Combinatorial Development of Polymer Nanocomposites Using Transient Processing Conditions in Twin Screw Extrusion

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A new approach is presented for combinatorial development of polymer nanocomposites with compositional gradients (CGs). The CGs were developed using transient processing conditions in twin screw extrusion with small quantities of expensive nanoscale fillers. Convolution of step input with normalized residence volume distributions (RVDs) was used to establish the processing–structure relationship for the CGs. The normalized RVD was established as a process characteristic independent of processing conditions and measured in situ using an optical probe. The CG determined nondestructively using the new combinatorial approach was validated through comparison with more time-consuming and destructive thermogravimetric analysis. The CG could also be established with relatively inexpensive microscale fillers using the normalized RVD obtained with nanoscale fillers, suggesting that transient effects of the mixing process are independent of the size of the filler. Finally, structure–property relationship of combinatorially developed polymer nanocomposites was established by characterizing their dynamic mechanical behavior (storage modulus, G', and loss modulus, G''). The dynamic mechanical behavior of the combinatorially developed composites correlated well with the batch-processed ones, indicating that the transient mixing conditions in extrusion do not affect the material properties. © 2008 American Institute of Chemical Engineers *AIChE J*, 54: 1895–1900, 2008

Keywords: composite materials, polymer processing, mathematical modeling, nanotechnology, polymer properties

Introduction

Fabrication of high-performance and multifunctional polymer nanocomposites on a commercial scale via extrusion holds great promise for applications in the civilian space arena. The processing–structure–microstructure–property relationships form the fundamental basis for a comprehensive understanding of how to develop novel polymer nanocomposites with the desired material properties. Identifying the appropriate processing parameters and melt formulation that lead to adequately dispersed nanoparticles in the matrix allows control over the resulting material properties.[1–3] However, thoroughly investigating the entire parametric domain, especially at different compositions with expensive nanoscale fillers, can be very expensive, time-consuming, and challenging. To address these issues, combinatorial materials science[4–8] offers systematic, high-throughput, and continuous experimental approaches for developing diverse novel polymer nanocomposites with rapid and efficient characterization tools. Specifically, continuous compositional gradients (CGs)

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with in situ compositional characterization are especially suited for inexpensive and rapid investigation of effects from processing conditions, such as dispersion of the nanoscale fillers, and/or compositional effects on composite material properties across the entire compositional domain of interest using smaller quantities of expensive nanoscale fillers when compared with batch-processed (i.e., one composition at a time) composites.

Ko et al.[9] combinatorially sputtered Zn-Sn-O films with continuous CGs from 16 at.% Sn to 89 at.% Sn for rapidly establishing the structure–property relationships. Gilman et al.[10–12] produced extruded composites of polyamide-6 or polystyrene and purified organoclay filler with specific emphasis on the combinatorial nature of the CGs. They indicated that a single experiment can provide samples for in situ or a posteriori characterization over the entire compositional domain of interest. Eidelman et al.[13] produced thin film CGs of poly(L-lactic acid) with poly(D,L-lactic acid) using a three-syringe pump system. They developed an elaborate Fourier transform infrared microspectroscopy technique that monitors the reflection-transmission spectra to obtain the composition. Potyrailo et al.[14] used a combinatorial extrusion system to generate polymeric CGs with two different material systems—polypropylene with model additives and polycarbonate with titanium dioxide filler. They characterized the CGs in situ by using an optical probe signal that tracks the changes in color of the blend. In fact, using an optical probe to measure changes in absorbance to obtain particle composition is not uncommon in areas related to dense suspensions,[15] two-phase flows,[16] reactive blending,[17] etc.

While there is no dearth of literature on the importance of CGs and characterizing the composition either in situ or a posteriori, there are certain limitations that are yet to be addressed.[18,19] Most of the nondestructive in situ characterization approaches developed so far with optical probes are limited to low composition of the filler in the composite. At higher compositions, especially of dark colored fillers, the optical probes tend to reach their saturation, i.e., detection limit. Furthermore, most of the prior works conducted to rapidly determine the CGs require a precalibration of the technique with known composition, thereby decoupling the processing from the evolution of the CG.

In this work, we investigate the combinatorial development of polymer nanocomposites using twin screw extrusion, where transient processing conditions are used to produce a CG. We present a novel nondestructive approach to rapidly predict the CGs involving high composition of fillers in the composite and validate it with experimental characterization of the CGs. This technique does not require precalibration because it is a physical consequence of the mixing occurring during extrusion. The applicability of the novel approach across different length scales is explored to study if inexpensive microscale fillers can be substituted for the expensive nanoscale fillers in identifying the appropriate processing conditions required to produce the desired CG. Furthermore, for complete validation of the new combinatorial approach by establishing the structure–property relationship, the dynamic mechanical behavior (storage modulus, G', and loss modulus, G'') of the polymer nanocomposites developed with this approach was compared with that of separately batch-processed ones.

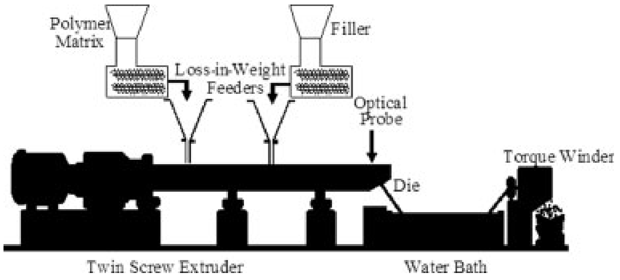

Figure 1. Schematic of the experimental setup.

The polymer and the filler were fed through loss-in-weight feeders. The optical probe was placed just before the die exit to measure the absorbance of the polymer melt.

Experimental Methods

Impact grade polystyrene (PS, weight-average molecular weight $\sim$ 150,000, polydispersity $\sim$2.73, density $\sim$1.04 g/cm^3) obtained from Nova Chemicals was used as the matrix material due to the ease of processing. The PR-19 grade carbon nanofibers (CNFs, dark colored filler, diameter $\sim$100–200 nm, length $\sim$10–30 μm, density $\sim$1.87 g/cm^3) obtained from Applied Sciences were used, because they were more affordable than the carbon nanotubes (CNTs). A relatively inexpensive filler, potassium chloride (KCl, bright colored filler, diameter $\sim$100 μm, density $\sim$2.00 g/cm^3), obtained from Indian Head Naval Warfare Center, was used to check the applicability of the approach across various filler length scales.

To prepare PS-CNF and PS-KCl composites combinatorially by twin screw extrusion, the PS pellets and the CNFs or KCl were fed into a Werner and Pfleiderer twin screw extruder (28-mm screw diameter, corotating, intermeshing, 30:1 L:D) using loss-in-weight feeders as shown in Figure 1. The extruder screw speeds in this work varied from 30 to 90 rpm and the polymer flow rates varied from 0.5 to 2 kg/h. The operating temperatures were 210°C for all the five barrel zones and 165°C for the die zone. The die zone of the extruder was designed to include a Cuda I-150 optical probe, which was used to obtain the residence distribution based on the absorbance of the processed material.

Two different kinds of experiments were conducted—impulse input and step input of the filler. In an impulse experiment, a small quantity of the filler ($\sim$1 g) was added to the polymer flow and the change in absorbance of the melt was monitored in situ by the optical probe to obtain the response as a residence distribution (Figure 2). In a step experiment, the filler was fed at a desired flow rate and the extrudate was collected to characterize: (a) the transient response to the step input, i.e., the CG, using small quantities of filler; and (b) the steady state response to the step input, i.e., the batch-processed composite, using large quantities of filler. The combinatorially developed CG was characterized via thermogravimetric analysis (TGA). A Cahn TG 2131 thermogravimetric analyzer was used to characterize the weight fraction of the filler in the composites. A detailed description of the procedure used is provided elsewhere.[20] The weight fraction (w) was converted to volume fraction (β) using a linear rule of mixtures:

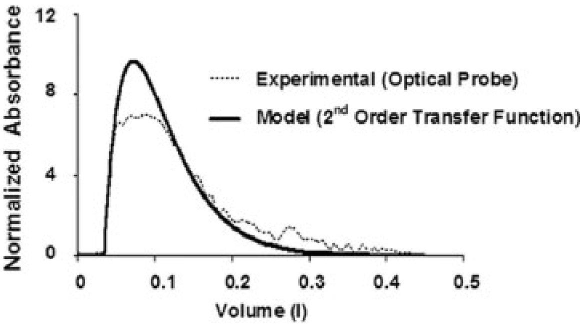

Figure 2. Modeling the normalized RVD using a second-order transfer function.

The peak of the experimental curve is slightly lower than that of the modeled curve because the optical probe measuring the absorbance reached its detection limit.

$$\beta = \frac{w\,\rho_{\mathrm{PS}}}{\rho_{\mathrm{filler}} + w\left(\rho_{\mathrm{PS}} - \rho_{\mathrm{filler}}\right)} \tag{1}$$

where ρ_{PS} and ρ_{filler} are the densities of PS and the filler, respectively.

To validate the new combinatorial approach, the dynamic mechanical behavior of PS-CNF composites that are combinatorially developed via transient extrusion was compared with that of batch-processed ones resulting from steady state extrusion. The dynamic mechanical behavior was characterized using a RDAIII strain controlled rheometer (TA Instruments) equipped with a convection oven. Parallel plate geometry (25-mm diameter) was used with a gap of 0.9 mm. Frequency sweeps were obtained at 190°C, the choice of temperature being dictated by the average processing temperature in extrusion. Frequency spectra from 0.02 to 100 rad/s were obtained at a strain of 0.5%, which was verified to be in the linear viscoelastic regime of the sample. Before recording each frequency sweep, the sample was equilibrated at the test temperature usually for a period of 30 min. All experiments were performed in a nitrogen atmosphere to avoid oxidative degradation of PS.

Prediction of the CG

In general, the response $y(t)$, from a linear, continuous, time-invariant system described by $\Phi(t)$ with input signal, $u(t)$, can be predicted using the convolution integral[21]:

$$y(t) = \int_0^t \Phi(t-\tau)\,u(\tau)\,d\tau \tag{2}$$

In the extrusion context, Eq. 2 can be transformed into the volume domain as

$$C(v) = \int_0^\infty \hat{\bar{g}}(v-v')\,H(v')\,dv' \tag{3}$$

where $\hat{\bar{g}}(v)$ is a characteristic of the process that is independent of processing conditions, $H(v)$ is the Heaviside function representing the step input of the filler and $C(v)$ is the response to the step input of the filler, i.e., the CG, assuming that the melt absorbance is linearly proportional to composition of the filler. This assumption is valid at low compositions of the filler where Rayleigh static light scattering principles predict that the scattered intensity of light scales linearly with number of particles,[22,23] i.e., composition of the filler.

To establish the processing–structure relationship and predict the CG, the characteristic of the process that is independent of the processing conditions has to be identified. This requires a good understanding of mixing in extrusion. Considering that the corotating TSE is open axially and involves a highly nonideal flow due to channeling, back-mixing, and stagnation, obtaining a complete knowledge of the flow patterns that govern mixing is impractical.[24] To address this problem, conventionally, mixing in extruders is understood via residence time distribution (RTD), which is a measure of how long the material takes to pass a given point.[25] The corresponding concept in the volume domain is called a residence volume distribution (RVD), i.e., it is a measure of the volume of the material that passes a given point. These distributions are typically expressed as normalized functions of time and volume in the following forms:

$$\bar{f}(t) = \frac{f(t)}{\int_0^\infty |f(t)|\,dt} \tag{4}$$

$$\bar{g}(v) = \frac{g(v)}{\int_0^\infty |g(v)|\,dv} \tag{5}$$

where

$$v = t \times Q \tag{6}$$

and $\bar{f}(t)$ is the normalized RTD, $\bar{g}(v)$ is the normalized RVD, Q is the throughput, t is time, v is volume, and f and g are the response functions associated with the amount of material that passes a given point in the extruder at the time, t, or along with a volume, v. In an earlier experimental work, Elkouss et al.[26] confirmed that in an extruder with a fixed screw design, in spite of varying the polymer flow rates, viscosity, and extruder screw speeds, all the normalized RVDs superimpose to form a single master curve, as long as the elastic effects were not predominant, because transient effects are dampened by the extruder as predicted by the model of material flow through the extruder by Mudalamane et al.[24] This indicates that as long as the Weissenberg number is less than 1, the normalized RVD can be used as a characteristic of the process that is independent of processing conditions. Leveraging these efforts, we propose to use the master curve ($\hat{\bar{g}}(v)$) obtained by modeling the normalized RVDs as a characteristic of the process in Eq. 2 to obtain the CG. The nature of the approach allows rapid characterization of the CG compared with a time-consuming and destructive approach such as TGA.

Results and Discussion

To obtain the master curve ($\hat{\bar{g}}(v)$), which is a characteristic of the process that is independent of the operating conditions, the normalized RVDs, obtained experimentally using the

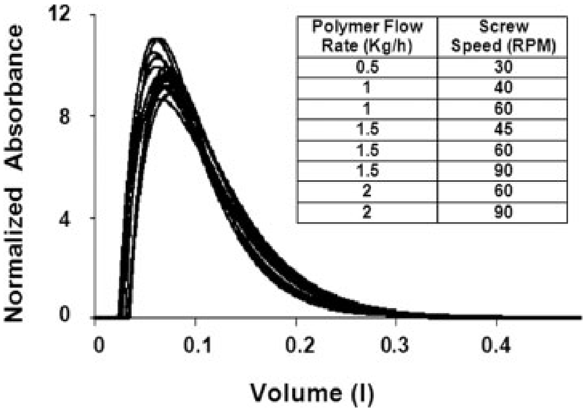

Figure 3. Modeled normalized RVDs.

The modeled normalized RVDs resulting from varying polymer flow rates and extruder screw speeds superimposed within reasonable error, thereby verifying the absence of predominant elastic effects.

in situ optical probe, can be modeled in various ways.[27–31] Without loss of generality, we demonstrate the applicability of our approach by modeling the normalized RVDs using simple empirical equations based on transfer functions that represent a series of perfect batch mixers.[32,33] A second-order transfer function that corresponds to the mixing occurring in the screw and the die zones of the extruder was used. In the Laplace domain, it can be represented as

$$G(s) = \frac{a^2 e^{-v_d s}}{(s+a)^2} \tag{7}$$

where v_d is the delay volume and a is the shape factor. The inverse transform gives the model in the volume domain as

$$g(v) = a^2(v - v_d)e^{-a(v-v_d)} \tag{8}$$

Figure 2 shows a representative normalized RVD that was obtained experimentally and the curve obtained by modeling it with the normalized form of Eq. 8, as shown in Eq. 5. The peak of the experimental curve is slightly lower than that of the modeled curve because the absorbance of the optical probe reached its saturation i.e., detection limit. The same argument explains why the peak was flatter than what would be expected. This is especially true with dark fillers such as CNFs and CNTs. This phenomenon was not observed in an earlier work using the same experimental setup with bright fillers.[18,19]

To leverage the earlier efforts by Elkouss et al.,[26] the absence of predominant elastic effects has to be verified. It was done by experimentally obtaining the normalized RVDs for the PS-CNF composites at varying polymer flow rates and extruder screw speeds for a fixed screw design. These normalized RVDs were modeled as described earlier and it was observed that all the curves superimposed within reasonable error (Figure 3). For the resulting master curve ($\hat{\bar{g}}(v)$) of PS-CNF composites, we obtained $v_d = 0.0521\ l$ and $a = 30\ l^{-1}$. Using Eq. 3, the convolution of $\hat{\bar{g}}(v)$ with a Heaviside step function of magnitude k, predicts the CG as

$$C(v) = k\int_0^v \hat{\bar{g}}(v)\,dv \tag{9}$$

Figure 4 compares the CG of PS-CNF composites ranging from an initial volume fraction of 0 to a final volume fraction of 0.06, i.e., $k = 6$, experimentally characterized using a TGA, with that theoretically predicted by Eq. 9. It is evident that the experimental results correlate well with those predicted by convolution confirming the validity of the nondestructive approach. This approach has significant implications in enhancing combinatorial techniques utilizing CGs. It allowed rapid characterization of the CGs when compared with the time-consuming and destructive tests like TGA. Furthermore, in contrast to batch-processed composites, the material resulting from transient extrusion state (i.e., before steady state in composition is reached) was not discarded, thereby significantly reducing the time and nanoscale filler consumed in producing samples at various compositions. This is especially important when using nanoscale fillers that are expensive or available in limited quantities. In this work, the amount of CNFs needed to obtain a CG containing all volume fractions between 0 and 0.06 was about 15 g, which was achieved by operating the PS feeder steadily at a rate of 2 lb/hr and the CNF feeder at 0.2 lb/hr for 10 min. Extending the operation of the CNF feeder beyond this time resulted in steady-state production of the PS-CNF composites with a volume fraction of 0.06 at a rate of 0.016 l/min.

In addition, the applicability of the approach for fillers across various length scales was studied by using inexpensive, bright colored KCl as the filler. Figure 5 compares the CG of PS-KCl composites ranging from an initial volume fraction of 0 to a final volume fraction of 0.18, i.e., $k = 18$, experimentally characterized using a TGA, with that predicted by Eq. 9. Here, the reader has to note that the master curve ($\hat{\bar{g}}(v)$) used in Eq. 9 was that obtained from modeling the normalized RVDs for the PS-CNF composites. In spite of this, the experimental results surprisingly correlated well with those predicted by convolution. Thus it can be concluded that the length scale of the fillers used in this work does not affect the evolution of CGs, thereby indicating that the transient effects

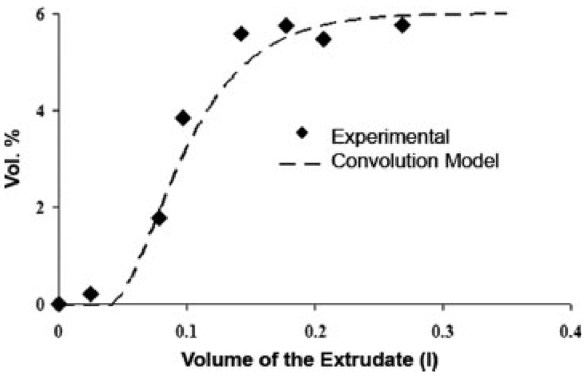

Figure 4. Comparison of PS-CNF compositional gradients.

The compositional gradient predicted via convolution correlates well with the experimental values obtained from TGA for the PS-CNF composite. This confirms the validity of the nondestructive approach.

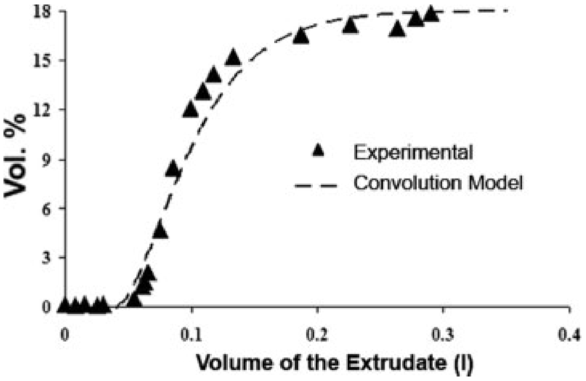

Figure 5. Comparison of PS-KCl compositional gradients.

The compositional gradient predicted via convolution correlates well with the experimental values obtained from TGA for the PS-KCl composite.This indicates that the approach is independent of the length scale of the fillers.

of the mixing process are independent of the size of the filler. Therefore, relatively inexpensive fillers such as KCl can be used to conduct impulse or step experiments to verify the absence of predominant elastic effects and to establish appropriate processing conditions for obtaining the desired CG, instead of using the more expensive nanoscale fillers.

In addition to rapidly predicting the CG, which is an aspect of the processing–structure relationships, the dynamic mechanical behavior of the combinatorially developed PS-CNF composites was characterized at various discrete compositions (see Figure 6a) in order to establish the structure–property relationship. At volume fractions exceeding 0.03, the storage modulus (G') of the PS-CNF composites exhibits a plateau at low frequencies indicating the formation of a percolated CNF network that responds elastically over long timescales. Similar, but less-predominant behavior is observed in loss modulus (G'') of the PS-CNF composites. Furthermore, the dynamic mechanical behavior of PS-CNF composites that are combinatorially developed via transient extrusion was compared with that of batch-processed ones (see Figure 6b) and it was observed that they correlated well. Therefore, the use of the new combinatorial approach for determining the processing–structure–property relationships for polymer nanocomposites was validated for the first time. This approach allows characterization of the material properties over a continuous range of composition without batch-to-batch variation in making the composites.

The deeper implications of this validation need further elucidation. In addition to the highly nonideal flow in the extruder, imposing a CG along the length of the screw further modifies the shear stress history experienced by the melt. Intuitively, this would indicate that the material properties of the composites that are combinatorially developed must be different from the batch-processed ones. However, a comparison of Figures 6a,b indicates that their dynamic mechanical behavior is very similar. This results in the counter-intuitive conclusion that the transient mixing conditions in extrusion do not affect the material properties, but is still consistent with the insensitivity of the RVD to the viscosity of the polymer as reported by Elkouss et al.[26] and the dampening of transient effects in the extruder modeled by Mudalamane et al.[24] Furthermore, although the entire approach is demonstrated for a fixed screw design and a fixed extruder, it is not difficult to extend it to varying screw designs and extruders. After testing for the absence of predominant elastic effects, every new screw design or extruder requires only a single impulse experiment to experimentally obtain the normalized RVD that can be modeled to obtain the master curve ($\hat{\bar{g}}(v)$). Subsequently, the CG can be predicted by using Eq. 9. The only limitation of this approach is that the normalized RVD cannot be used as a characteristic of the process that is independent of processing conditions, if the elastic effects are predominant as indicated by a Weissenberg number greater than 1.

Conclusions

In summary, a nondestructive approach to rapidly predict the CGs resulting from transient extrusion response has been developed by using small quantities of CNFs. The CGs were predicted by convolution of a step input with the normalized RVD, which was identified to be the characteristic of the process that is independent of the processing conditions. The normalized RVD was experimentally obtained for the PS-CNF composites by using in situ optical probe measurements and modeled using a second-order transfer function that

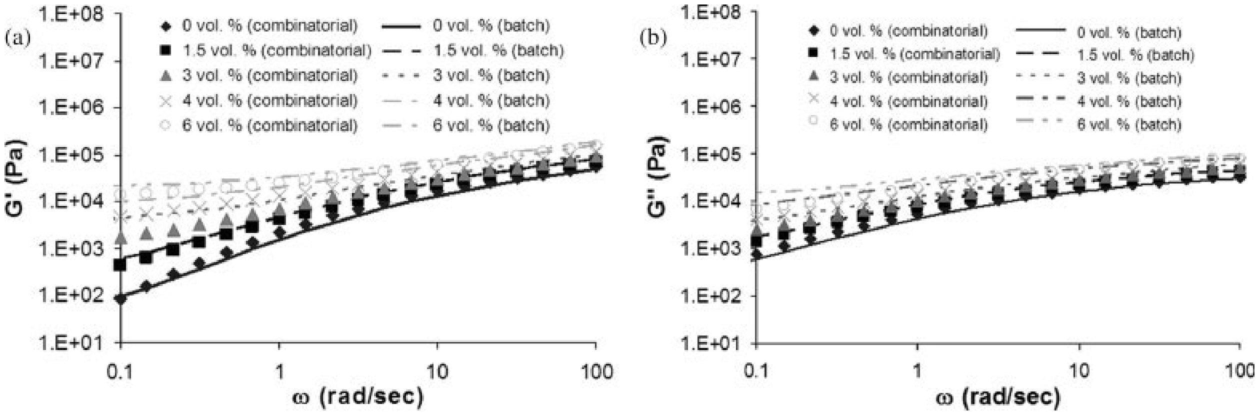

Figure 6. Comparison of dynamic mechanical properties of the polymer nanocomposites developed using the new combinatorial approach and batch-processed validating the new combinatorial approach.

physically represents the screw zone and the die zone as two perfect batch mixers in series. The CGs of PS-CNF nanocomposites thus predicted correlated well with those characterized experimentally using time consuming and destructive TGA, thereby confirming the validity of the nondestructive approach. Furthermore, in contrast to the batch-processed composites, the CGs required significantly less time and nanoscale filler to produce samples at various compositions, which is especially important when using nanoscale fillers that are expensive or available in limited quantities.

In addition, the CGs of PS-KCl composites were characterized experimentally and, rather surprisingly, correlated well with those predicted by convolution of the step input with the normalized RVD obtained from the PS-CNF composites. Thus it can be concluded that the length scale of the fillers used in this work did not affect the evolution of CGs, thereby indicating that the transient effects of the mixing process are independent of the size of the filler. Therefore, it is possible to use inexpensive microscale fillers to establish appropriate processing conditions for obtaining the desired CG.

For complete validation of the new combinatorial approach by establishing the structure–property relationship, the dynamic mechanical behavior of the combinatorially developed PS-CNF composites was compared with that of batch-processed ones. Results indicated that both the storage modulus, G', and the loss modulus, G'', correlated well between the combinatorially developed and the batch-processed PS-CNF composites. While it validates the use of the new combinatorial approach for determining the processing–structure–property relationships for polymer nanocomposites, it also results in the counter-intuitive conclusion that the transient mixing conditions in extrusion do not affect the material properties.

Acknowledgments

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