Enhancing the Mechanical and Thermal Properties of Polyacrylonitrile Through Blending with Tea Polyphenol

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ABSTRACT: Several polyacrylonitrile (PAN)/tea polyphenol (TP) blends were prepared with various mixing weight ratios (percentage). With a commercial acrylonitrile–butadiene–styrene (ABS) as reference, the results show that the PAN/TP blends with 12.5 wt % TP had a better antiwear ability and similar hardness to those of ABS. All of the prepared PAN/TP blends showed a lower impact strength than the referenced ABS. However, some values were indeed higher than those reported for engineering materials in the literature, for example, polystyrenes and some ABS blends. Differential scanning calorimetry, differential thermogravimetry, and dynamic mechanical analysis indicated that the PAN/TP blends had enhanced the thermal stability compared to the pure PAN. Fourier transform infrared spectral analysis suggested that the H bonds increased in the PAN/TP blends. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40411.

INTRODUCTION

Polyacrylonitrile (PAN) is a copolymer made from a mixture of monomers, and acrylonitrile (AN) is the main component. As an important polymeric material, PAN is broadly applied as the main precursor of carbonaceous materials, including carbon fibers, porous/activated carbon materials, and nanofibers,[1–6] because of its high carbon yield, for example, up to 56%.[7] PAN is also broadly applied to the production of textile fibers and ultrafiltration membranes because of its good flexibility and stability.[7–10]

Notably, although PAN is an AN-based copolymer, its mechanical properties are weak compared with those of other AN-based copolymers, for example, AN–butadiene–styrene (ABS),[11–15] because ABS is superior in its hardness, gloss, toughness, and electrical insulation properties.[16]

To enhance the mechanical properties of PAN, some developments have been reported in the literature. For example, the use of nanomaterials, for example, carbon nanotubes, to reinforce PAN is one method, and it has been tried by some researchers.[17–19] Although this method is available for enhancing mechanical properties, a problem is subsequently presented in its reduced biodegradation.[19] Because PAN blended with other

synthetic polymers is rarely compatible because of the strong dipole–dipole interactions of nitrile groups,[20,21] the use of natural polymers is expected and has been focused on. For example, recently, Unlu et al.[22] used a natural polymer, xylan, to graft PAN and found this could improve the thermal properties of PAN. This is interesting because xylan is a component of hemi-celluloses with a structure of *O*-acetyl-4-*O*-methylglucurono-*d*-xylan. As we previously reported,[23] its mechanical properties are weak compared with those of ring-based plant polyphenols.[24] Therefore, the application of ring-based natural polymers to blends with PAN was considered.

Tea polyphenol (TP) is a natural polymer with known advantages as an antioxidant in eliminating free radicals in the human body to protect against UV effects, as a resisting agent for the treatment of cancer and tumors, and as an antiviral, anti-inflammatory, and deodorization agent with radiation protection properties.[25–30] Recently, we applied TP to blends with poly(vinyl alcohol) (PVA) and found that this improved the thermal and biodegradation properties of PVA.[24]

Therefore, in this study, we aimed to apply TP to blends with PAN to modify and enhance the mechanical properties of PAN. Experimentally, we prepared several PAN/TP blends by varying the weight ratios and characterized the mechanical and thermal

properties. Considering that the AN-based ABS had good mechanical properties,[11–16] we used a commercial ABS sample as a reference for comparison with all of the prepared PAN/TP blends.

EXPERIMENTAL

Raw Materials

A commercial PAN obtained from Shanghai Petrochemical Co. with known molecular weight (number-average molecular weight = 18,000) was used as received. This PAN was used and studied previously.[1]

TP was obtained from Zhejiang Tea Research Institute (China) and was used as received.[24] According to the producer, this TP had a purity of about 98.3%.

Analytical grade N,N-dimethylformamide (99.0%) was purchased from a local chemical store and was used as received.

The referenced ABS was a commercial sample obtained from a local plastic market in Shanghai, China.

Preparation of PAN/TP Blends

By oven drying for about 2 h at 80°C and then cooling to 25°C to remove the moisture, we dissolved the PAN powder in N,N-dimethylformamide at 80°C under stirring conditions for about 2 h to form a PAN solution. In this case, the PAN solutions were prepared with different concentrations: 5, 10, 15, and 20%. The TP solution was directly prepared by dissolution in water at 25°C.

The PAN/TP blending solutions were prepared by the mixture of the PAN and TP solutions under stirring conditions at 25°C and at various weight ratios, for example, 100/2, 100/5, 100/10, 100/15, and 100/20 wt % PAN/TP, respectively. After at least 2 h of mixing, the PAN/TP blending solutions were oven-dried for about 24 h at 80°C to form solid samples. Observation of all of these solid blends presented a dark color.

Measurement and Characterization

The Fourier transform infrared (FTIR) spectra were recorded with a NEXUS-670 FTIR spectrometer (Nicolet Co.). For each spectrum, a 50-scan interferogram was collected that corresponded to a single-beam mode with a 4-cm^{-1} resolution.

The wear properties of the PAN/TP blends were evaluated with a pin-on-disc machine (MM-200, Shanghai, China). The pins were cut to a size of 30 × 7 × 6 mm^3. A fixed sliding velocity of 200rpm and a suggested force of 300 N were applied. The tests were performed at room temperature (25°C) when the blend specimens were rotated against a GCr15 stainless steel disc with a thickness of 25 mm, a diameter of 40 mm, and a Rockwell hardness between HRC values of 58 and 63. Before this test, the disc was initially cleaned with acetone. Before and after the wear test, the blend specimens were weighed, respectively, to obtain the mass removed during the wear process. The removed mass weight was also measured after different wearing times. The presented data was averaged by three independence measurements with a standard deviation of ±5 mg.

The impact measurement was performed with a multifunction impact tester (Chengde Kaosi Tester Co., China). Before mea-

surement, the samples were prepared with a size of 5 × 50 × 6 mm^3 with a V-type gape at a depth of 1.5 mm and a width of 2 mm. The presented data were averaged by five independence measurements, and the standard deviation was ±5 kJ/m^2. This measurement was performed at 25°C.

The Rockwell hardness was measured with an XHR-150 tester (Shanghai Hugong Too Co., Ltd. China). The presented value was averaged after five independence measurements, and the standard derivation was ±5 HRC. The measurement temperature was 25°C.

The thermomechanical properties were analyzed with dynamic mechanical analysis (DMA; DMAQ800, TA Instruments) with known sensitivity tan at 0.0001. By mounting the sample in the tension mode, we sealed the furnace off and scanned over a temperature range from −50 to 250°C at a fixed frequency of 5 Hz. The heating rate was 2°C/min, and the strain amplitude was 0.01 mm within the linear viscoelastic region for all of the temperature scanning tests.

Thermogravimetry (TG) analyses were conducted on a Netzsch TG 209 at a heating rate of 20°C/min and in a range of 50–400°C when the nitrogen flow rate was set at 20 mL/min.

Differential scanning calorimetry (DSC) measurements were performed under an N_2 atmosphere with a DSC Q20 (TA Instruments). The temperature was initially increased from 25 to 300°C at a fixed rate of 10°C/min; it was then cooled to 25°C. During measurement, the sample weight was kept at 7 mg under a nitrogen environment.

RESULTS AND DISCUSSION

Structure of the PAN/TP Blends

The IR spectra of the PAN/TP blends with different mixing ratios are shown in Figure 1, where the pure TP also appeared as a reference. Because the IR spectrum of PAN has been done elsewhere, we knew that those distinct absorption bands at 2930 cm^{-1} ($v_{C—H}$ in CH$_2$), 2244 cm^{-1} ($v_{C≡N}$ in CN), 1662 cm^{-1} ($\delta_{C—H}$ in CH$_2$), 1447 cm^{-1} ($\delta_{C—H}$ in CH), 1388 cm^{-1} ($\delta_{O—H}$ vibration), 1248 cm^{-1} ($v_{C—O—C}$ stretching), and 1092 cm^{-1} ($v_{C—O—C}$ stretching) appeared in the blends corresponded to the PAN structure.[1–6] With the IR spectrum of TP as taken as a reference (Figure 1), it is also known that the typical TP peaks, such as those located at 1697 cm^{-1} ($v_{C=O}$ stretching), 1622 cm^{-1} ($v_{C=C}$ vibration on the ring), 1452 cm^{-1} ($\delta_{C—H}$ bending), 1348 cm^{-1} ($\delta_{O—H}$ bending), 1243 cm^{-1} ($v_{C—O—C}$ stretching), 1144 cm^{-1} ($v_{C—O—C}$ stretching), and 1034 cm^{-1} ($v_{C—O—C}$ stretching[24] overlapped or uniquely appeared in those blends. This clearly indicated that the formed blends were contributed by both PAN and TP.

Because the PAN/TP blends showed a new peak located at about 1450 cm^{-1}, which corresponded to the CH$_2$ vibration, this peak was considerably characteristic of such blends. In terms of Figure 1, the TP-based peak located at 1622 cm^{-1} due to the C=C vibration appeared for all of the blends. This suggests that the TP molecules interpenetrated into the network of PAN. In Figure 1, the TP content decreased from 15 to 10%, and 5% was found to lead the peak located at 1697 cm^{-1}
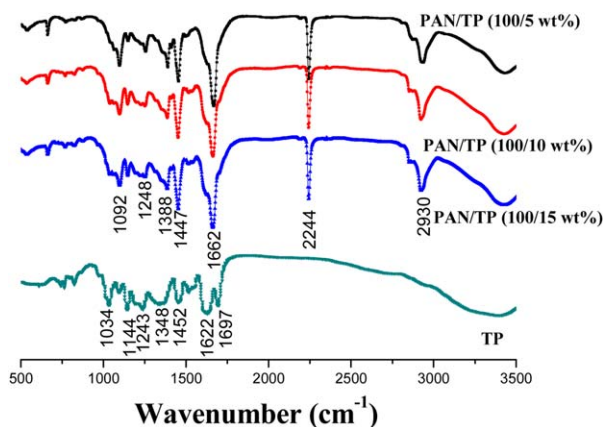
Figure 1. FTIR spectra of the pure TP and PAN/TP blends with different mixing weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(C=O stretching vibration) initially to reduce its intensity (TP 10%) and then fully disappeared (TP 5%). Obviously, this supported the aforementioned formation of an interpenetration network structure and also indicated that the TP percentage is a factor for formation of such a structure. Because the TP weight percentage within the blends increased from 5 to 15%, this caused some peaks located within the areas of 1050–1300 cm^{-1} (C-O group vibrations) and 3000–3500 cm^{-1} (H-bonding vibrations) to increase the peak width. These structural changes led us to consider that the interpenetration network was mainly formed by H bonds.

Mechanical Properties of the PAN/TP Blends

In this case, the wear, Charpy impact, and hardness were taken as the mechanical parameters and were investigated for all of the prepared PAN/TP blends, including the referenced ABS sample.

We describe the wear behavior by taking the weight loss as a function of the wear time in Figure 2, of which the weight loss was also taken as a function of the TP percentage, as shown in the inset. We observed that the weight loss increased with increasing wear time or decreased with increasing TP percentage for the PAN/TP blends, and among the prepared blends, the samples with 10% or more TP seemed to be better than that of the referenced ABS. This good wear behavior of the PAN/TP blend was considerable because of the formed interpenetration network structure. According to Figure 2, the preparation of an ABS-like PAN was possible through blending with TP.

According to the plot shown in the inset in Figure 2, a relationship between the weight loss and TP content for those blends was deduced, as presented in eq. (1), where W is the weight loss due to wear:

$$W = 98.67 \times e^{[(TP)/3.19]} + 54.45 \qquad (1)$$

In terms of eq. (1), we quantitatively estimated the required TP amount for application to the PAN/TP blends with the enhanced wear behavior.

The impact strength is a parameter of the materials and refers to the toughness. The measured Charpy impact strength (I_m) of
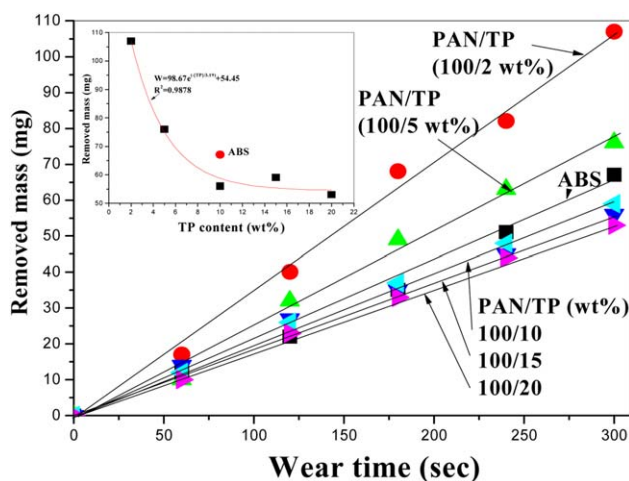

Figure 2. Comparison of the wear properties of the PAN/TP blends with various mixing weight ratios and referenced ABS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

those prepared PAN/TP blends is shown in Figure 3. We observed that the I_m of those PAN/TP blends was decreased quickly with increasing TP content and followed a nonlinear fit (Figure 3). The reason that all of the prepared blends presented a lower impact strength compared with the referenced ABS was reasonable because the crystallinity of PAN might have been reduced through the blending of the TP molecules.[31] Considering the fact that the ABS had a crosslinking network because of the copolymerization of the AN monomer with styrene and butadiene and was thus capable against crack expansion[17–21] to enhance the impact strength, we, therefore, considered the structure of ABS to be strong in impact strength compared to that of the interpenetration network structure of the PAN/TP blend.

Although all of those blends showed a lower I_m than ABS (Figure 3), some values of these blends were exactly greater than those of some known engineering materials,[17–21,31–33] for example, 197, 8350, and WT1235 polystyrenes (Atochem, United Kingdom)[32] and even some ABS blends.[33]
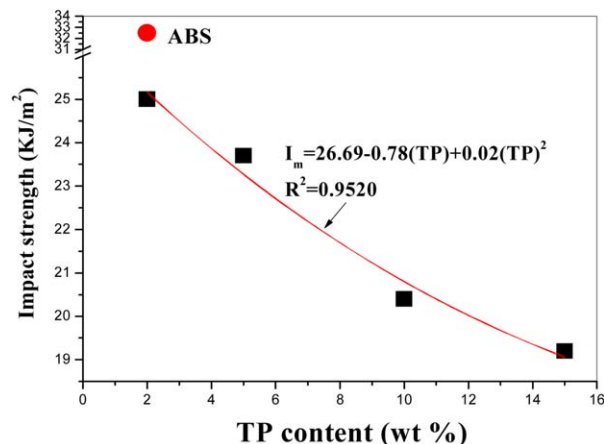

Figure 3. Comparison of the impact strength of the PAN/TP blends with various mixing weight ratios and referenced ABS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Comparison of the hardness of the PAN/TP blends with various mixing weight ratios and referenced ABS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
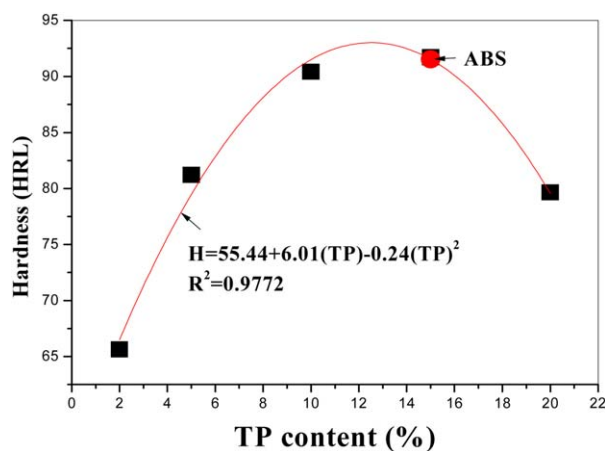
According to Figure 3, a relationship between I_m and the TP content for these blends was also deduced and presented by eq.z#(2):

$$I_m = 26.69 - 0.78(TP) + 0.02(TP)^2 \qquad (2)$$

Hardness is a main measure of materials because it is related to the resistance to plastic flow and the tensile strength of materials.[15,31] To compare to the referenced ABS, Figure 4 shows that the HRL hardness (H) of those PAN/TP blends varied, and only one blend with about 12.5 wt % TP had a similar hardness to that of ABS. This was interested because this critical TP percentage was in good agreement with the wear measurement result (Figure 2). In fact, the information in Figure 4 is interesting because it may explain the interpenetration network of the PAN/TP blends. For example, the hardness decreased with either decreasing TP or increased because a few of the TP molecules were interpenetrated in the PAN network in a small role and were unable to enhance the hardness and the wear behavior (Figure 2). The TP molecules within the PAN network crammed in with each other to expand and damage the network and reduce the hardness. This was reasonable because the small molecules of TP squeezed in an interpenetrated network would damage the polymer network;[7] this was in good agreement with Guhanathan et al.[31]

In terms of Figure 4, the relationship between the TP percentage and the hardness of the PAN/TP blends were described by eq. (3):
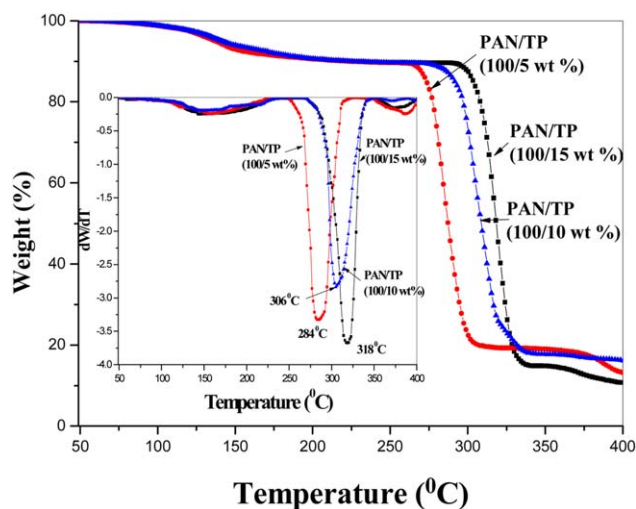

Figure 5. TG and DTG curves of the PAN/TP blends with different mixing weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$H = 55.44 + 6.01(TP) - 0.24(TP)^2 \qquad (3)$$

Thermal Properties of the PAN/TP Blends

TP is an antioxidant[25–30] and, when it was blended with PVA, it has been found to improve the thermal properties of PVA,[24] studying the thermal properties of these prepared PAN/TP blends is interesting. Figure 5 shows the TG and differential thermogravimetry (DTG) analysis results, where these blends presented different degradation temperatures (T_d's), and these T_d's obviously increased with increasing TP percentage. For example, the T_d values were 284, 306, and 318°C for blends with TP percentages of about 5, 10, and 15 wt %, respectively, and all of them were higher than that of the pure PAN, which were about 210–220°C,[34] and lower than that of the ABS, which were about 600–700°C (Table I).[11–15] This clearly indicated that these PAN/TP blends had better thermal stability than the PAN. From these thermal results, although the antioxidant behavior of TP was important, the blending-induced interpenetration network structure was also considered to play a positive role. In fact, the enhancement of the thermal stability of the polymer through the addition of an antioxidation agent was reported by Mousavi et al.[34] in the case of polyester (PET). According to the results of Mousavi et al.,[34] we concluded that the enhancement of the thermal stability of these PAN/TP blends (Figure 5)

Table I. Comparison of the T_g, T_c, and T_d Values of the PAN/TP Blends with Different Mixing Ratios as Measured with DSC, DMA, and DTG

Sample	DMA-based T_g (°C)	DSC-based T_c (°C)	DTG-based T_d (°C)	β-Transition temperature (°C)
PAN	–	275	210–220	
PAN/TP (100/5 wt %)	141	266	284	1
PAN/TP (100/10 wt %)	126	258	306	−3
PAN/TP (100/15 wt %)	123	256	318	−5
TP	–	–	–	
ABS			600–700	

occurred because the presence of TP in the PAN network eliminated the occurrence of free radicals.

In the cooling-process recorded DSC curves, all of prepared PAN/TP blends showed a unique peak, as shown in Figure 6; this obviously indicated that these two materials blended with good miscibility. As shown in Figure 6, the crystallization temperature (T_c) of these blends was found to shift from higher to lower, corresponding to the TP percentage increase but was always smaller than that of the pure PAN. This was reasonable because the TP molecules interpenetrated into the PAN network should have damaged the original crystal structure of PAN to reduce its degree of crystallization. The DSC measured T_c for all of the blends (Figure 6) are also summarized in Table I.

The dynamic mechanical properties of the PAN/TP blends determined from DMA measurements are illustrated in Figure 7, and two temperature peaks appeared in relation to the α and β transitions. As is known, the α transition was caused by the segmental motion corresponding to the glass-transition temperature (T_g), and the β transition was an aspect of the hydrogen-bond formation between the cyan groups of PAN and polyphenols, which could be applied to the identification of engineering materials.[17–21] In fact, the observed β transition showed good support for the formation of an interpenetration network for the PAN/TP blend. According to Figure 7, the T_g of those blends decreased with increasing TP percentage; this was similar to the T_c change, whereas the β transition was the same for all of the blends. These thermal behaviors suggested that the interactions occurred between the polyphenols, and the cyan groups of PAN decreased with increasing TP percentage because the crystal area decreased in the formed interpenetration network. This was possible and was supported by the literature, as a similar thermal phenomenon was also found for some PAN/biomaterial blends.[35,36]

The α and β transitions related to two temperatures for all of the prepared blends were compared and are summarized in Table I.

Because the tan δ was directly proportional to the storage modulus, Figure 7 also shows which related curves in the inset indi-
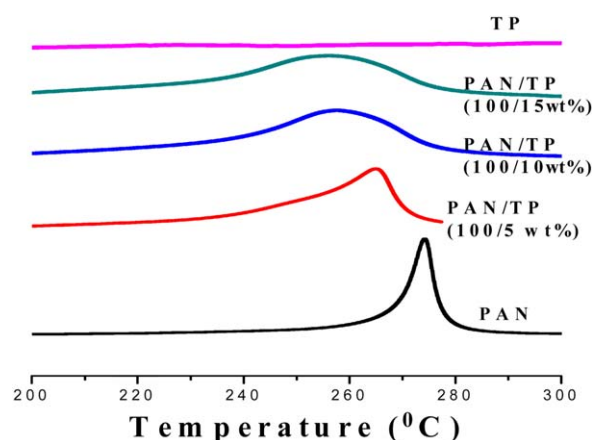

Figure 7. DMA curves of the PAN/TP blends with different mixing weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
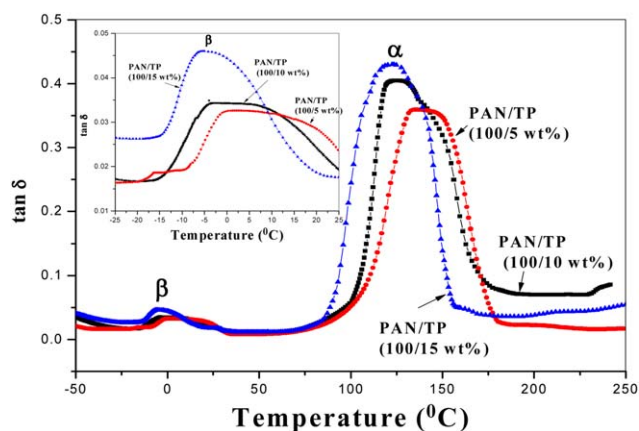
cate that increase in the TP percentage increased the storage modulus for the PAN/TP blends.

CONCLUSIONS

Experiments have proven that the application of natural TP to blends with synthetic PAN was very miscible, and the blend may have had an interpenetration network. The PAN/TP blends prepared with about 12–13% TP had better antiwear ability and a hardness that was comparable to that of with the ABS. The impact strength of the PAN/TP blends was lower compared to that of the referenced ABS. However, it was greater than those reported for some engineering materials, for example, PS and some ABS blends. These PAN/TP blends also showed enhanced thermal stability compared with the pure PAN.

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Figure 6. DSC curves of the PAN/TP blends with different mixing weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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