

Supporting Information

Preparation and compatibility mechanism study of the polyurethane-polysiloxane copolymer with tunable polysiloxane content for the TPU/MVQ blends with comfortable human touch

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Characterization Synthesis and text

The FTIR structure characterization of different PDMS content compatibilizers. The FTIR spectra of compatibilizers are shown in *Figure S1*. Through the FTIR spectrogram normalization of -NHCOO-, the characteristic peak of -Si-O-Si- appeared at 1084 cm^{-1} , and the telescopic vibration peak of -Si-C- appeared at 800 cm^{-1} and 1189 cm^{-1} , indicating that the PDMS segment successfully reacted with MDI. There was no obvious feature peak at $2250\text{--}2280\text{ cm}^{-1}$ in the FTIR spectrogram of the compatibilizer, which is the absorption peak position of the -NCO in MDI, indicating that -NCO was fully reacted with -OH group in PTMG and PDMS. Meanwhile, it was found that the vibration peak of -Si-C- exhibited a significant enhancement, which verified the increase of PDMS content from PU-PDMS-20% to PU-PDMS-100%.

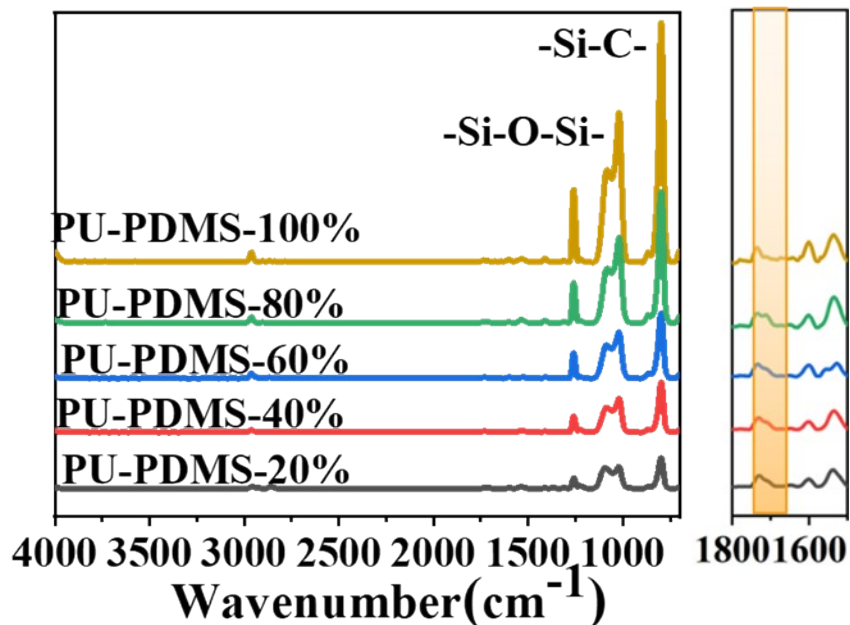


Figure S1. The FTIR spectra of different PDMS content compatibilizers

The ^1H NMR structure characterization of different PDMS content compatibilizers. ^1H NMR spectrum was also applied here to prove the structure of different PDMS content compatibilizers. As shown in **Figure S2**, according to the ^1H NMR spectra of the compatibilizers with different PDMS content, the characteristic peak of -NH was observed at about 1.90 ppm, indicating the successful synthesis of the reaction. At the same time, the content of PDMS segment in the compatibilizers can be verified by the -Si- CH_3 signals, which was calculated by normalizing the ^1H NMR spectra, and the actual content of PDMS segment was obtained, which confirmed the increase of PDMS content. The actual PDMS content of PU-PDMS (marked as m) is obtained via the integral area of the corresponding signals:

$$m = \frac{n_{PDMS}}{n_{PDMS} + n_{PTMG}} = \frac{S_3/4}{S_1/12} * 100\%$$

The actual PDMS content in PU-PDMS copolymer was increased with PDMS monomer in feed.

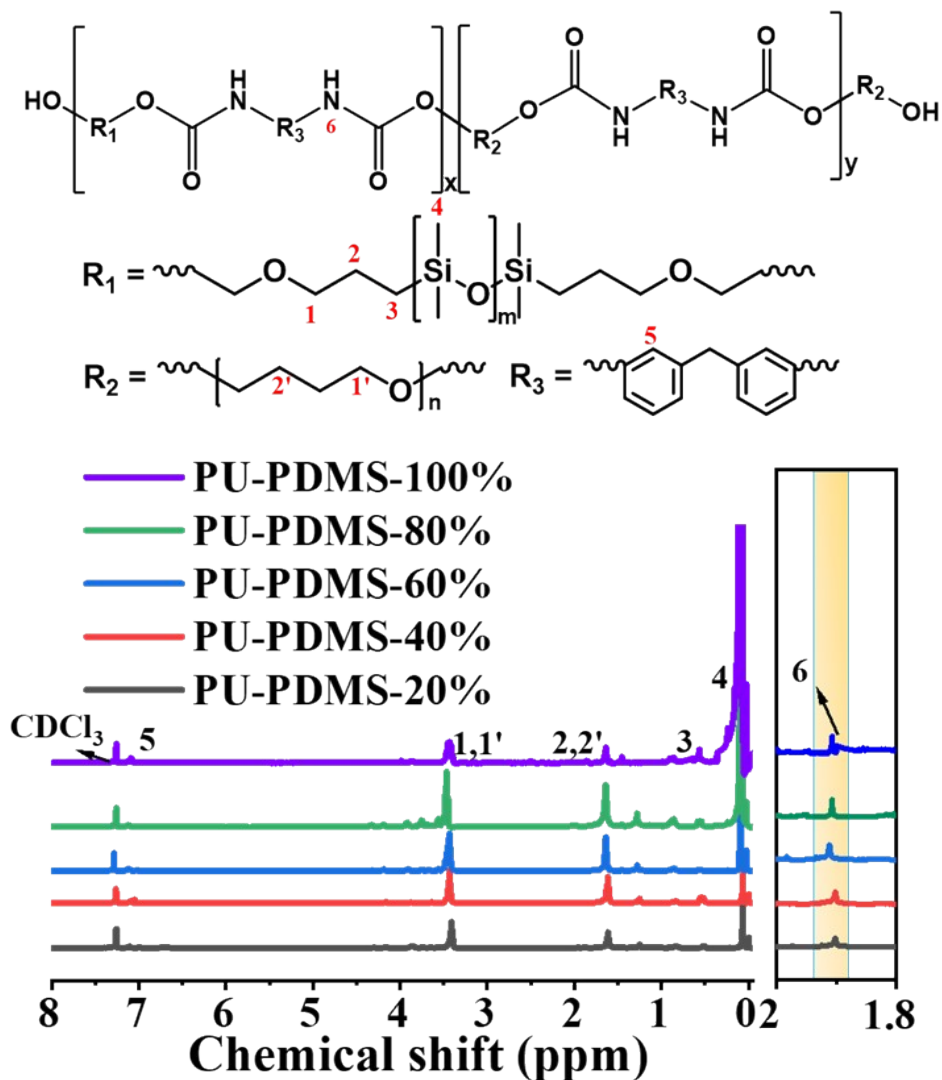


Figure S2. The ¹H NMR spectra of different PDMS content compatibilizers

The surface tension analysis of the polyurethane-polysiloxane compatibilizers with different PDMS content. To determine the surface

tension (γ) and wetting parameters (ω) of the compatibilizer in blends,^{1, 2} the position of the compatibilizers in the blend as shown in **Figure S3**.

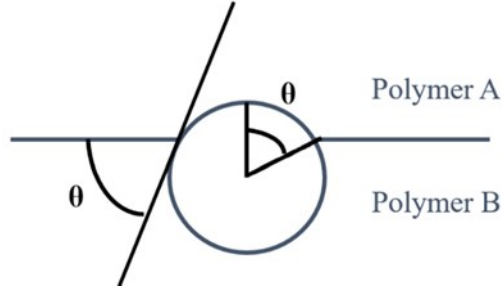


Figure S3. The position of the compatibilizers in the blend

The Harmonic Equations (Formula S1) can be used to estimate

$$\text{interfacial tension} \quad (1 + \cos \theta_{H_2O}) \gamma_{H_2O=4} \left(\frac{\gamma_{H_2O}^d \gamma^d}{\gamma_{H_2O}^d + \gamma^d} + \frac{\gamma_{H_2O}^p \gamma^p}{\gamma_{H_2O}^p + \gamma^p} \right)$$

$$(1 + \cos \theta_{C_2H_5OH}) \gamma_{C_2H_5OH=4} \left(\frac{\gamma_{C_2H_5OH}^d \gamma^d}{\gamma_{C_2H_5OH}^d + \gamma^d} + \frac{\gamma_{C_2H_5OH}^p \gamma^p}{\gamma_{C_2H_5OH}^p + \gamma^p} \right)$$

θ_{H_2O} and $\theta_{C_2H_5OH}$ represent the contact angle of water and ethanol on MVQ and TPU samples.

$$\gamma = \gamma^d + \gamma^p \quad (\text{Formula S2})$$

γ is the surface tension of MVQ or TPU, d is the non-polar component, and p is the polar component. The surface tension of water and ethylene glycol is substituted into the Formula S1 to calculate the surface tension of MVQ and TPU matrix.

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (\text{Formula S3})$$

γ_1 is the surface tension of MVQ, γ_2 is the surface tension of TPU. γ^d and γ^p represent the non-polar and polar parts of the components of the polymer. The position of the compatibilizers in the blend can be determined by the wetting coefficient ω :

$$\omega = \frac{\gamma_{\text{compatibilizer-MVQ}} - \gamma_{\text{compatibilizer-TPU}}}{\gamma_{\text{MVQ-TPU}}}$$

(Formula S4)

$\gamma_{\text{compatibilizer-TPU}}$, $\gamma_{\text{compatibilizer-MVQ}}$, $\gamma_{\text{MVQ-TPU}}$ represents the interface tension of the two phases of the compatibilizer-TPU, the compatibilizer-MVQ, and the TPU-MVQ. When $\omega > 1$, the compatibilizer is located in the TPU phase, when $\omega < -1$, the compatibilizer is located in the MVQ phase, when $-1 < \omega < 1$, the compatibilizer is located at the two-phase interface of the TPU/MVQ blend.

The SEM micrographs obtained for blending at pure TPU/MVQ. The structure of the compatibilizer PU-PDMS plays a key role in adjusting the morphology of TPU/MVQ, the TPU/MVQ blend was prepared at a weight ratio of 7/3, in order to eliminate the influence of temperature, shear rate, blending time, and other processing conditions, the samples were prepared by the solution mixing as shown in ***Figure S4***.

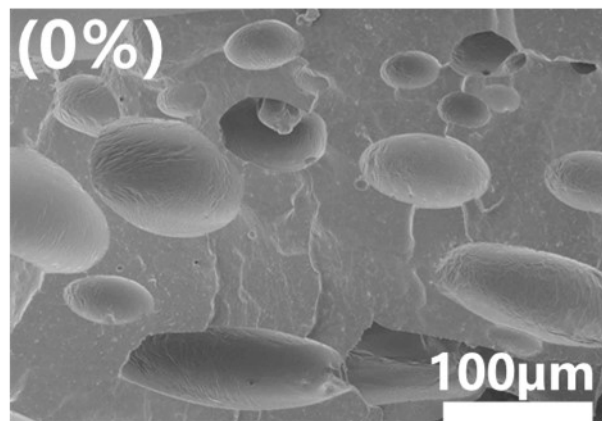
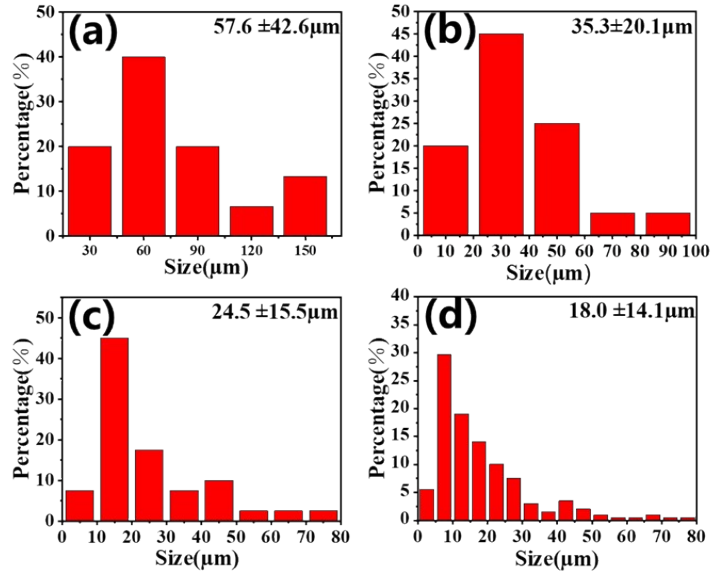


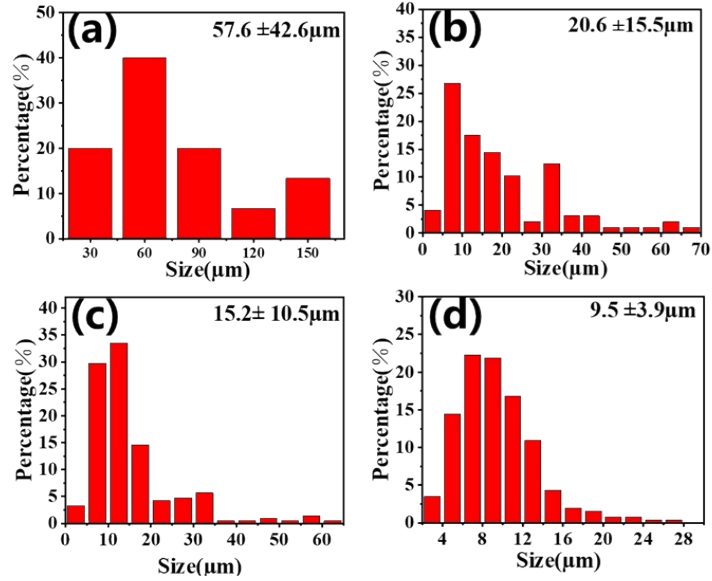
Figure S4. The SEM micrographs obtained for blending at TPU/MVQ without compatibilizer

The average diameter of the MVQ phase in TPU/MVQ (7/3) compatibilized by PU-PDMS with varied PDMS content. The structure of PU-PDMS was adjusted by varying the PDMS content from 20% to 100%, which was expected to orient at the interface and exhibited good compatibilization effect. In order to investigate the effect of synthetic PU-PDMS amphiphilic copolymer on the compatibilization of TPU/MVQ blends, the TPU/MVQ blends were prepared at a weight ratio of 7/3 with various amounts of PU-PDMS compatibilizers from 1 wt.% to 10 wt.% content. The average diameter of the MVQ phase of TPU/MVQ blends are shown in *Figure S5*.

PU-PDMS-20%



PU-PDMS-80%



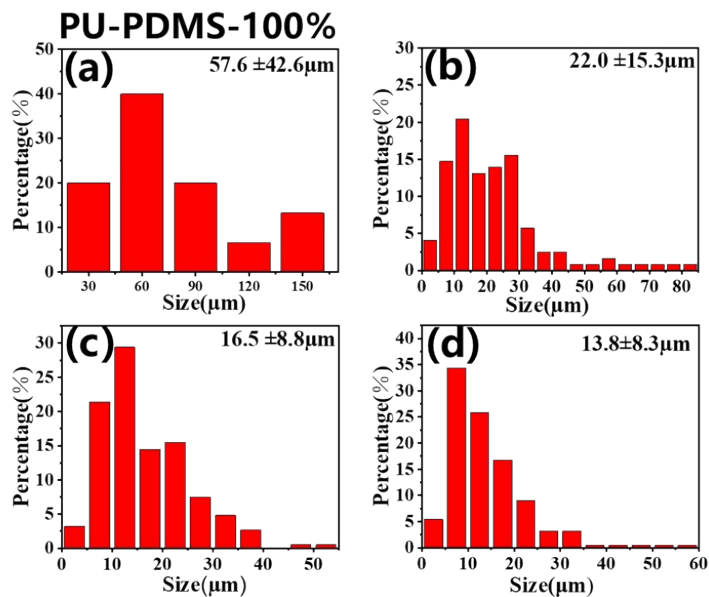


Figure S5. The dispersion phase size distribution of TPU/MVQ blends compatibilized by the compatibilizers with different PDMS content, (a), (b), (c), and (d) represent the amount of compatibilizers addition is 0%, 1%, 5%, and 10%, respectively. The blends were obtained by solution blending.

The Mechanical properties of the TPU/MVQ blends compatibilized by the compatibilizers with different PDMS content. The interfacial adhesion is necessary for stress transfer to suppress crack at the interface.³ As a result, the compatibility and the enhanced interfacial interactions can be reflected by the stress-strain curve of the blends. The effect of the structure of PU-PDMS on the mechanical properties of TPU/MVQ blends is investigated, which reflects the influence of varied PU-PDMS structure on the interface adhesion of TPU/MVQ blends by the changes of the elongation at break, and the stress-strain curves are shown in **Figure S6**. Meanwhile, the mechanical data are

shown in *Table S1*.

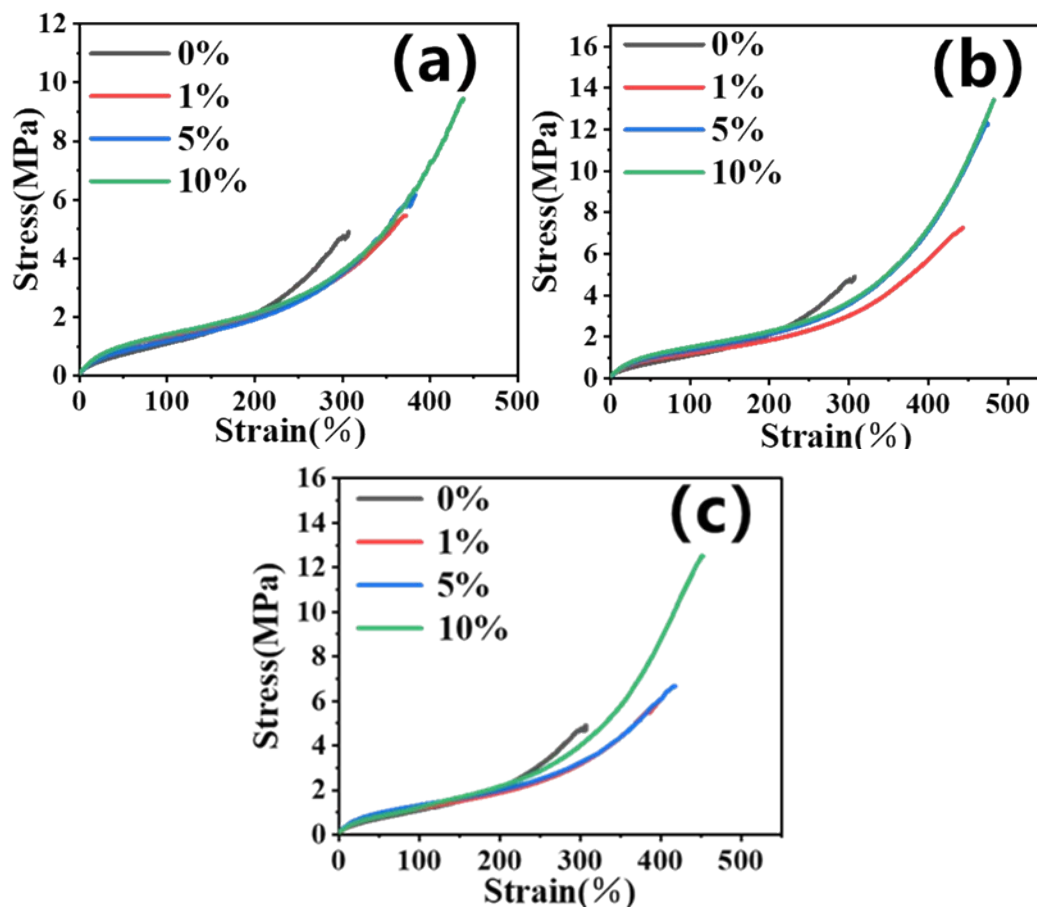


Figure S6. The stress-strain curve of the TPU/MVQ blends compatibilized by the compatibilizers with different PDMS content, (a) PU-PDMS-20%, (b) PU-PDMS-80%, (c) PU-PDMS-100%

Table S1. The tensile strength and elongation at break of TPU/MVQ/PU-PDMS-X blends

Sample	Compatibilizer dosage (wt.%)	Tensile strength (MPa)	Elongation (%)
TPU/MVQ/PU-PDMS-20%	0	4.9±2.6	307±47
	1	5.5±2.2	371±42
	5	6.2±1.8	383±42
	10	9.9±1.7	456±37
TPU/MVQ/PU-PDMS-80%	1	7.3±1.9	443±35
	5	12.3±1.5	472±30
	10	13.4±0.9	482±25
TPU/MVQ/PU-PDMS-100%	1	6.0±2.1	397±42
	5	6.7±1.7	418±37
	10	12.5±1.3	451±33

*The average diameter of the TPU/MVQ blends compatibilized by PU-PDMS-80%. In order to verify whether PU-PDMS-80% compatibilizer also exhibits obvious effect in the preparation of TPV materials, the melt blending method is used in the preparation of the TPU/MVQ blends, which is similar as the conditions of dynamic vulcanization. The dispersion phase size distribution of the TPU/MVQ blends compatibilized by PU-PDMS-80% as shown in **Figure S7**.*

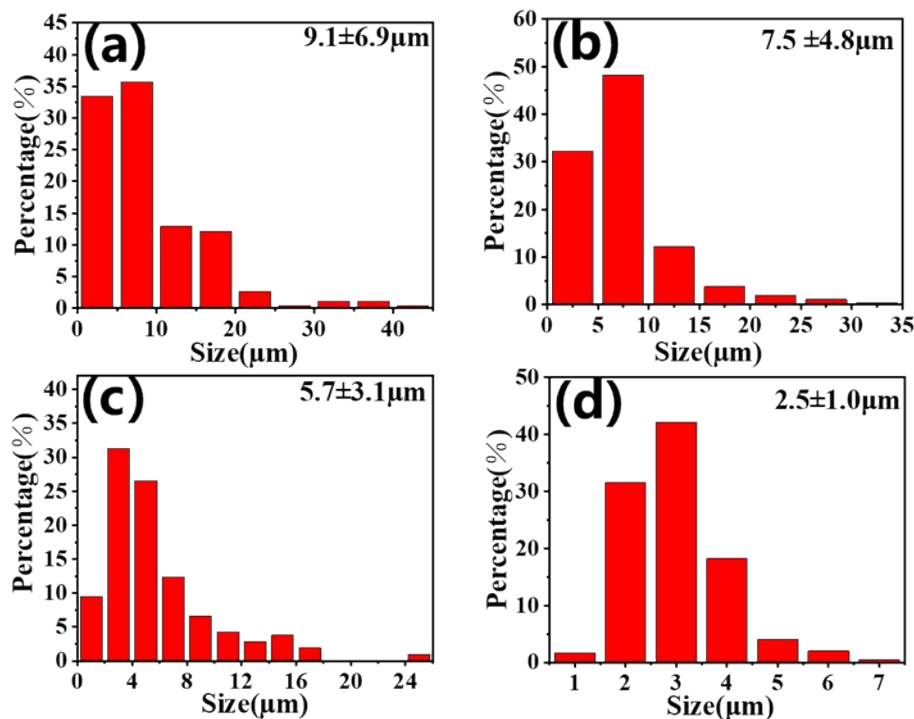


Figure S7. The dispersion phase size distribution of the TPU/MVQ blends compatibilized by PU-PDMS-80%, (a), (b), (c), and (d) represent the amount of compatibilizers addition is 0%, 1%, 5%, and 10%, respectively. The blends were obtained by melting blending.

References

- [1] M. Sumita, K. Sakata, S. Asai, K. Miyasaka, H. Nakagawa. Dispersion of fillers and the electrical conductivity of polymer blends filled with carbon black, *Polymer Bulletin*, 1991, **25**, 265-271.
- [2] F. Fenouillot, P. Cassagnau, J.C. Majesté. Uneven distribution of nanoparticles in immiscible fluids: Morphology development in polymer blends, *Polymer*, 2009, **50**, 1333-1350.
- [3] N. Bitinis, R. Verdejo, P. Cassagnau, M.A. Lopez-Manchado. Structure and properties of polylactide/natural rubber blends, *Materials Chemistry and Physics*, 2011, **129**, 823-831.