SUPPORTING INFORMATION

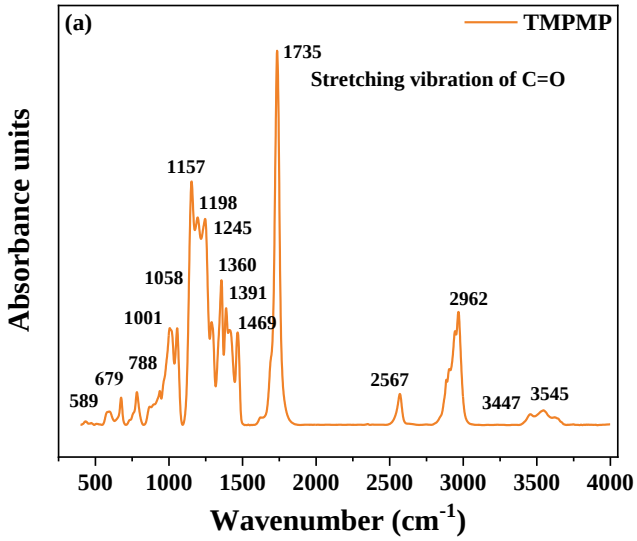
Enhanced Interfacial Compatibility and Dynamic Fatigue Crack Propagation Behavior of Natural Rubber/Silicone Rubber Composites

Qingyuan Han [†], *Liqun Zhang* [†,‡], *Youping Wu*[*, †,‡]

[†]State Key Lab of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China

[‡]Beijing Engineering Research Center of Advanced Elastomers, Beijing University of Chemical Technology, Beijing 100029, PR China

The FT-IR spectrums of TMPMP; pure NR (T0-D0) and extracted T-NRs (T0.5-D0.05, T1-D0.1, T1.5-D0.15) are shown in **Figure S1 (a)** and **(b)**, respectively.



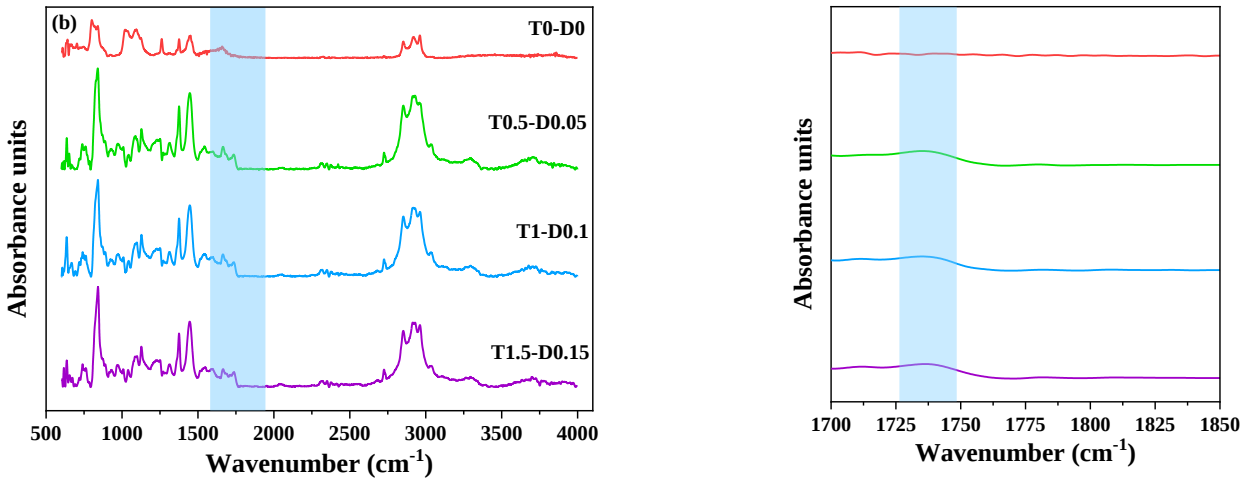


Figure S1. FT-IR spectrums of **(a)** TMPMP; **(b)** pure NR (T0-D0) and extracted T-NRs (T0.5-D0.05, T1-D0.1, T1.5-D0.15), including enlarged details

Comparing with pure NR (T0-D0), the stretching vibration peaks of carbonyl groups (C=O) in TMPMP around 1735 cm^{-1} (**Figure S1 (a)**) have been retained in the extracted T-NRs (enlarged details in **Figure S1 (b)**), which proves the successful grafting of TMPMP on NR.

The interfacial adhesive energy (W_{rf}) between rubber and filler could be calculated by Fowkes model [26], which is an effective criterion for evaluating the interfacial interaction degree between rubber and filler:

$$W_{rf} = 2\left(\sqrt{\gamma_r^d \gamma_f^d} + \sqrt{\gamma_r^P \gamma_f^P}\right) \quad \textbf{(S1)}$$

where γ_r^d and γ_r^P are dispersive and polar part of surface energy for rubber, respectively, and γ_f^d and γ_f^P are dispersive and polar part of surface energy for filler, respectively. The surface energy (γ) and its dispersive/polar part (γ_D/γ_P) for NR and VMQ were measured in our earlier study [9], and the surface energy of silica has referred to the result of Heinrich et al [27], for the same brand VN3 used, then the W_{rf} was determined as listed in **Table S1**. The higher W_{rf} of NR-silica than that of VMQ-silica indicates the stronger interfacial interaction between NR phases and silica.

In addition, according to **Equation (S2)**, the interfacial energy (γ_{12}) between any two components is correlated to their surface energy γ_1 and γ_2, then the phase selective distribution of silica could be further assessed by the wetting coefficient ($\omega_{NR\text{-}VMQ}$) [28], which is a function of interfacial energy among silica, NR and VMQ: $\gamma_{silica\text{-}NR}$, $\gamma_{silica\text{-}VMQ}$ and $\gamma_{NR\text{-}VMQ}$. As for $\omega_{NR\text{-}VMQ} > 1$, silica would distribute in NR phases; with regard to $\omega_{NR\text{-}VMQ} < -1$, silica would distribute in VMQ phases; when $-1 < \omega_{NR\text{-}VMQ} < 1$, silica would distribute at the interface of the two phases.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1\gamma_2)^{\frac{1}{2}} \quad \textbf{(S2)}$$

$$\omega_{NR-VMQ} = \frac{(\gamma_{silica-VMQ} - \gamma_{silica-NR})}{\gamma_{NR-VMQ}} \quad \textbf{(S3)}$$

Corresponding interfacial energy and wetting coefficient have also been determined in **Table S1**. As for $\omega_{NR\text{-}VMQ} = 9 >> 1$, demonstrating the selective location tendency of silica in NR phases.

Therefore, these two parameters: W_{rf} and $\omega_{NR\text{-}VMQ}$, could both reasonably explain the reason why part of pre-mixed silica in VMQ/silica master-batch has migrated from VMQ phases internal into NR phases after compounding, as the result shown in **Figure 4**.

Table S1. Surface energy (γ) and its dispersive/polar part (γ_D/γ_P) for NR, VMQ and silica; interfacial adhesive energy (W_{rf}), interfacial energy (γ_{12}) among them (NR-silica, VMQ-silica, NR-VMQ) and wetting coefficient ($\omega_{NR\text{-}VMQ}$)

Surface energy (mN/m)	Total γ	Dispersive part (γ_D)	Polar part (γ_P)
NR	25.2	25.2	0
VMQ	23.0	23.0	0
silica	34.9	19.7	15.2

Interfacial adhesive energy (mN/m)	W_{rf}
NR-silica	44.6
VMQ-silica	42.6
Interfacial energy (mN/m)	γ_{12}
NR-silica	0.79
VMQ-silica	1.24
NR-VMQ	0.05
Wetting coefficient	$\omega_{NR\text{-}VMQ}$
	9

RPA was conducted to investigate the agglomeration degree of silica in composites, the storage modulus (*G'*)-strain sweeping curves of T-NR/VMQ composites are shown in **Figure S2**. The high *G'* level at lower strains and its rapid decrease at higher strains is called Payne effect [29], which is mainly caused by the existence of filler network under lower strains and its progressive collapse and destruction under higher strains. The more *G'* decrease amplitude ($\Delta G'$), the stronger structure of filler network, the worse dispersion of filler in rubber matrix, the lower rubber-filler interaction. As could be seen, with the increase of TMPMP grafting degree, the $\Delta G'$ gradually decreases, which indicates the weakened filler network, the explanations for this result are as below: as discussed above, due to the small amount of silica (10.5 phr) was pre-mixed in VMQ/silica master-batch, after compounding with NR, part of silica has migrated into the large amount of NR matrix (70 phr), which is helpful to weaken the packing of silica network; besides, under the

modification via TMPMP, the smaller sized and more evenly distributed VMQ phases in NR matrix is another assistance to facilitate a more homogeneous dispersion of silica in composites.

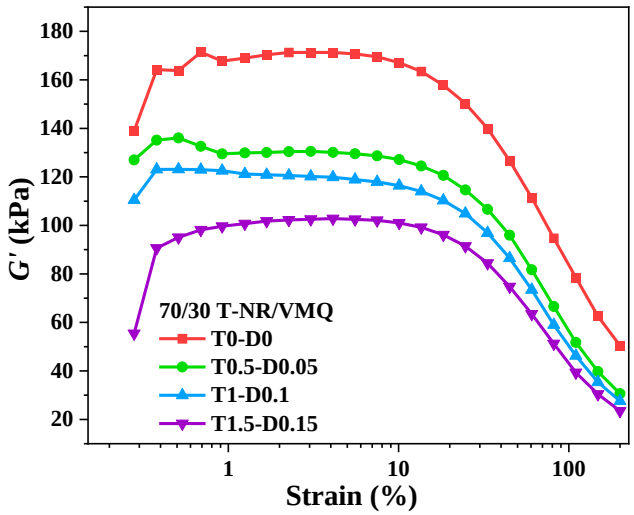
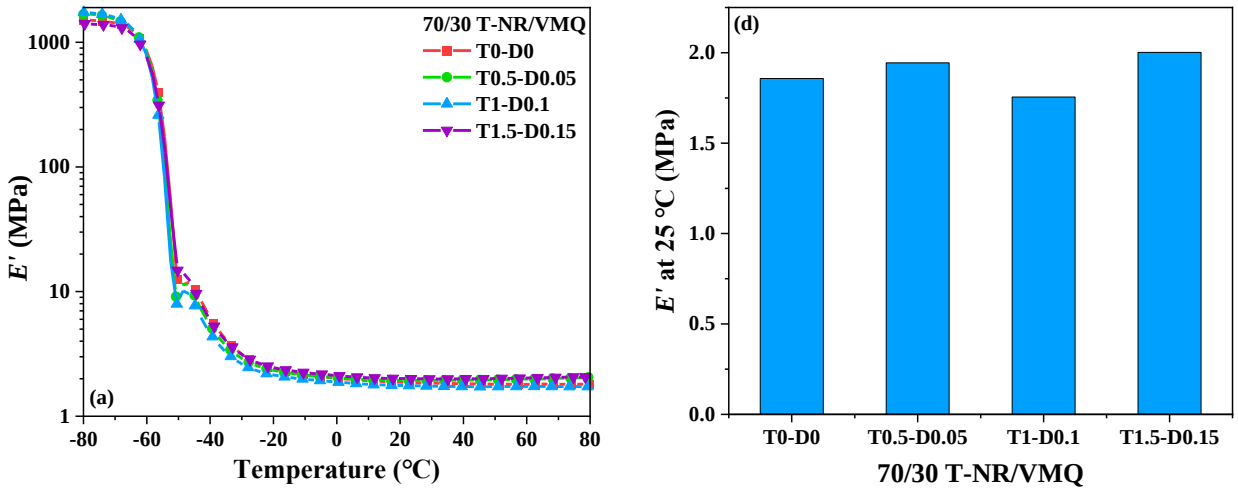


Figure S2. RPA storage modulus (*G'*)-strain sweeping curves of T-NR/VMQ composites

The temperature dependency of storage modulus (*E'*), loss factor (*tan δ*) and loss compliance modulus (*J''*) measured via DMTA is shown in **Figure S3 (a)-(c)**, respectively, and the corresponding values at 25 ℃ (consistent with the testing temperature of dynamic fatigue crack growth) are listed in the histograms of **Figure S3 (d)-(f)**, respectively.



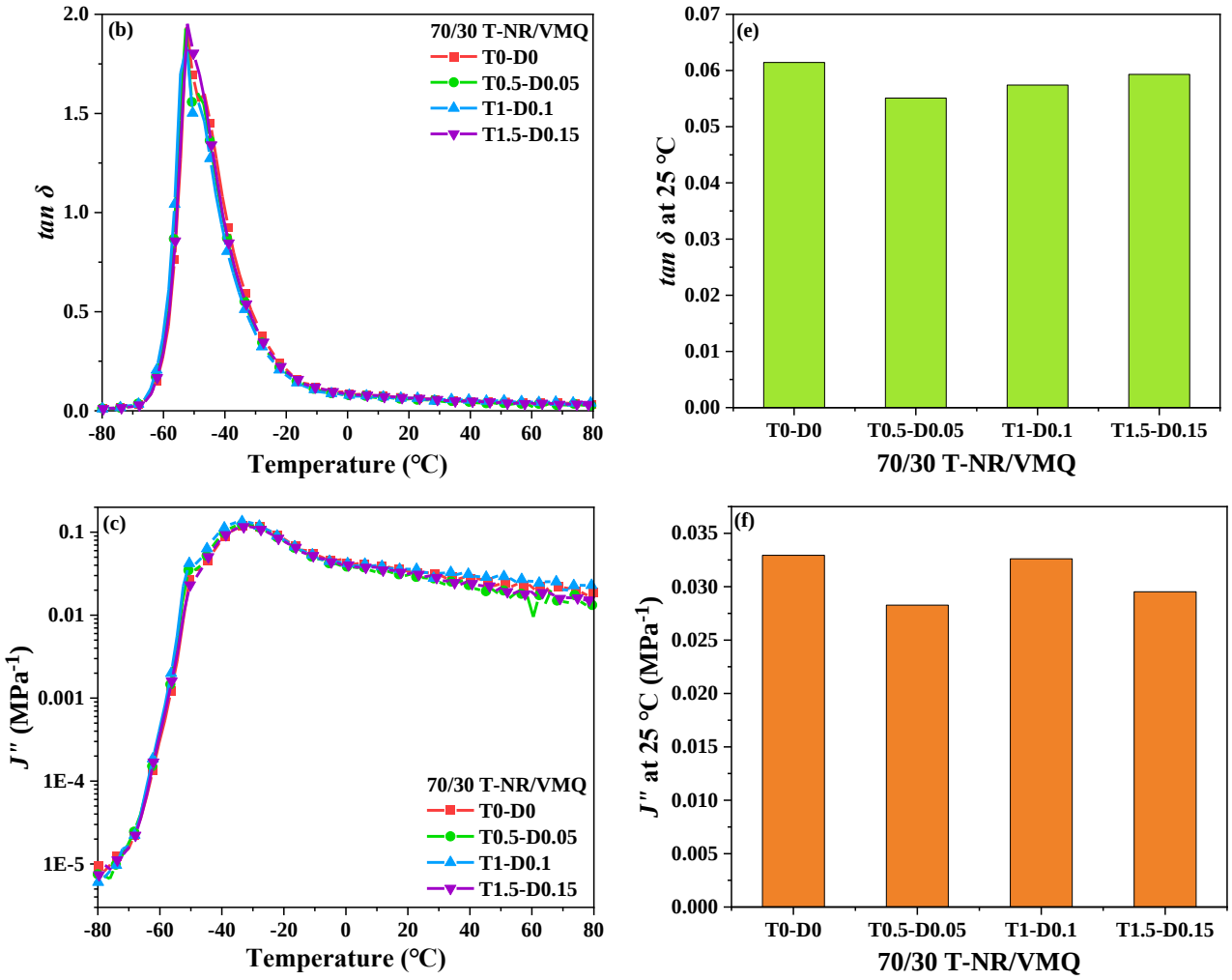


Figure S3. Temperature dependency of **(a)** storage modulus (*E'*), **(b)** loss factor (*tan δ*) and **(c)** loss compliance modulus (*J''*); **(d)-(f)**: corresponding values at 25 ℃ for T-NR/VMQ composites via DMTA

The cyclic stress-strain curves recorded in the real-time during crack growth are shown in **Figure S4**, as for the strain amplitude is about 20 %, the composites exhibit approximately a linear stress-strain behavior, which is consistent with the hypothesis of **Equation (3)** for Persson's theory.

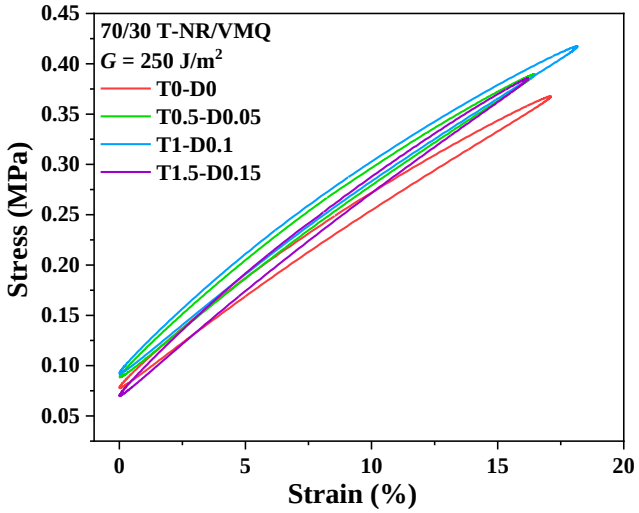


Figure S4. The cyclic stress-strain curves during crack growth for T-NR/VMQ composites