APPLICATION OF TWO-DIMENSIONAL CORRELATION ANALYSIS TO EXPLOSIVES DETECTION AND POLYMER CRYSTALLIZATION

THESIS BY

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ABSTRACT

This thesis presents two novel applications of two-dimensional (2D) correlation analysis: (1) long standoff detection of explosives using Raman spectroscopy and (2) examination of morphology development in semicrystalline materials. The power of 2D correlation analysis is its ability to expose and quantify the relationship between changes in distinct observables characterizing a system as it evolves in response to a perturbation. Most frequently, the observables are spectroscopic (intensity $I(\nu_i)$ at distinct values of the spectral variable, ν_i), so the method is often called “2D correlation spectroscopy.” Diverse perturbations, such as mechanical stress, change in thermodynamic conditions (e.g., temperature or pressure), and extent of reaction, have been applied to reveal desired information that is obscured in the absence of the perturbation. Even small, subtle changes in response to the perturbation become readily resolved with 2D correlation analysis, which effectively excludes static observables and greatly enhances correlated changes relative to random variations.

Improvised explosive devices (IEDs) are currently the number one killer of both troops and civilians in Iraq and Afghanistan. Effective detection of explosives at standoff distances is important to ensure human safety. Implementation of 2D correlation spectroscopy can increase detection success due to the following advantages of the analysis: (1) simplification of complex spectra by separation of overlapped peaks, (2) enhancement of spectral resolution and enhancement of signal to noise ratio (SNR) through the spreading of peaks over a second dimension, (3) probing specific sequential order of spectral intensity changes, and primarily (4) exclusion of stable compounds and selective exclusion of unsta-

ble explosives. By taking advantage of the unstable nature of explosive compounds through the imposition of thermal degradation, it is possible to further separate spectral features corresponding to explosives both from a noisy background and any contaminants based on their rate of response to heating.

A temperature ramp is used to probe Raman features of explosives and their mixtures with choice contaminants. Implementation of 2D correlation analysis results in significant enhancement of explosive signal relative to background. Effective separation of explosive features is demonstrated for two biogenic contaminants: saliva, which represents proteins, lipids and saccharides, and diesel soot, which contains heteroaromatic species. We discovered that correlation analysis can further provide information on the physical state of the unstable compounds, distinguishing crystalline from amorphous states. The well-established spectral shifts of organic crystals with increasing temperature provide strong 2D spectral features, which could be utilized for further sample identification. Several aspects of the 2D correlation analysis are examined to optimize effectiveness of detection. Use of the time-averaged spectrum as the reference for calculating dynamic spectra yields the best performance. Normalization schemes are found to be of limited utility: some of them enhance specific features, but their application also can result in false positives. The only data pretreatment recommended for the application of long standoff detection in arbitrary environments is the removal of data offset by the subtraction of the minimum value from each spectrum.

The ultimate physical properties of semicrystalline materials, such as strength, toughness, and transparency, are directly related to their morphology through their molecu-

lar characteristics and processing conditions. Morphology is examined using small-angle and wide-angle x-ray scattering (SAXS and WAXS, respectively), for which 2D correlation analysis is well suited due to its simplification of complex scattering curves through the de-convolution of overlapping features, the determination of sequential order of intensity changes, and the enhancement of spectral resolution by spreading data over a second dimension. The effects of different molecular characteristics on crystallization of semi-crystalline polymers are examined by conventional techniques and 2D correlation analysis of x-ray scattering data.

Model short-chain branched (SCB) polyethylenes are found to crystallize in three regimes during quiescent temperature ramps. “Primary-irreversible” crystallization occurs at the highest temperatures and is marked by large changes in the morphological parameters (crystallinity, long period, and overall scattering power) as primary lamellae propagate relatively rapidly through unconstrained melt. Once the majority of unconstrained melt is consumed, secondary lamellar growth occurs in the largest non-crystalline regions between primary lamellae marks slower “secondary-irreversible” crystallization that occurs at intermediate temperatures. At low temperatures, the values of the morphological parameters are equal during cooling and subsequent heating marking the slow formation of fringed micelles that occurs in the “reversible” crystallization regime. While irreversible and reversible crystallization have been observed previously in SCB materials, this is the first time that a physical justification is presented for the separation of the irreversible crystallization into primary- and secondary-irreversible regimes.

Each regime is identified by unique features in the 2D correlation plots. Specifically, 2D heterospectral analysis of SAXS/WAXS data reveals identical qualitative behavior between a series of branched hydrogenated polybutadienes in each regime: the primary-irreversible regime is characterized by the intensity redistribution (sign change) only in SAXS, the secondary-irreversible regime is characterized by the intensity redistribution only in WAXS, while the reversible regime is characterized by the intensity redistribution in both SAXS and WAXS. Additionally, two-dimensional correlation analysis provides a unique approach to gain insight into subtle changes during morphology development, such as the development of density heterogeneities in the non-crystalline regions.

The presence of short-chain branches is found to have a profound, diminishing effect on the formation of oriented structures in response to flow-induced crystallization. Crystallization of SCB materials is examined in the presence of high density polyethylene (HDPE) in order to expose the effectiveness of the branched materials to propagate oriented morphology. HDPE is found to serve as an effective clarifying and nucleating agent for a metallocene copolymer with complex concentration dependence. The SCB material is found to be incapable of propagating oriented growth on large length scales. Evidence presented suggests that this behavior is the result of a buildup of chain defects at the growth front which results in a transition from oriented to isotropic crystallization. Hence, it is proposed that size of crystal structures can be controlled by dictating the amount of copolymer incorporated during oriented structure formation via the crystallization temperature, allowing for the fine-tuning of ultimate material properties. Ultimately, it is found that both quiescent and flow-induced crystallization is dominated by short-chain branching.

Two-dimensional correlation analysis in conjunction with thermal decomposition is demonstrated as an effective means to increase the success of detection of energetic compounds using Raman spectroscopy. This combination of analysis and a perturbation that elicits a unique response in the compound can be applied to variety of other detection systems. Additionally, 2D correlation analysis is demonstrated to provide unique insight into the morphology evolution during crystallization of semicrystalline materials, which can be used to control their material properties. The ideas presented here can be easily applied to study phase transitions in other systems, such as block copolymers.

TABLE OF CONTENTS

LIST OF FIGURES AND TABLES

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Appendix B

NOMENCLATURE

a	unit cell parameter
$A(q)$	autocorrelation intensity
$\hat{A}$	amplitude of response to perturbation
b	unit cell parameter
c^*	overlap concentration
d	sample thickness
DSC	Differential Scanning Calorimetry
FIC	Flow-Induced Crystallization
G	relaxation modulus
G_N^0	plateau modulus
HDPE	high density polyethylene
HPBD	hydrogenated polybutadiene
$I(q)$	scattering intensity
I_{perp}, I_{para}	light intensity transmitted through crossed and parallel polarizers, respectively
Im	imaginary part of complex number
$J(q)$	Lorentz-corrected scattering intensity
L_p	long period
LCB	long chain branch
m	total number of discrete spectra
$\mathrm{M_e}$	molecular weight of entanglements
$\mathrm{M_n}$	number-average molecular weight
$\mathrm{M_w}$, $\mathrm{M_{w,tot}}$	total weight-average molecular weight
$\mathrm{M_{w,a}}$	weight-average molecular weight of long chain branch (‘arm’)
$\mathrm{M_{w,b}}$	weight-average molecular weight of chain backbone
N_a	Avogadro’s number
Δn	birefringence
P	performance parameter

PDI	polydispersity
PE	polyethylene
q	scattering wavevector
Q	total SAXS scattering power
R_g	radius of gyration
Re{}	real part of complex number
SALS	Small Angle Light Scattering
SAXS	Small Angle X-ray Scattering
SCB	short chain branch
t	perturbation variable
t_c	isothermal crystallization time
T_c	experimental isothermal crystallization temperature
t_{hold}	hold-time at elevated temperatures
T_{hold}	elevated temperature used in nucleation studies
T_m	peak melting temperature as determined by DSC
t_{max}	peak crystallization time
T_{min}, T_{max}	limits of perturbation variable
t_s	shearing time
T_x	peak crystallization temperature as determined by DSC
ΔT	apparent subcooling
$\mathbf{v}$	velocity vector
WAXS	Wide Angle X-ray Scattering
Wi	Wiessenberg number
X_c	WAXS crystallinity index
y_i	discrete Raman spectrum
$\tilde{y}$	dynamic spectrum
$\tilde{z}$	orthogonal spectrum
δ	sample retardance

θ	azimuthal angle
ϑ	time
λ	wavelength
μ	viscosity
ν	spectral variable
ρ	density
σ_w	wall shear stress
τ_r	terminal relaxation time
ϕ	cospectrum
Φ	2D synchronous spectrum
ψ	quad-spectrum
Ψ	2D asynchronous spectrum
ω	frequency