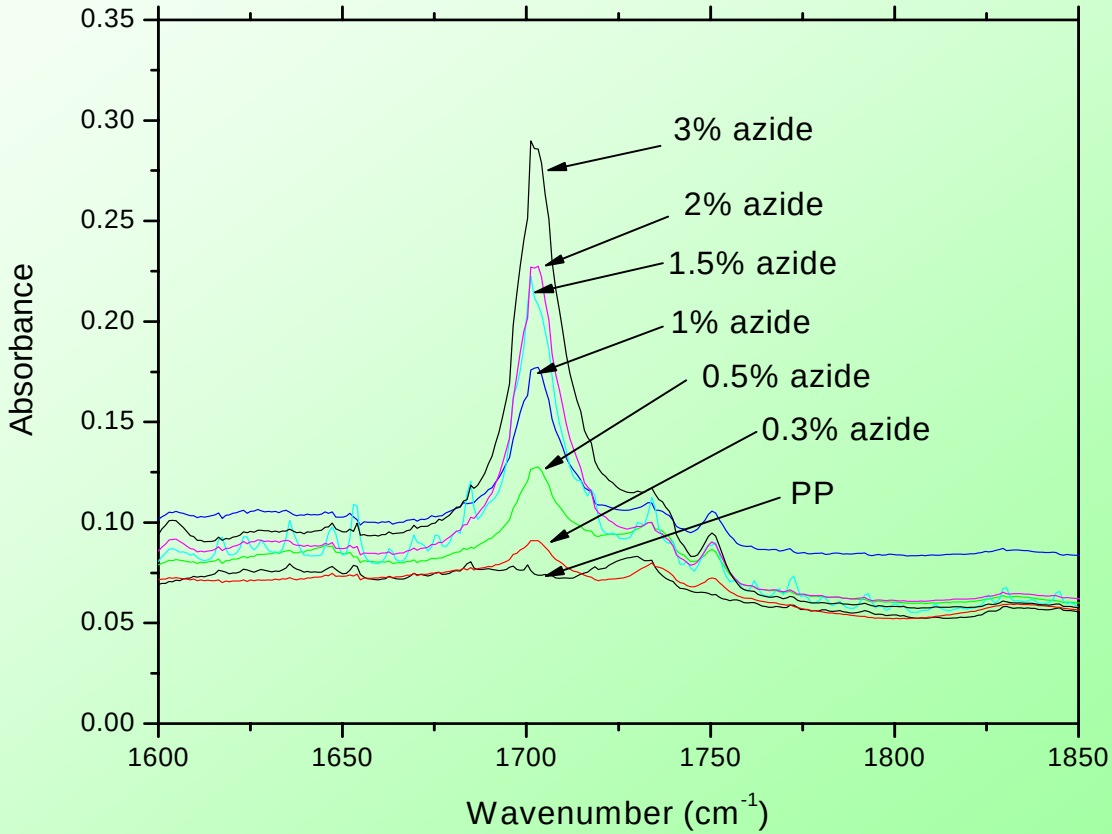
- ^{1}H-NMR spectrum for grafted PP(1.5% azide feed)





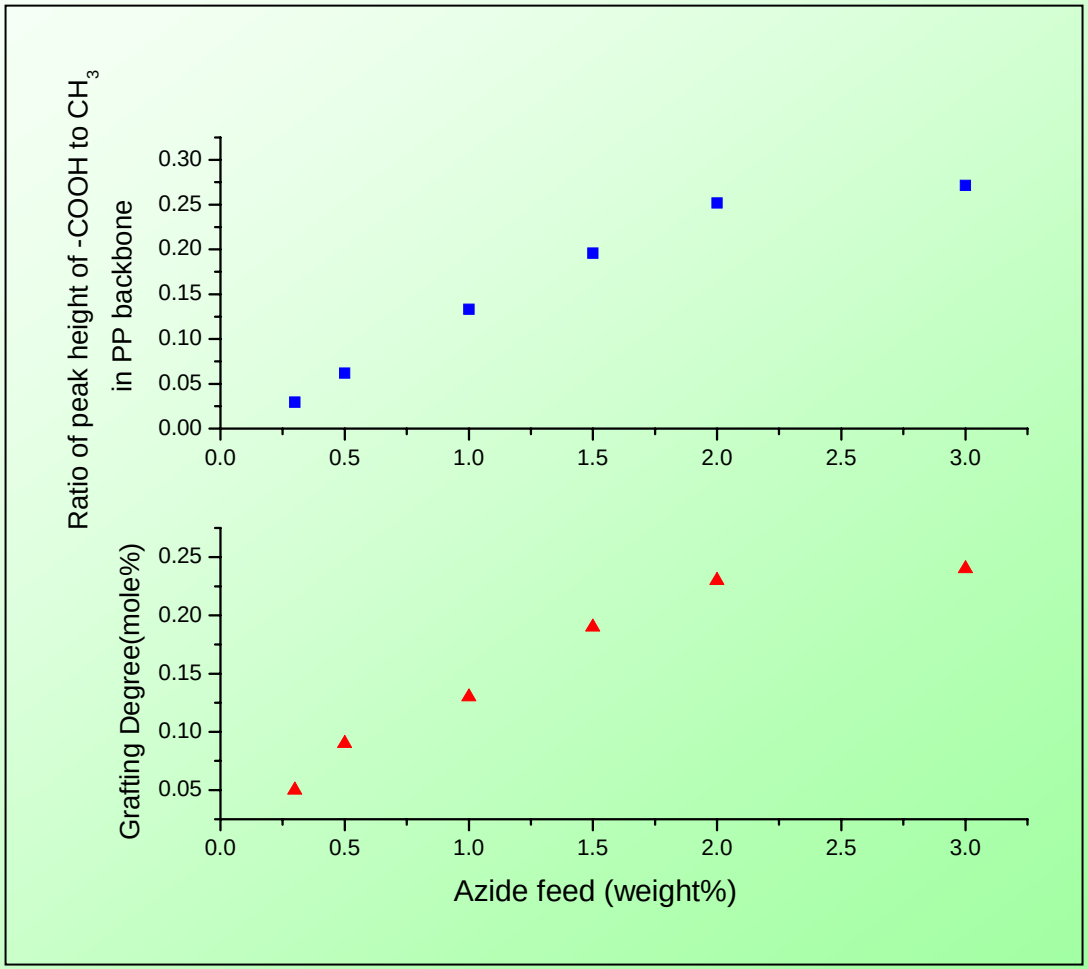
Results and Discussion

- FTIR peak height intensity as function of azide feed



Results and Discussion

- Influence of azide feed on grafting degree



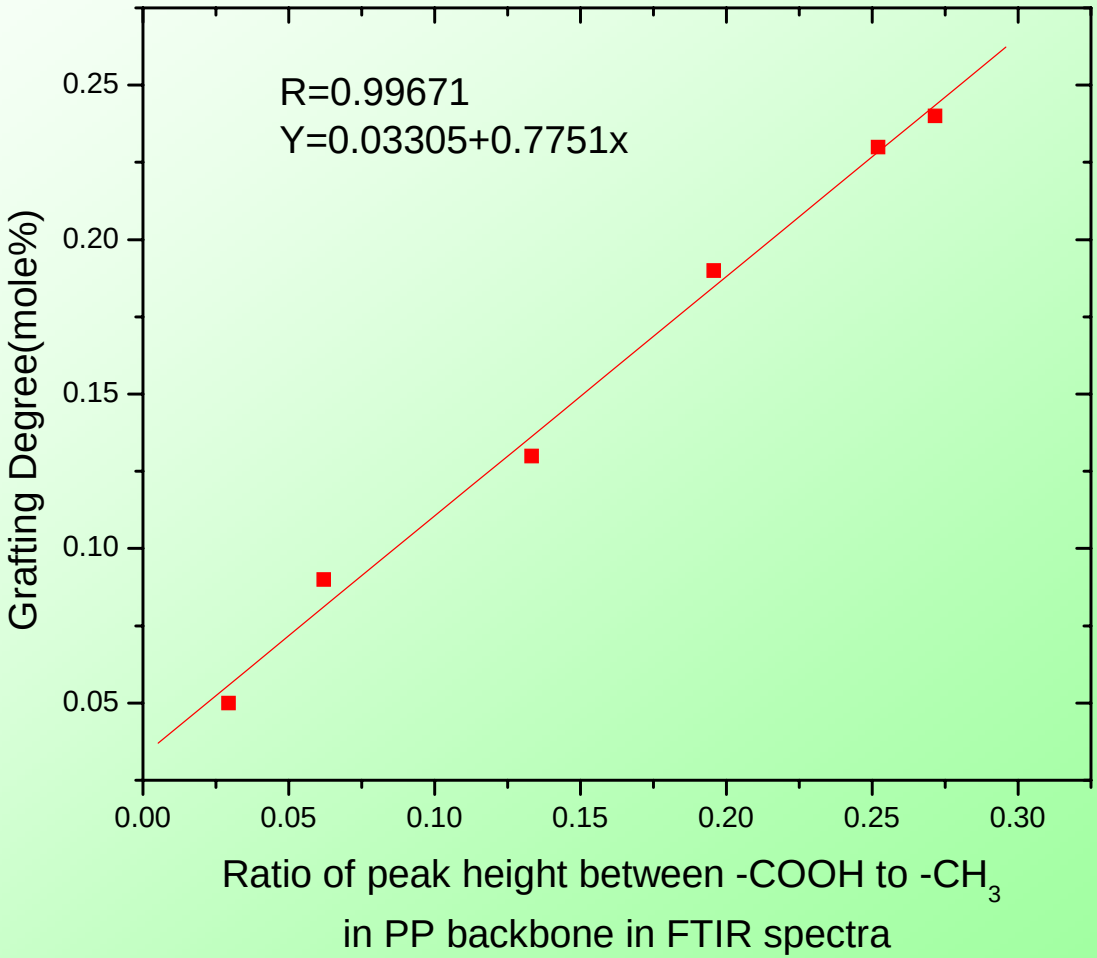
Results and Discussion

Table 1 FTIR and ^{1}H-NMR results for different azide feed

feed azide (wt %)	grafting degree (mole %)	peak height ratio of 1701cm^{-1} to 973cm^{-1} in IR measurements
0.30	0.05	0.0294
0.50	0.09	0.0620
1	0.13	0.1333
1.50	0.19	0.1957
2	0.23	0.2520
3	0.24	0.2716

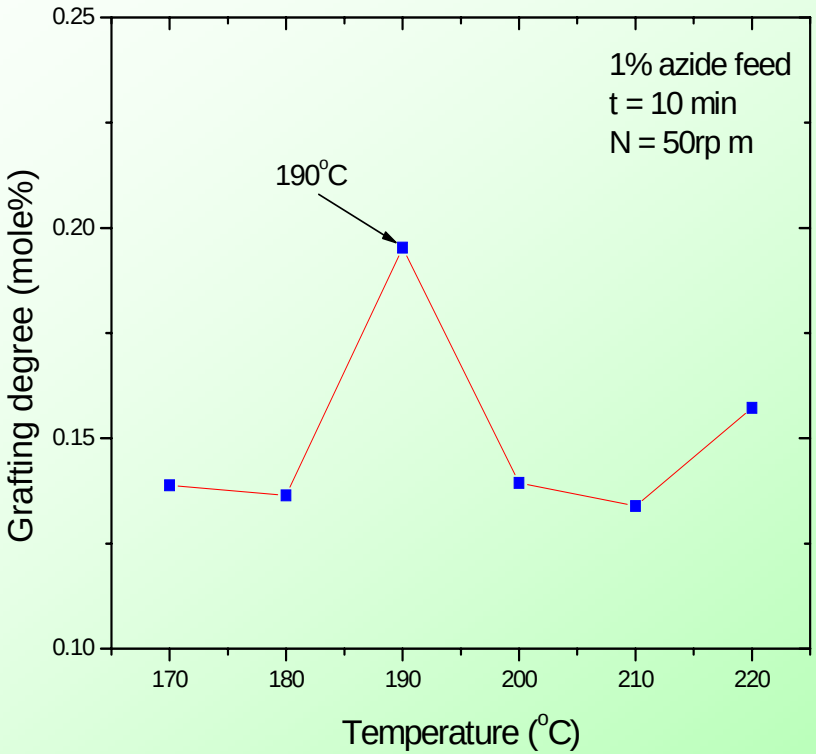
Results and Discussion

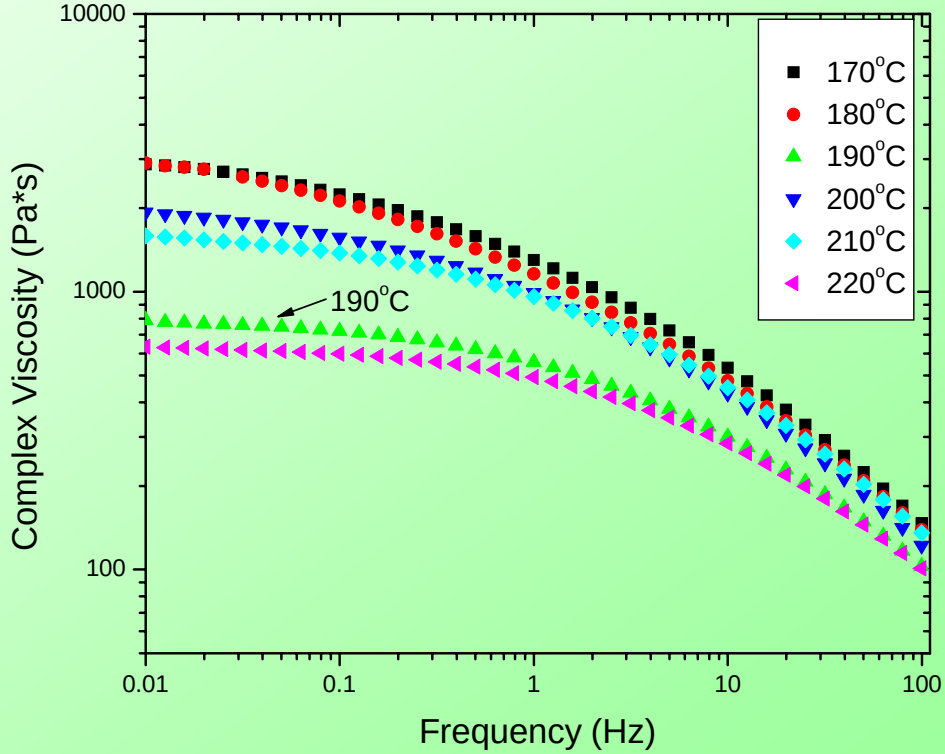
- Relationship between the ratio of –COOH to –CH_3 in FTIR spectrum and the grafting degree in ^{1}H-NMR spectrum



Results and Discussion

- Effects of Reaction Temperature on Grafting Degree and Viscosity

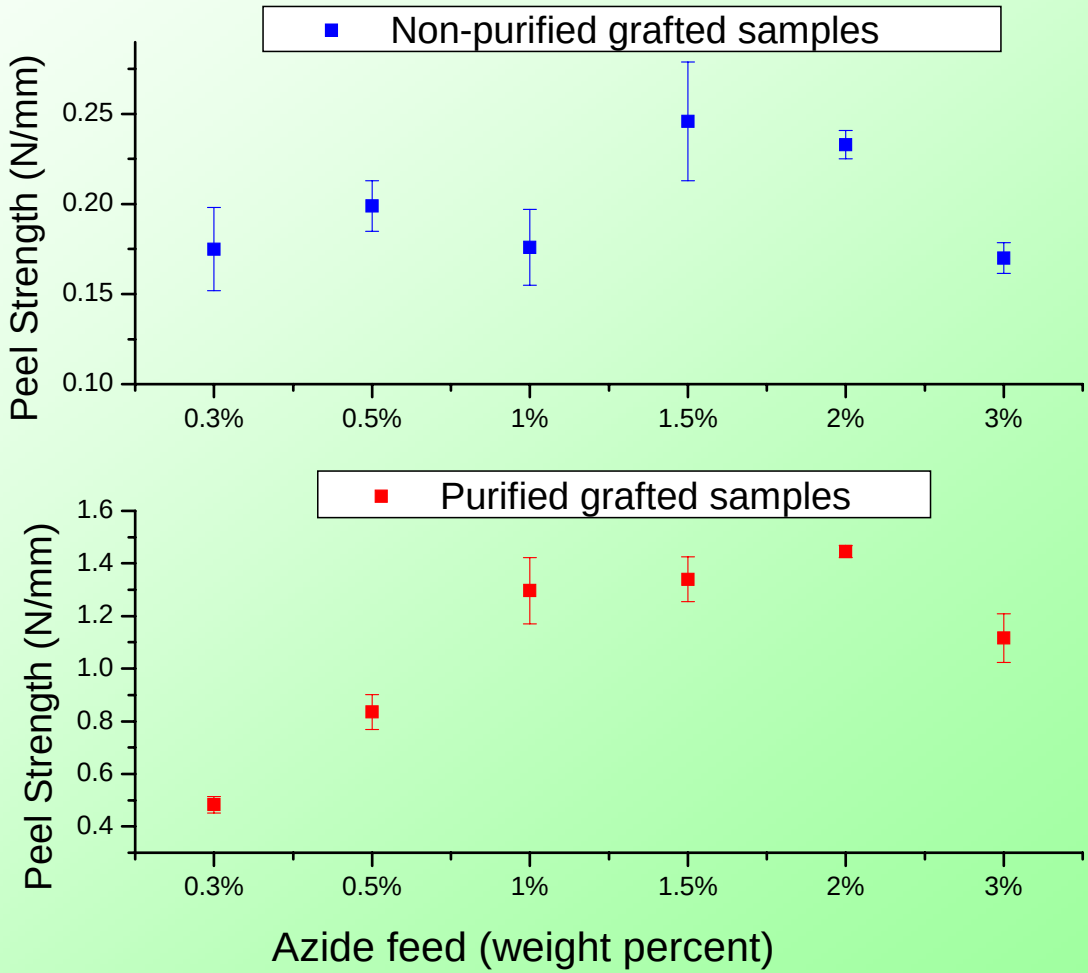




Results and Discussion

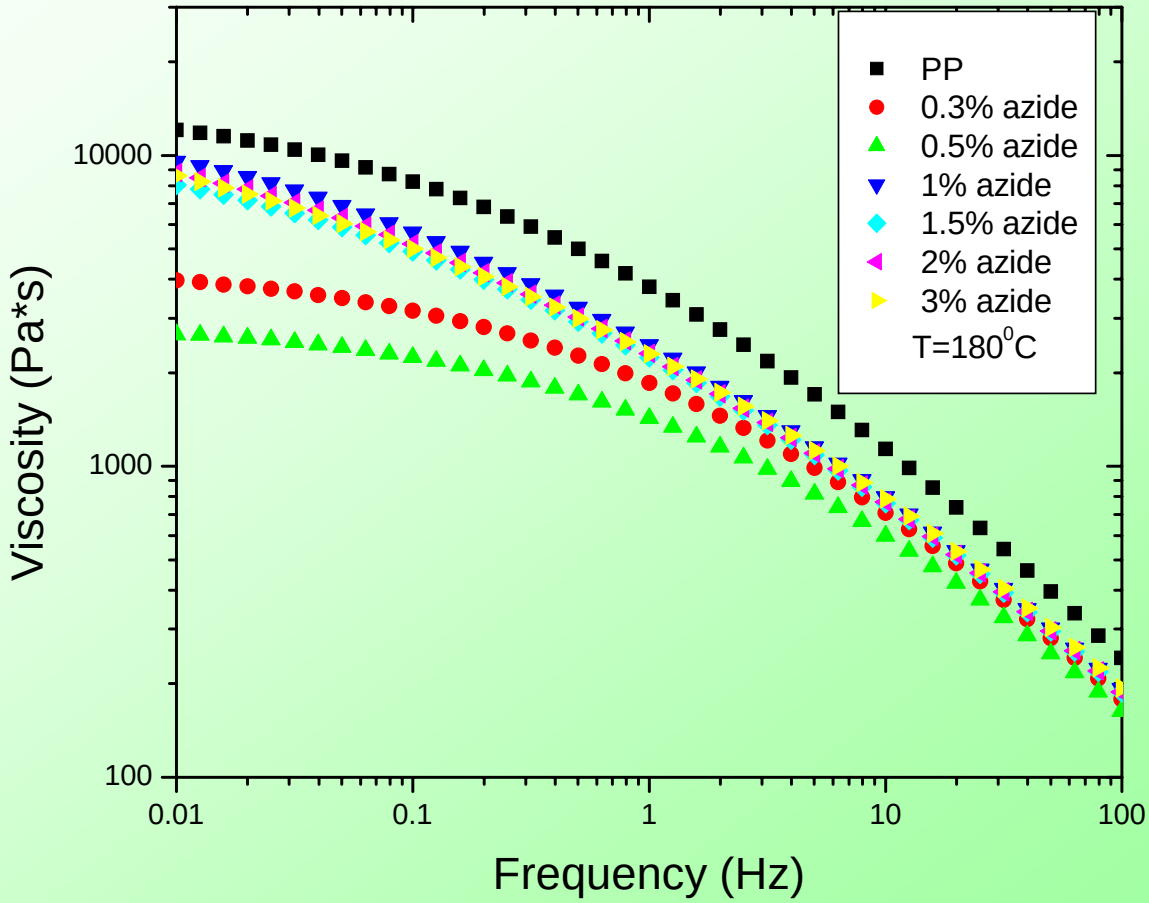
- Adhesive Strength

  Influence of azide feed on peel strength of grafted PP



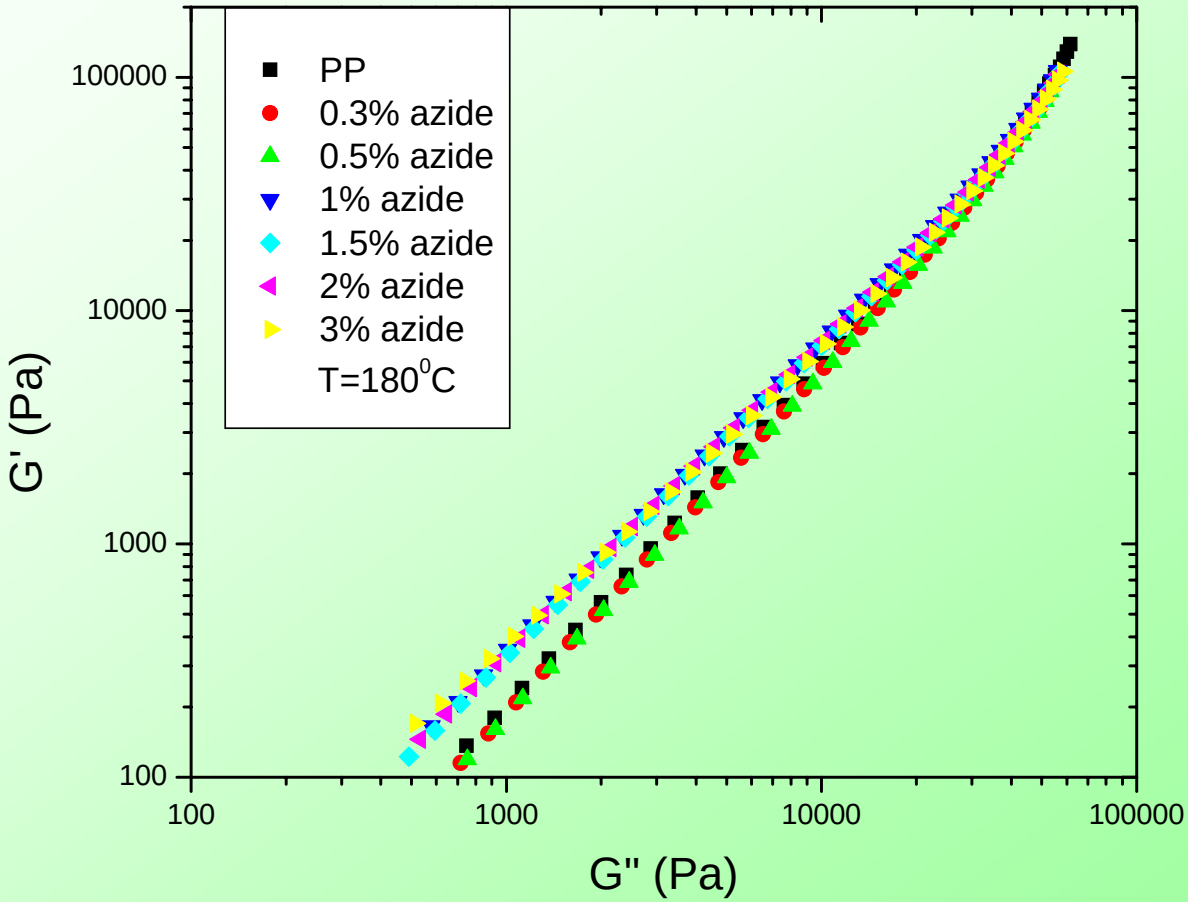
Results and Discussion

- Complex viscosity



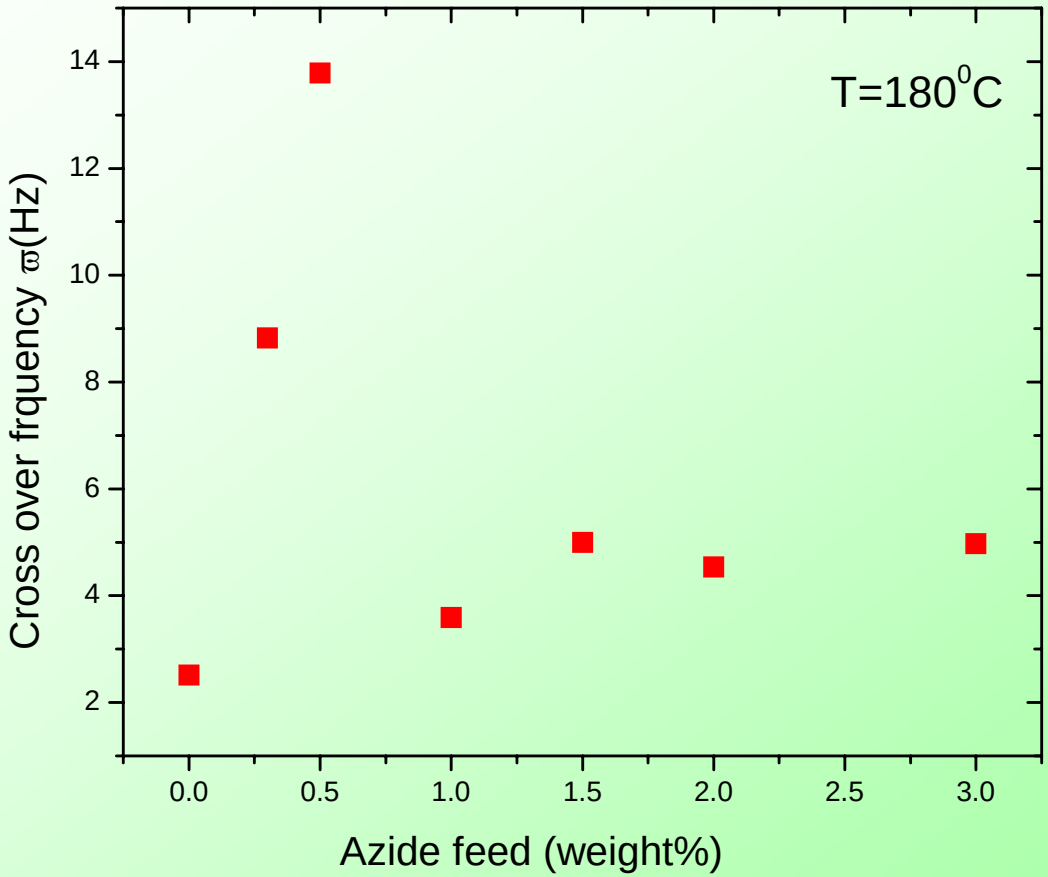
Results and Discussion

- Correlations of G' and G" at T=180^{0}C



Results and Discussion

- Plot of crossover frequency (ω) as function of azide feed concentration



$$\omega \approx (M_w)^b$$

M_w: weight-average molecular weight

b: negative exponent

(From R.M.Ho et al., Polymer, 34, 3264-3269 (1993))

Applications

- TPO Blends (grafting degree: 1.5 wt%)
  - Mechanical Properties

	Tensile Strength (Mpa)	Young's Modulus (Mpa)	Flexural Modulus (MPa)	Flexural Strength (MPa)
TPO	10.2± 0.25	353.6± 55.04	907.8 ± 18.60	21.1 ± 0.36
20% graft + 80% TPO	15.2± 0.47	581.3± 26.11	1302.9 ± 61.19	33.8 ± 0.72

Applications

- TPO Blends (grafting degree 1.5wt%)
  - Adhesion Properties (Aluminum substrate)

	Peel Strength (N/mm)
20% grafted PP + 80% TPO	1.78 ± 0.04
Azide grafted PP (purified)	1.43 ± 0.09
100% TPO	Negligible
20%PP + 80% TPO	Negligible

Conclusions

- Functionalization of PP by CBSA was successfully carried out via melt mixing.
- The grafting degree increases with the CBSA content initially, and then after 2% azide feed, it levels off.
- An excellent agreement between FTIR and ^{1}H-NMR results was achieved.
- Potential applications in automotive and packaging industries are expected.

Acknowledgements

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Comments or Questions?