

RHEOLOGICAL PROPERTIES OF RECYCLED POLYCARBONATE AND ABS MELTS

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PLASTICS RECYCLING

- Beverage bottles & milk jugs relatively easy to recycle
- Post-consumer plastics are commingled. Mixed plastics are difficult to use
 - Poor mechanical properties
 - Batch-to-batch composition variations
 - Problems of labels, foam, screws and inserts
- Separation of plastics is critical but costly
- Large collection & transportation costs



POLYMERS FOR ELECTRONIC APPLICATIONS

- 150 million pounds of polymer used each year for computer & printer housings etc.
 - More than 50% are PC, ABS, PC/ABS
- Plastics used are relatively expensive
- Products are discarded relatively quickly
- Landfilled as hazardous waste



ISSUES AND APPROACHES

- Numerous types of plastics and presence of contaminants.
 - Negligible resale value
- Plastics separation by chemical type is essential
 - Needed purity level?
- Variations in mw, mwd and chain branching
 - Variations in viscosity & mechanical properties



OBJECTIVE

- To re-use recycled polymers in their original applications via blending with virgin resins
- To increase the recycled content to as much as 50% in any compounded product
- To achieve a minimum of batch-to-batch variation in properties



RHEOLOGICAL CHARACTERIZATION

- Rheometric RMS 800
 - Parallel plates ϕ 25mm, gap 1mm
 - Temperature 250C for PC; 200C for ABS
 - Dynamic modulus (G' , G'') & complex Viscosity η
 - Shear viscosity η & relaxation modulus $G(t)$
- Molecular weight & mwd calculation
 - Relaxation spectrum from linear VE data
 - Using Rheometric Scientific software

CHARACTERISTICS OF RECYCLED POLYMERS TESTED

DESIGNATION	PURITY LEVEL	CONTAMINANTS
Recycled PC I R-PC	>99%	No appreciable contamination
Recycled PC II R-528	99%	HIPS 0.016%, PC/ABS 0.03% PMMA 0.05%, PE 0.07%
Recycled PC III R-630	98%	HIPS 0.29%, PC/ABS 0.11%, PMMA 0.25%, PE 0.07%, ABS 0.6%, POM 0.16%
Recycled ABS I R-ABS	99.9%	No appreciable contamination
Recycled ABS II R-594	96%	HIPS 2.4% PPO + Nylon 1.3%
Recycled ABS III R-612	88%	ABS-FR 9.8%, HIPS 1.4% PC/ABS 0.2%
Virgin PC V-PC		(Lexan 101, GE Plastics)
Virgin ABS V-ABS		(Cycolac GPM 5500, GE Plastics)

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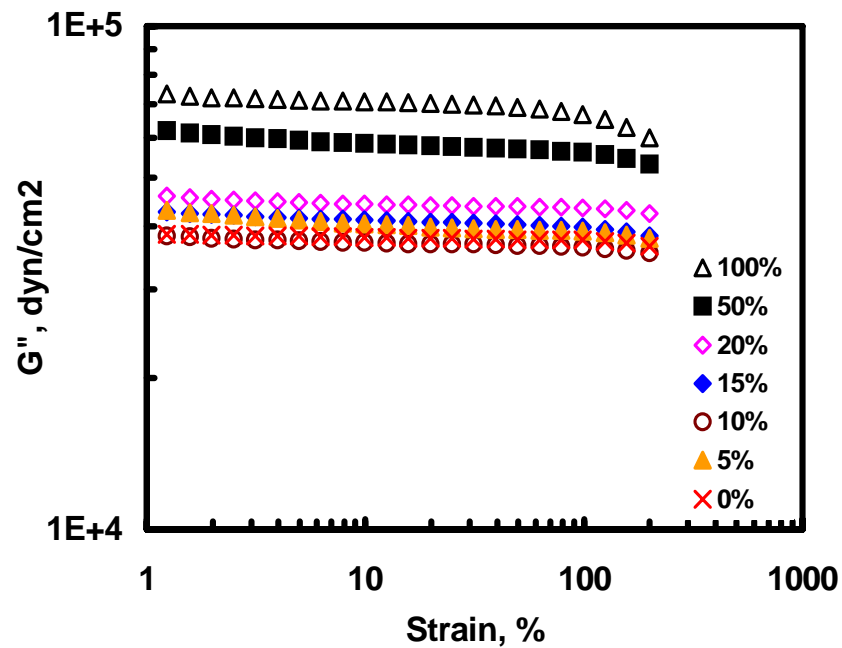


SAMPLE PREPARATION

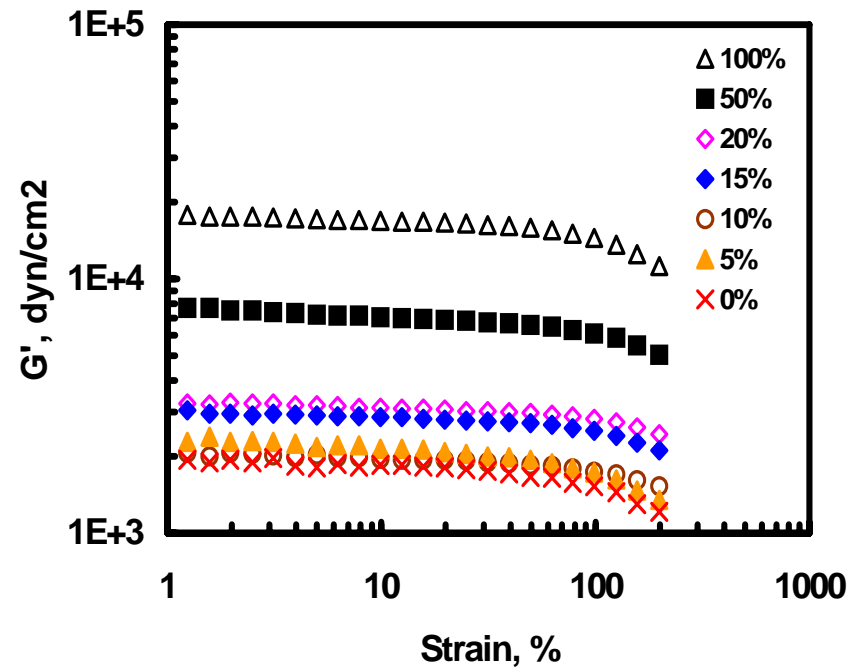
- **Recycled/virgin resin blending ratio**
 - 0, 5, 10, 15, 20, 50, 100 wt% of recycled content for R-PC & R-ABS
 - 0, 15, 100 wt% of recycled content for other purity levels
- **Drying in a vacuum oven at 120C for PC; 90C for ABS**
- **Brabender twin screw extruder**
 - Temp. settings
 - 220C, 265C, 315C, 300C for PC blends
 - 160C, 175C, 190C, 195C for ABS blends
 - Screw speed 30rpm for PC and 20rpm for ABS
- **Pelletizing extrudate into pieces, cooling in water & drying in vacuum oven**
- **Using a heated press to make sheets of thickness 1mm at 200C (PC) /180C (ABS) for testing**

DETERMINATION OF LINEAR VISCOELASTIC STRAIN

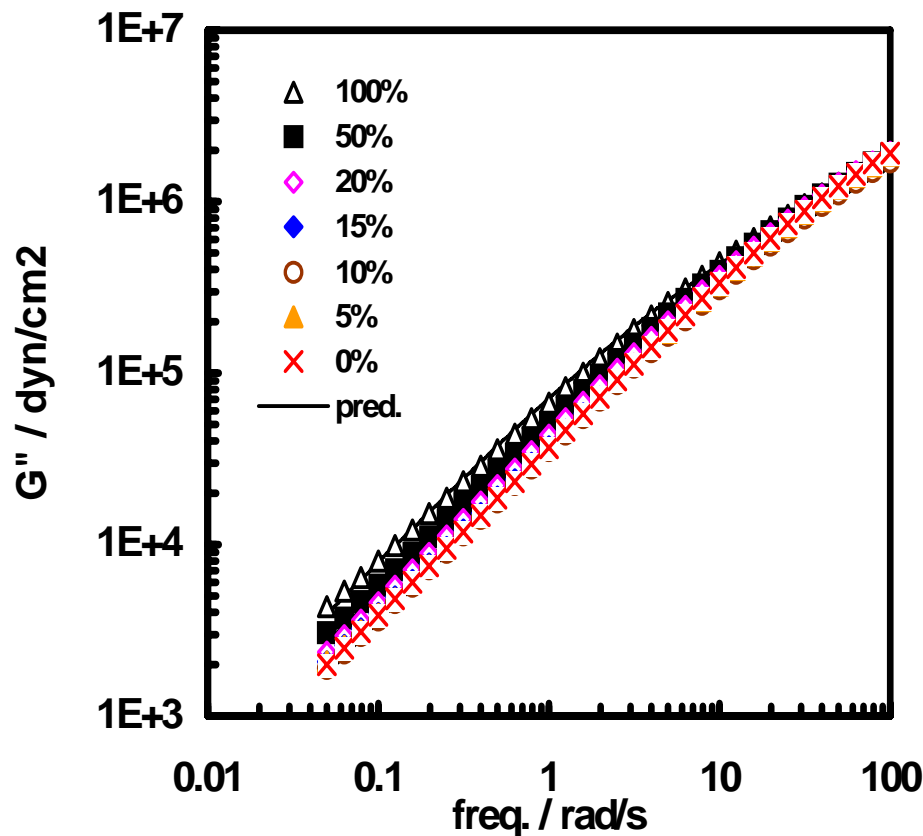
Loss modulus for recycled PC blends (250C, 1rad/s)



Storage modulus for recycled PC blends (250C, 1rad/s)



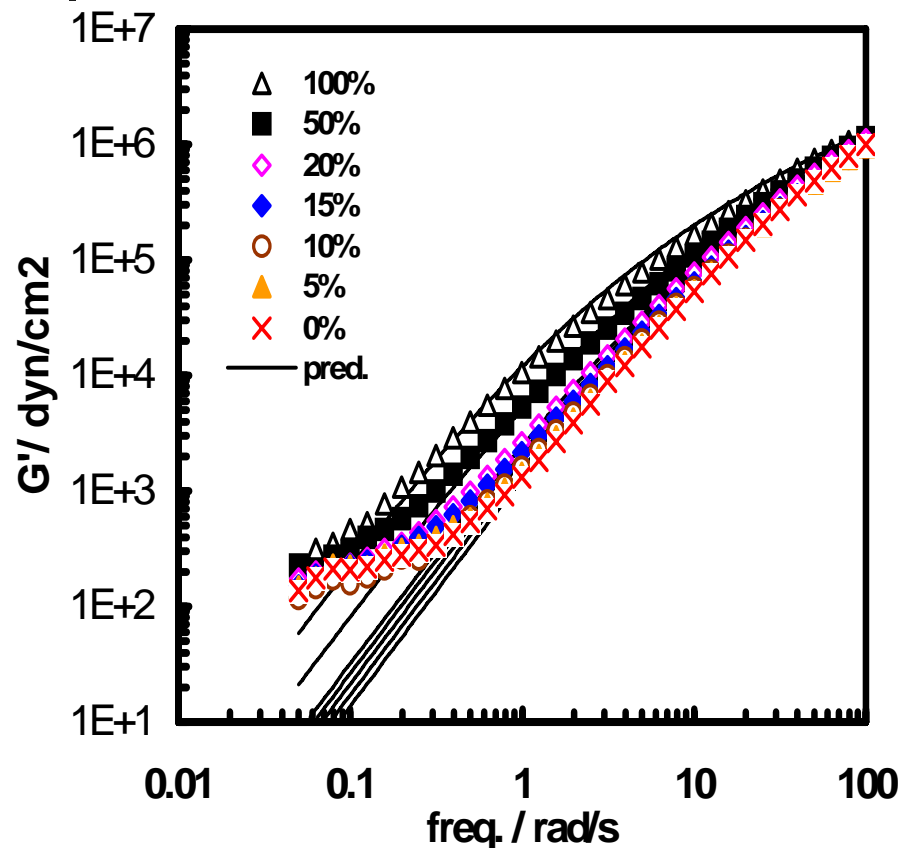
LOSS MODULI OF RECYCLED PC BLENDS



Data for R-PC blends
(250C, strain 10%)

- The virgin PC (0%) has lower G'' than the recycled PC
- The blends behave in a way between the recycled and virgin PC melts
- The G'' of the blends with R- PC content less than 15% are hardly distinguishable from those of virgin PC
- Solid lines represent data predicted using MWD data of 0% and 100% PC samples

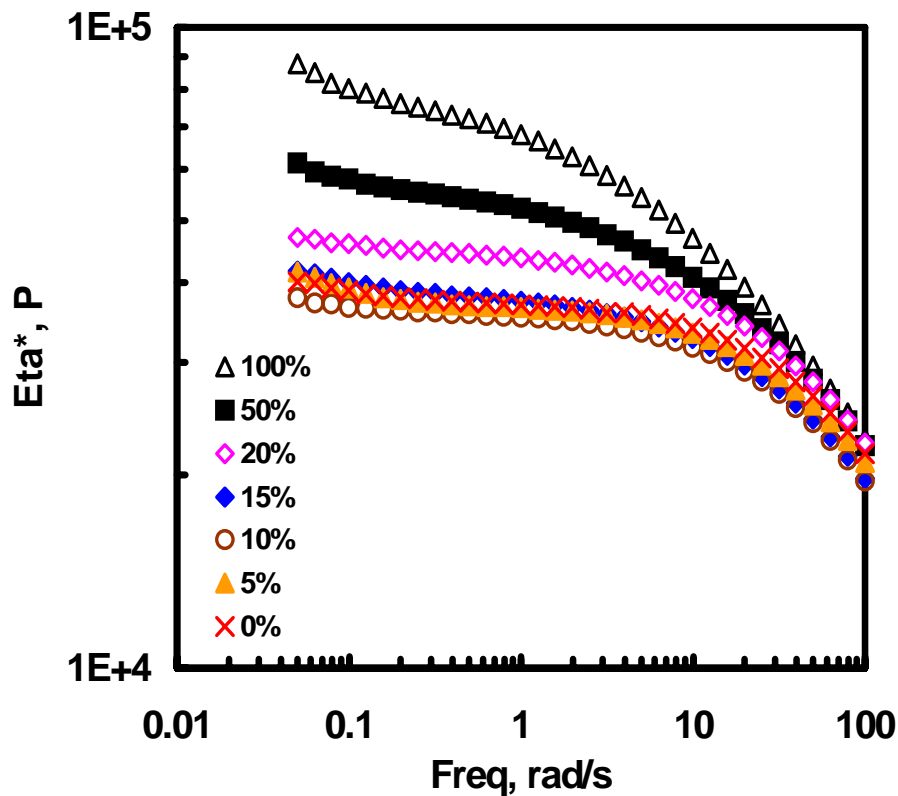
STORAGE MODULI OF RECYCLED PC BLENDS



Data for R-PC blends
(250C, strain 10%)

- The blends behave in a way between the recycled and virgin PC melts
- The G' of the blends with R- PC content less than 15% are hardly distinguishable from those of virgin PC
- The G' plateaus appear at low frequencies, more or less, for all the samples
- Solid lines represent data predicted using MWD data of 0% and 100% PC sample

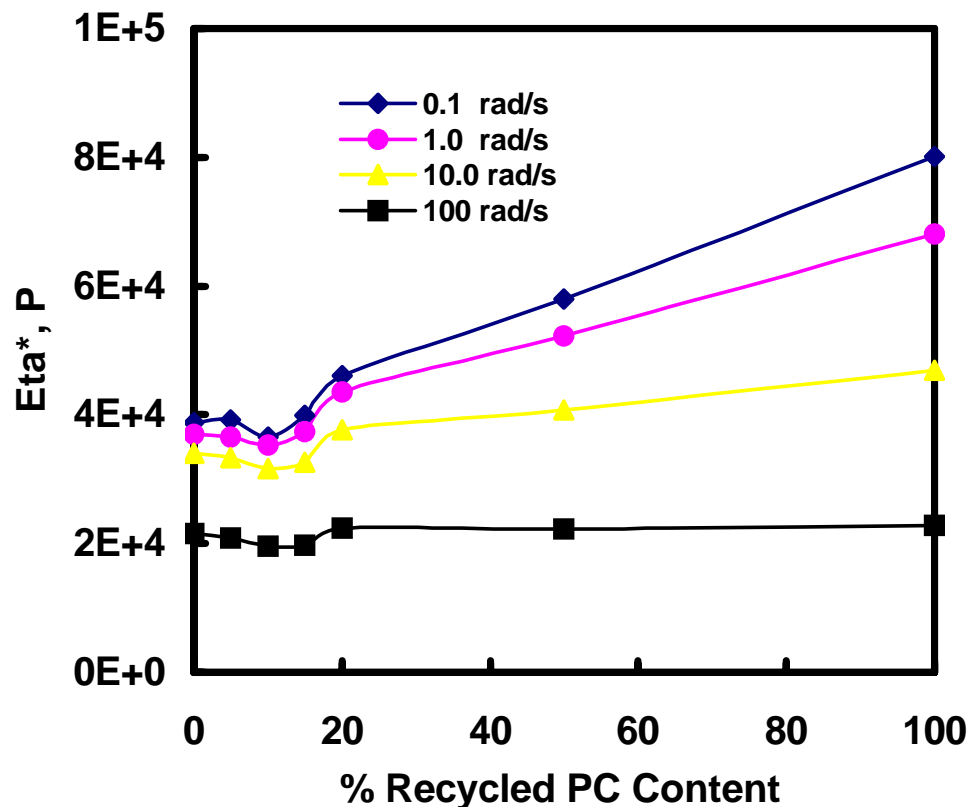
COMPLEX VISCOSITY OF RECYCLED PC BLENDS



Data for R-PC blends
(250C, strain 10%)

- Recycled PC has a higher viscosity than virgin PC
- The samples with recycled PC content less than 15% have nearly the same properties as that of the virgin resin

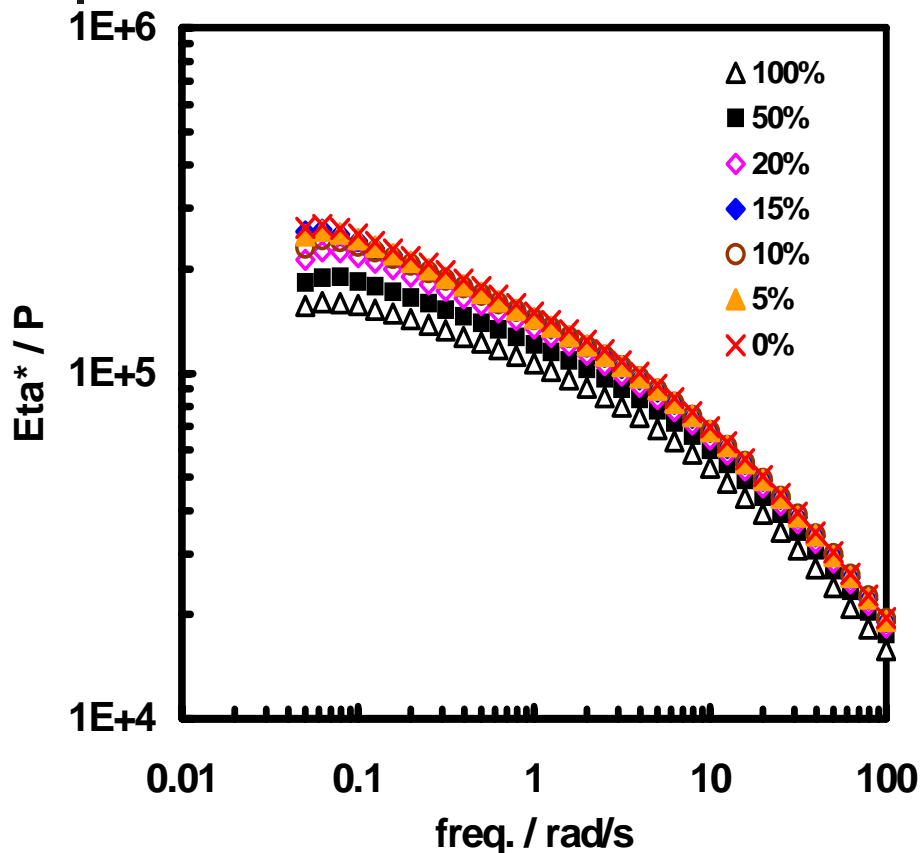
COMPLEX VISCOSITY AS A FUNCTION OF RECYCLED PC CONTENT



Data for R-PC blends
(250C, strain 10%)

- remains unchanged when recycled PC content is less than 15%
- shows a slight increase when recycled PC content is 20%
- approaches the magnitude of the recycled PC as the recycled PC content further increases

COMPLEX VISCOSITY OF RECYCLED ABS BLENDS



Data for R-ABS blends
(200C, strain 10%)

- In contrast to R-PC blends, R-ABS has a weaker viscoelasticity and lower viscosity than virgin ABS
- The samples with R-ABS content less than 15% have nearly the same properties as those of the virgin resin
- **'15% blending rule'** - The minimum virgin content needed to mask the effect of addition of recycled material was about 85%

DOUBLE REPTATION MIXING RULE FOR MWD CALCULATION

For linear flexible polymers

$$G(t) = G_N \left[\int_0^{\infty} F^{1/2}(M, t) W(M) dM \right]^2$$

where

$$F^{1/2}(M, t) = \exp\left\{ \frac{-t}{2\lambda(M)} \right\}$$

$$\lambda(M) = K(T) M^x$$

$$K(T) = K(T_0) \exp\left[\frac{E_A}{RT} \right]$$

$G(t)$	Relaxation modulus	$\lambda(M)$	Characteristic relaxation time
$F^{1/2}(M, t)$	Relaxation function	$W(M)$	Weight based MWD
G_N	Plateau modulus	x	Relaxation time exponent
$K(T)$	Front factor dependent on temperature with activation energy E_A		
$K(T_0)$	Front factor at the reference temperature		



MATERIAL PARAMETERS FOR MWD CALCULATION

For Polycarbonate, 250C

1. Relaxation time exponent χ

$$\chi = 3.40$$

2. Plateau modulus G_N

Ellis model data fitting

$$G' = G_N + \frac{c_1}{\omega^{c_2}}$$

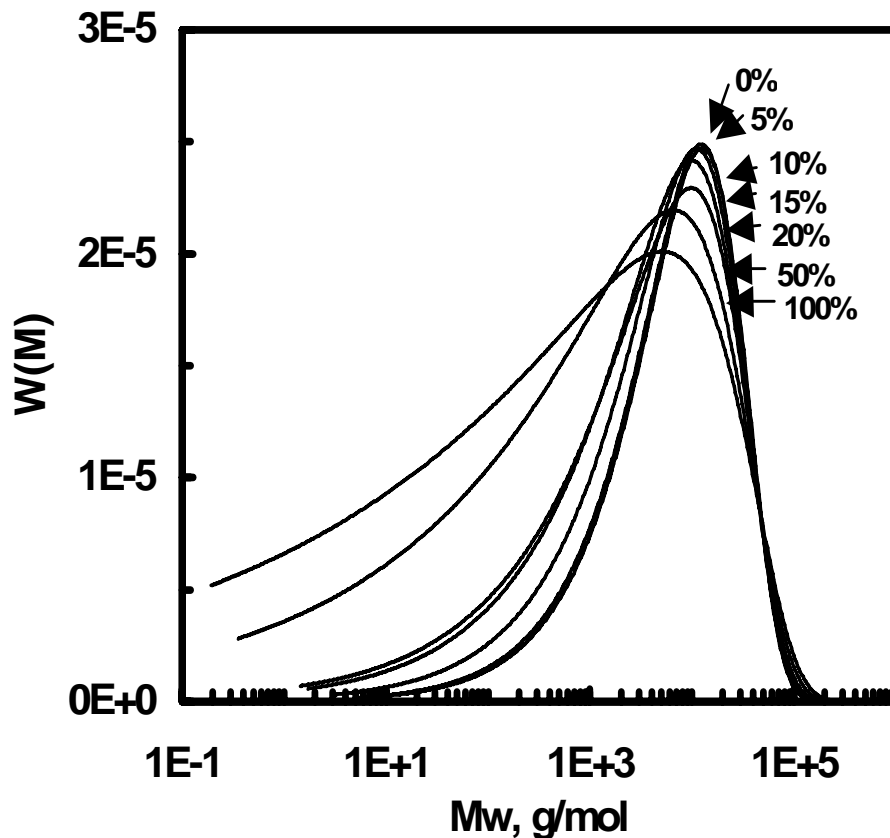
giving $G_N = 2.52 \times 10^6 \text{ dyn/cm}^2$

3. Front factor K_λ

Using χ , G_N and GPC data ($M_w = 3.0 - 3.5 \times 10^4$, $PI = 2.3$)

giving $K_\lambda = 3.5 \times 10^{-18}$

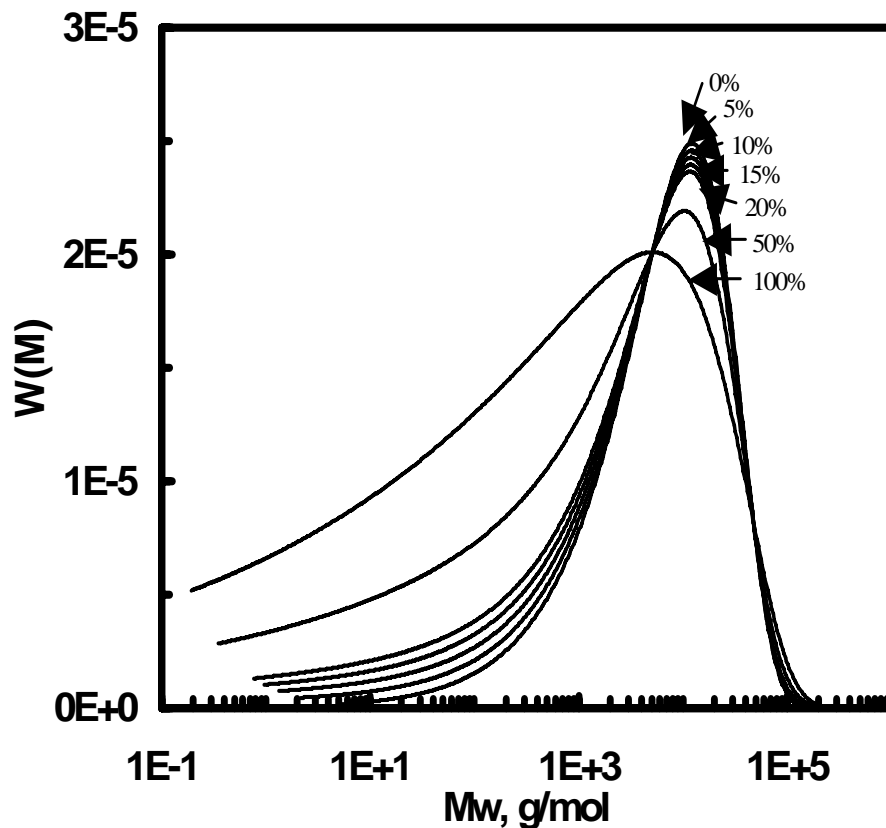
MWD CURVES CALCULATED USING L.V.E. DATA



Weight based MWD curves of recycled PC blends, calculated using experimental linear viscoelasticity data of each sample

- The recycled PC has a higher molecular weight and much wider MWD than the virgin polymer

MWD CURVES PREDICTED USING 0% AND 100% SAMPLE MWD DATA

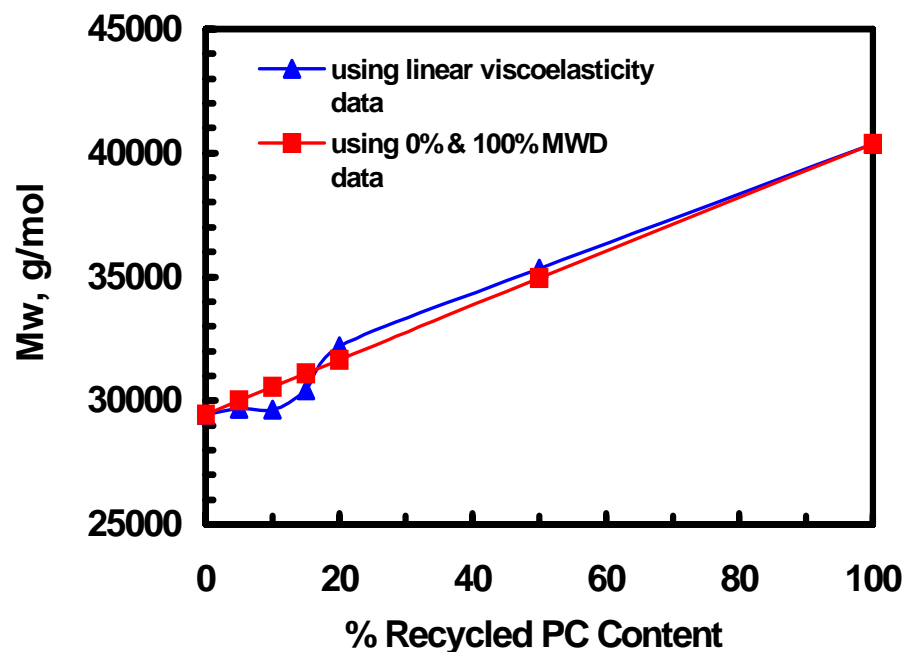


Weight based MWD curves of recycled PC blends, predicted using MWD data of 0% and 100% samples in terms of a simple, linear addition rule

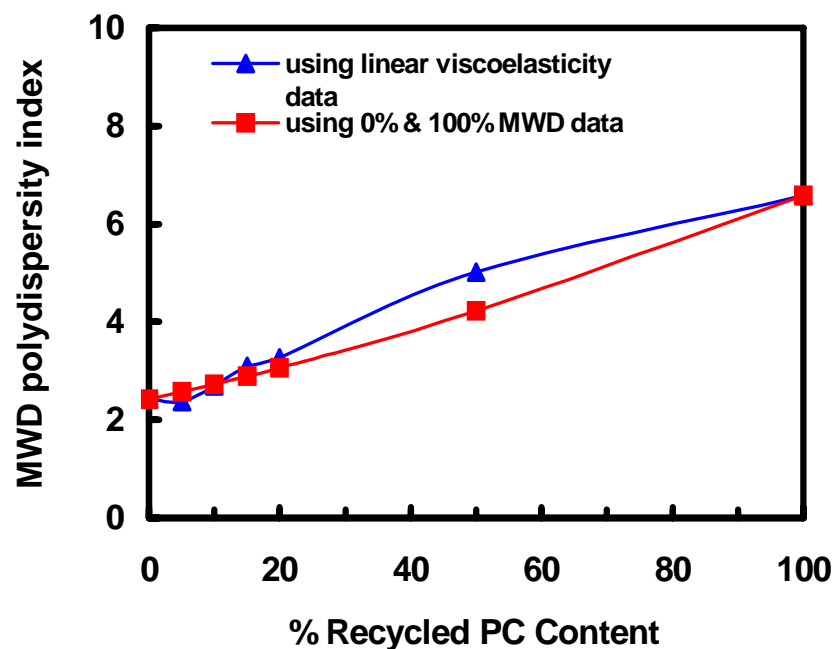
- showing a good agreement with data calculated using exp. linear viscoelasticity data of each sample

WEIGHT AVERAGE MOLECULAR WEIGHT AND POLYDISPERSITY INDEX

Weight Average Molecular Weight for R-PC Blends



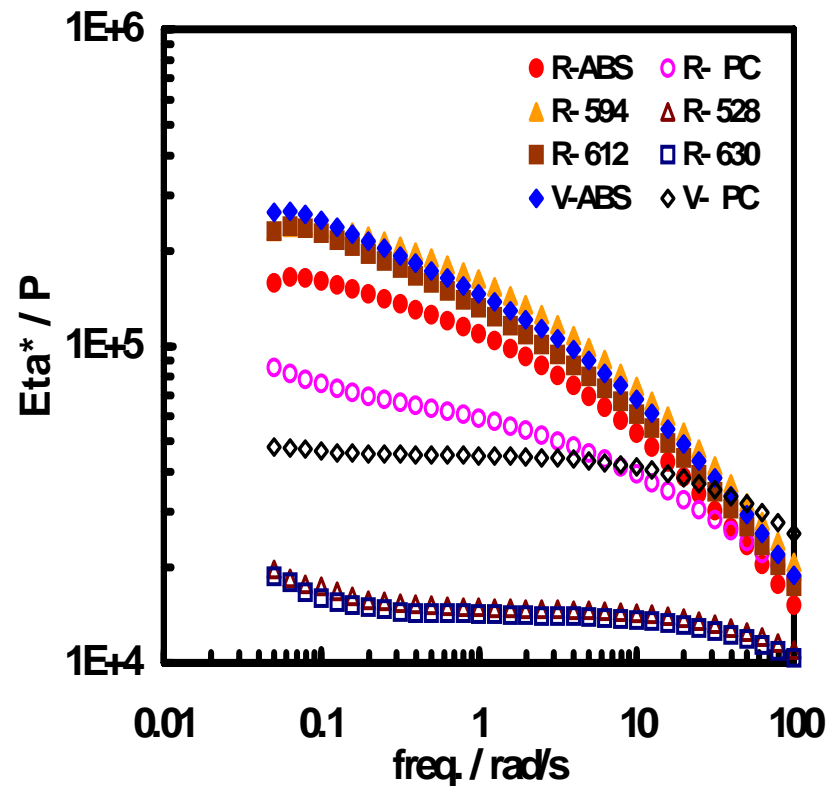
MWD Polydispersity Index for R-PC Blends



BATCH-TO-BATCH VARIATIONS OF RECYCLED PC & ABS MELTS VISCOSITY

Complex viscosity vs. freq. for three recycled PC and three recycled ABS materials with different purity levels

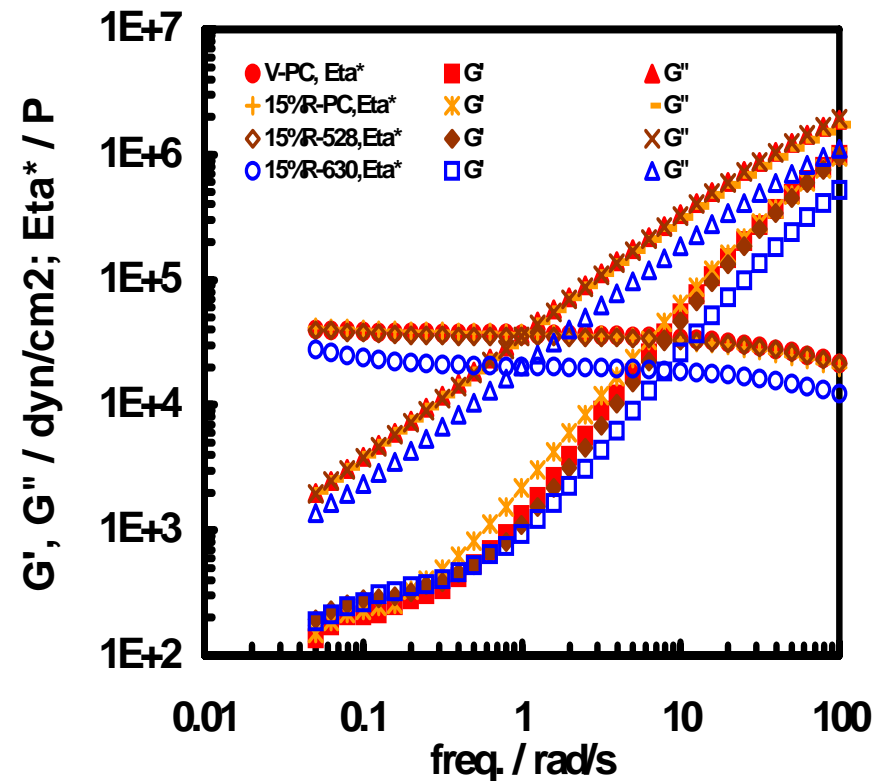
- Material purity and batch-to-batch variations have a large influence on the observed rheology



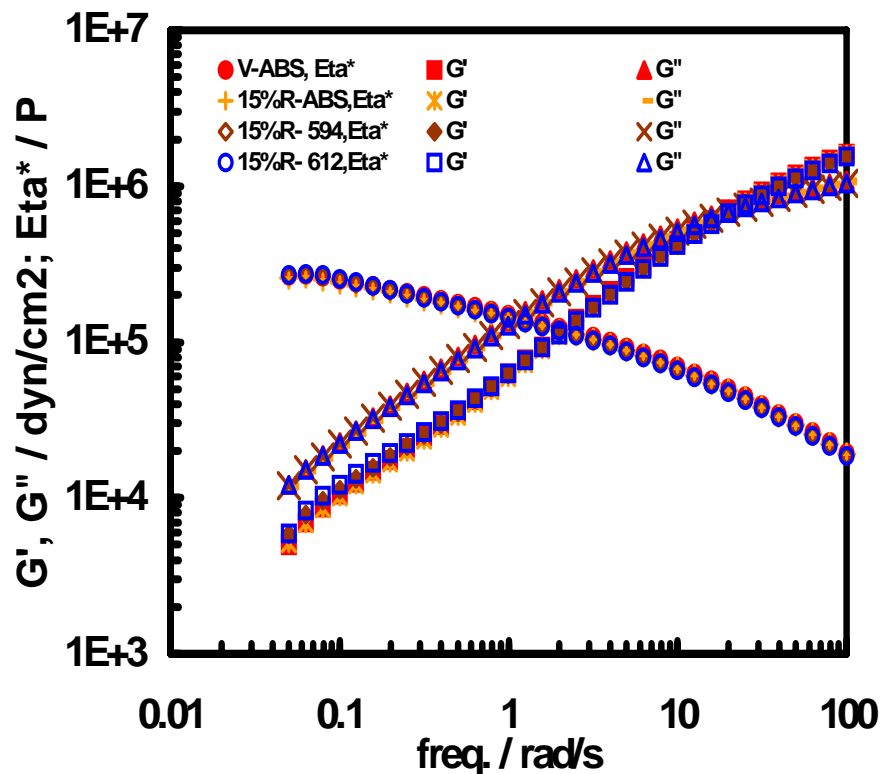
PURITY EFFECT ON DYN. PROPERTIES OF 15% RECYCLED PC BLENDS

Dynamic properties of three 15% recycled PC blends in comparison with virgin PC

- Except R-630PC, the results verify the '15% blending ratio rule'



PURITY EFFECT ON DYN. PROPERTIES OF 15% RECYCLED ABS BLENDS

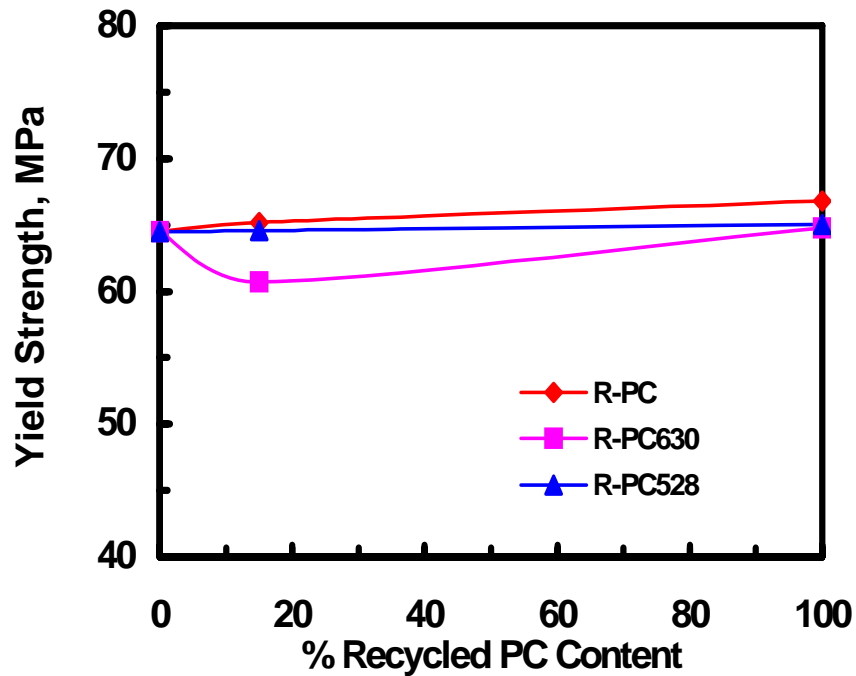


Dynamic properties of three 15% recycled ABS blends are compared with virgin ABS

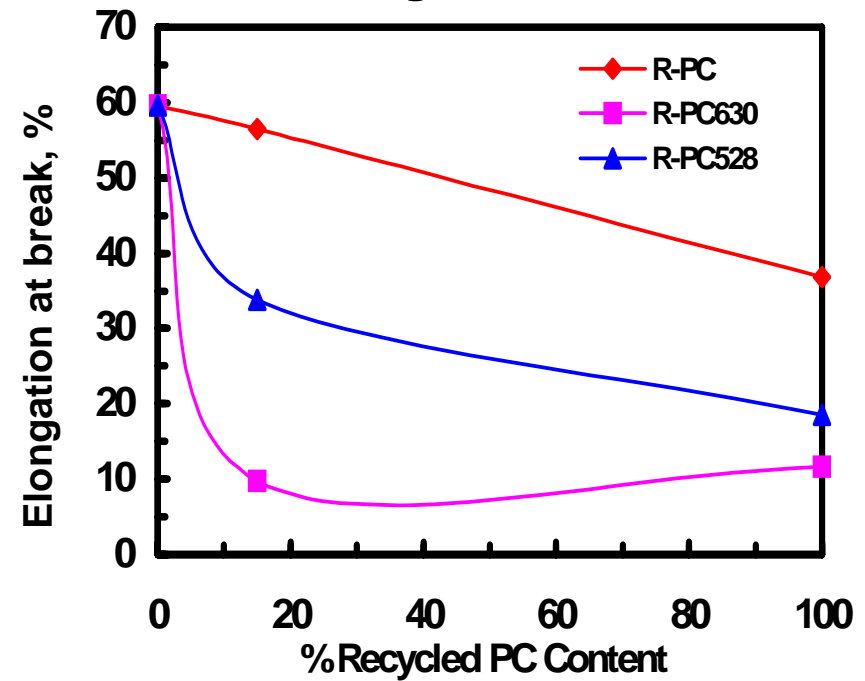
- All three blends have the same values as those of the virgin resin
- These data of different purity levels further verify the '15% blending rule'

CORRELATION WITH TENSILE PROPERTIES

Effect of Recycled PC Purity on Tensile Yield Strength

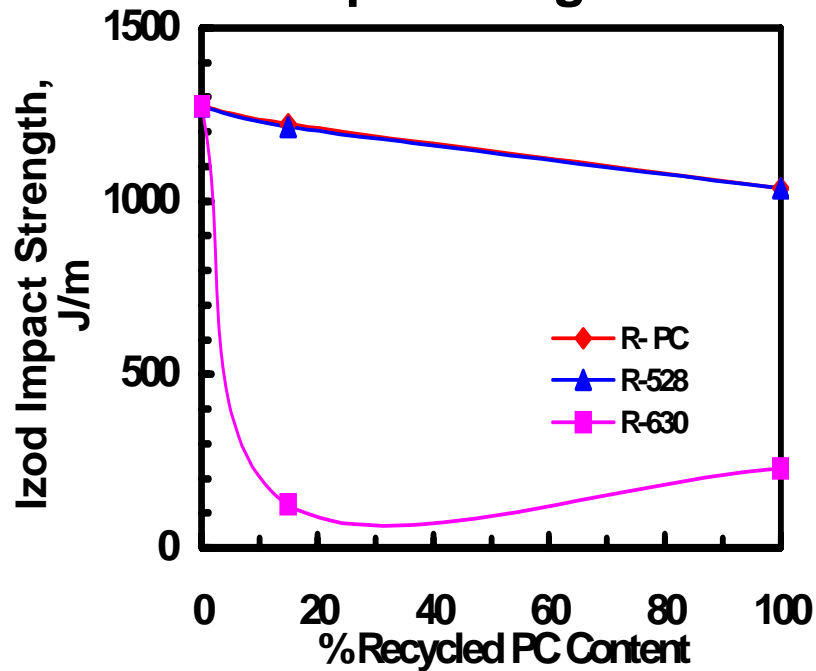


Effect of Recycled PC Purity on Elongation at Break

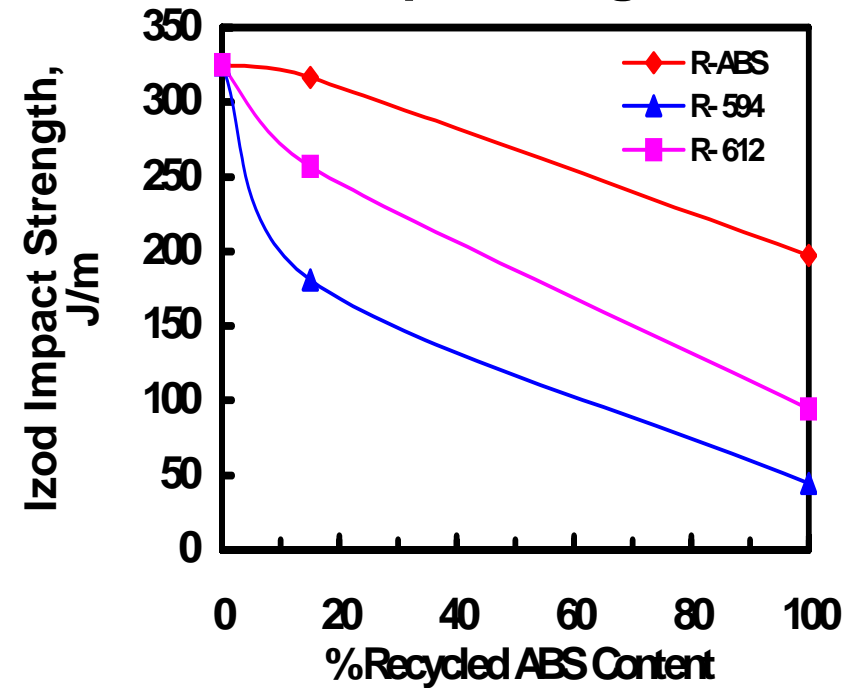


CORRELATION WITH IZOD IMPACT STRENGTH

Effect of Recycled PC Purity on Impact Strength



Effect of Recycled ABS Purity on Impact Strength





CONCLUSIONS

- Recycled PC or ABS melts
 - Linear viscoelastic rheol. behavior
 - Variations from batch-to-batch - Purity level effect
 - Recycled PC has a wider mwd
- Recycled polymer blends with virgin resin
 - The batch-to-batch variations minimized
 - '15% blending rule' for high purity recycled content
- Rheology in simple shear seems less sensitive to impurities than some mech. properties



CURRENT RESEARCH DIRECTION

- Rheological responses under more complex shear deformation and in extensional flow
- Further examine impurity effect & correlate to compatibility of polymers
- Formulate and characterize PC/ABS blends, filled /reinforced blends



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