Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Molecular Interfacial Structure and Plasticizer Migration Behavior of "Green" Plasticized Poly (vinyl chloride)

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SFG and CARS system

The EKSPLA SFG system used in this research is composed of a pico-second laser, a harmonics unit, an optical parametric generation (OPG)/optical parameter amplification (OPA)/difference frequency generation (DFG) system and a detection system. To be specific, the output of the Nd:YAG laser is a 20 Hz, 20 ps 1064 nm near-IR beam. The visible 532 nm input beam for SFG experiments is generated by frequency-doubling part of this 1064 nm IR beam. The IR input beam for SFG study is frequency tunable (from 1000 cm^{-1} to 4300 cm^{-1}). For all the SFG experiments performed here, the incident angles of the visible and the IR input beams were 60° and 55° with respect to the surface normal, respectively. The diameters of the two input beams at the surface were around 500 µm. ssp (s-polarized signal output, s-polarized visible input, and p-polarized IR input) polarization combination was used in all SFG experiments.

As shown in our previous work, our SFG system can be easily converted to a CARS system.[1] For CARS experiments, the 532 nm visible beam was overlapped with a frequency tunable visible beam generated from the OPG/OPA system other than the frequency tunable IR beam. In this paper, all CARS spectra were collected using the ssss polarization combination (s polarized signal output, pump, probe, and Stokes input beams). Both SFG and CARS spectra were measured using the reflection geometry (Figure S1). For each sample, spectra were collected at least at five different spots; for each spot, five spectra were detected to examine the film homogeneity and reduce the influence of the detection noise.

FTIR system

FTIR experiments were performed using a Nicolet Magna 550 spectrometer in transmission mode. Each spectrum shown in this paper was collected with a resolution of 4 cm^{-1}, 128 scans, and in the wavenumber range of 1000 to 3200 cm^{-1}. CaF_2 windows were used as substrates. The FTIR sample chamber was purged with nitrogen gas during and before measurements to avoid interferences from water or CO_2 in the atmosphere.

Surface static contact angle

Static water contact angle measurements were performed using a CAM 100 Optical Contact Meter (KSV Instruments). At least three samples of each type of plasticized polymer were used for contact angle goniometry measurements. Water contact angles were measured on four spots on each sample and then averaged.

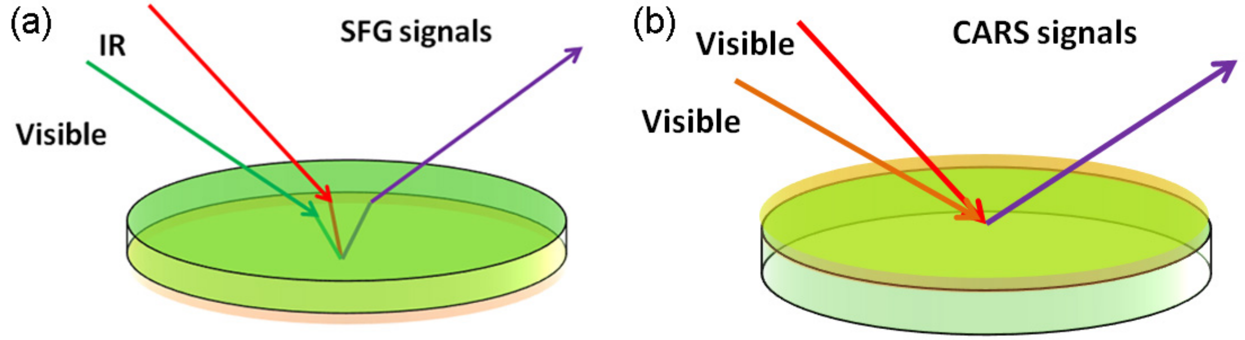

Figure S1 Schematic illustration of SFG samples using window face-down geometry (a) and CARS sample window face-up geometry (b).

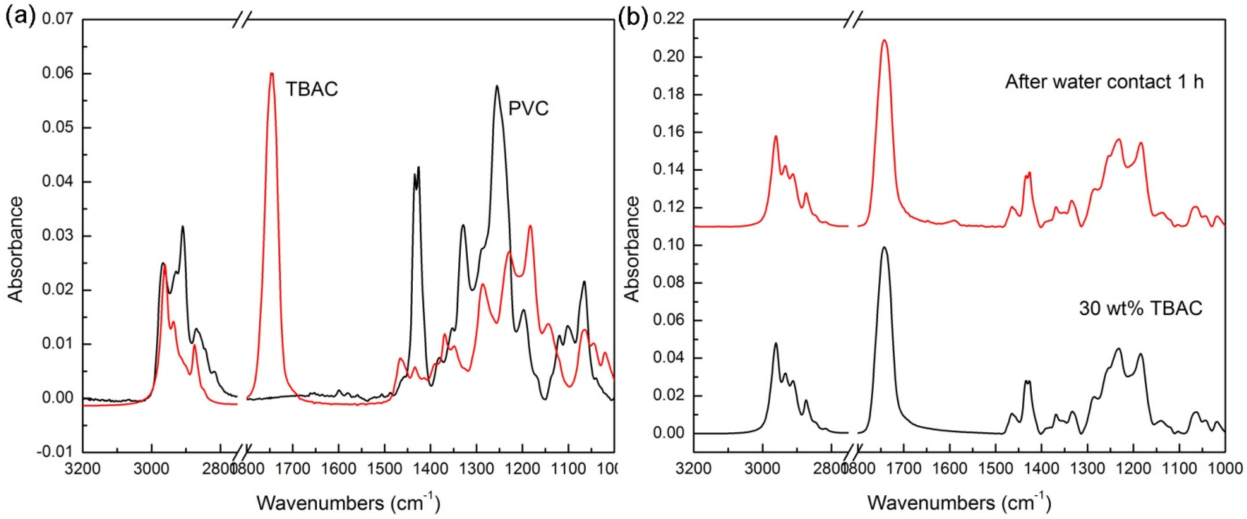

Figure S2 FTIR spectra of pure PVC and TBAC (a), as well as 30 wt% TBAC before and after water contact for 1 h (b).

Representative FTIR spectra of pure PVC, TBAC thin films and 30 wt% TBAC thin film before and after exposing to water for 1 h are shown in Figure S2 (a) and S2(b) respectively. For pure PVC, a pronounced peak around 2906 cm^{-1} (assigned to the symmetric stretching mode of CH_2) is observed in the CH stretching frequency region (2800-3000 cm^{-1}). Two strongest peaks, one around 1428 cm^{-1} assigned to the CH bending mode and the other at 1256 cm^{-1} contributed from CH_2 bending modes, were chosen to represent PVC in the FTIR spectra in the fingerprint region (1000-1800 cm^{-1}). In contrast, for pure TBAC, two peaks around 1725 cm^{-1} (C=O stretch) and 1280 cm^{-1} (conjugated aromatic ester COO groups in citrate) were chosen to represent the plasticizer in the fingerprint region.[2-4]

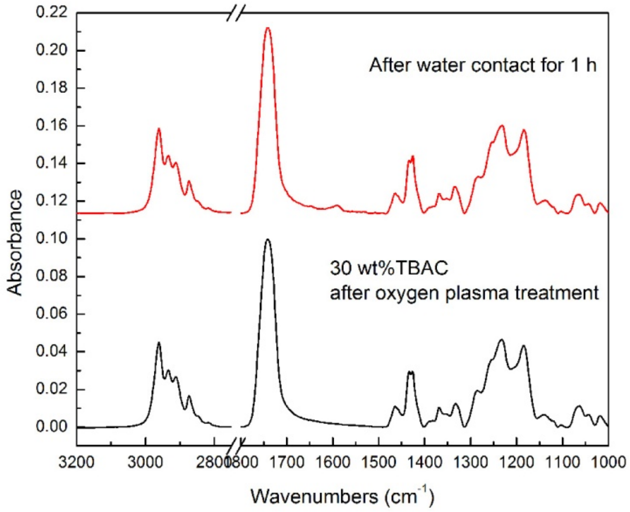

Figure S3 FTIR spectra of 30 wt% TBAC after oxygen plasma treatment and before and after water contact for 1 h.

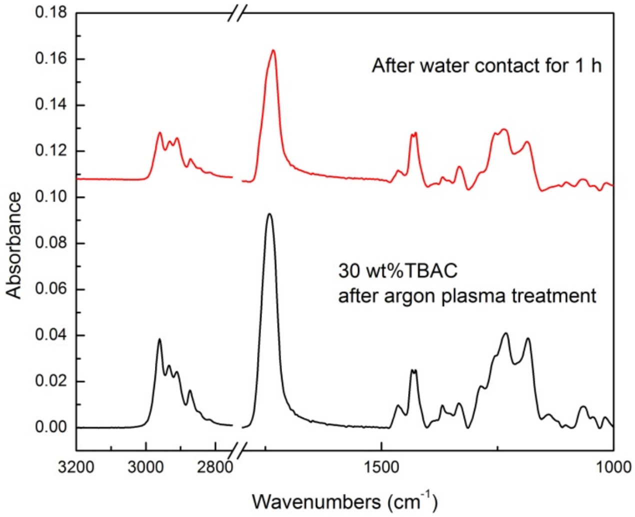

Figure S4 FTIR spectra of 30 wt% TBAC after argon plasma treatment and before and after water contact for 1 h.

Table S1. Polar and dispersive surface energy components of the three liquids used [5, 6]

Test liquids	**γ_l (mJ/m^2)**	**γ_l^p (mJ/m^2)**	**γ_l^d (mJ/m^2)**
Water	72.8	51.0	21.8
Methylene Iodide	50.8	0	50.8
Glycerol	64.0	30.0	34.0

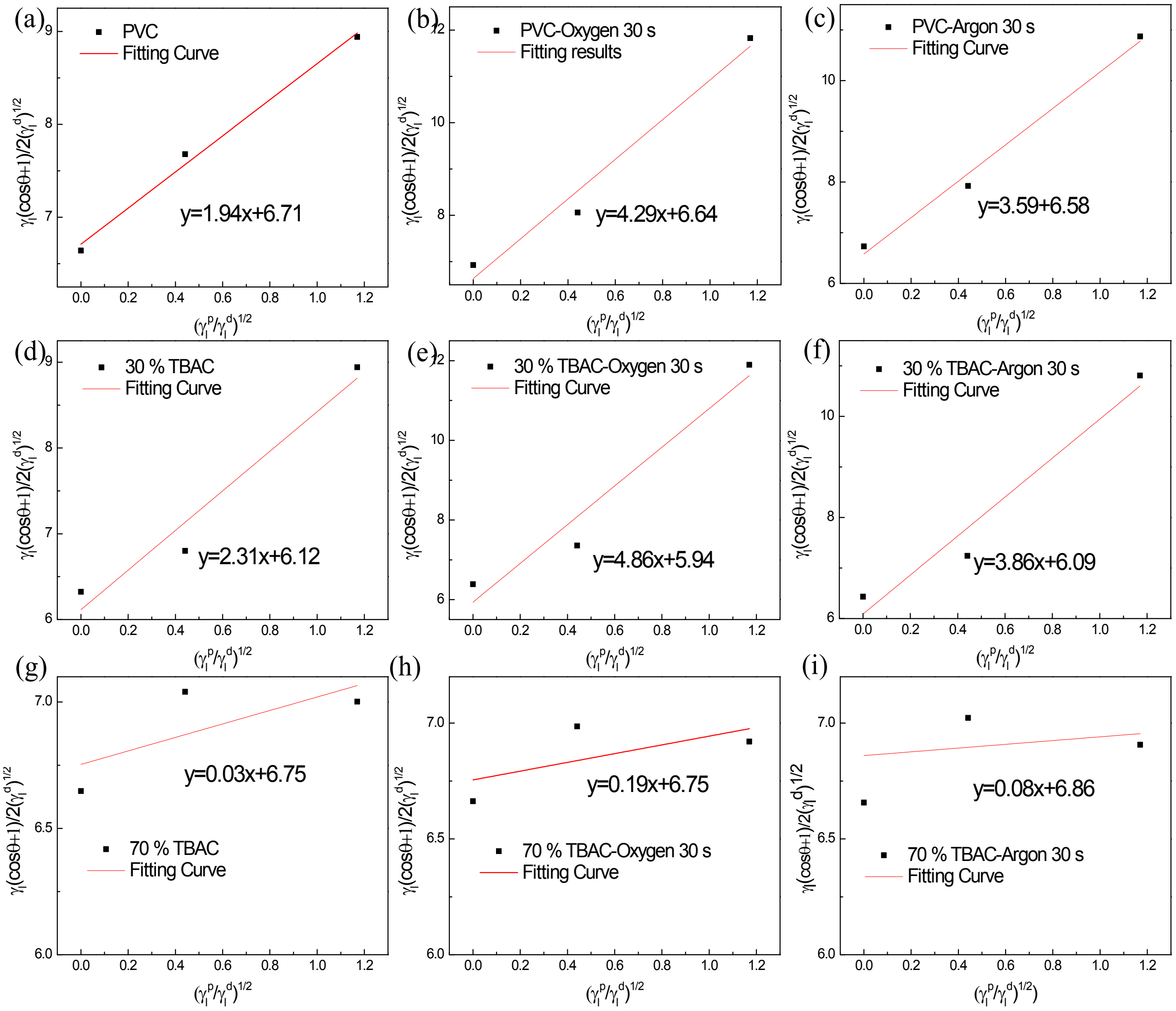

Figure S5 Contact angle plots and fitting results using the Owen-Wendt model for (a) - (c) PVC, (d) - (f) 30 % TBAC, and (g) – (i) 70 % TBAC before and after oxygen or argon plasma treatment.

Various models are commonly used to characterize surface energies and debates on the accuracy of these models are ongoing.[5-7] Here we measured the contact angles of three liquids including water, methylene iodide and glycerol on various sample surfaces, and then choose a widely-used Owens-Wendt (extended Fowkes) model to calculate the polar and nonpolar (dispersive) components of the surface energy (Table S1). In this model, surface energy dissociates liquid (l, the media which is used to perform contact angle measurements) and solid (s, the surface under investigation) surface energy into its polar and nonpolar components:

$$\frac{\gamma_l(\cos\theta + 1)}{2(\gamma_l^d)^{1/2}} = (\gamma_s^p)^{1/2}\frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}} + (\gamma_s^d)^{1/2}$$

equation 1[8]

Where γ_l is the liquid surface free energy, and γ_l^p and γ_l^d are the liquid surface energy polar and nonpolar components, respectively. Similarly, γ_s is the solid surface free energy, and γ_s^p and γ_s^d are the solid surface energy polar and nonpolar components, respectively. θ is the surface contact angle. The liquid polar and nonpolar components are known (listed in Table S1), and the surface contact angles on sample surfaces using different testing liquids were measured (listed in table 1).

Plotting the value on the left side of equation 1 as a function of value $\frac{(\gamma_l^p)^{1/2}}{(\gamma_l^d)^{1/2}}$, produces a line of data points (shown in Figure S5). By fitting the data points with a line, we can deduce the γ_s^p term as the square of the slope and the γ_s^d term as the square of the intercept. The corresponding

Owen-Wendt plots for various PVC/TBAC samples before and after plasma treatment are also exhibited in Figure S5. By squaring the slope and intercept in the fitting curve (insets of Figure S5), we can thus get surface energy values and the two polar and nonpolar components for the PVC/TBAC samples. (Table 1)

References:

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