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Electronic Supplementary Information

Revealing the Dynamic Heterogeneity of PMMA/PVDF Blends: From the Microscopic Dynamics to Macroscopic Properties

Bo Lu,[a] *Khalid Lamnawar,*[b, *] *Abderrahim Maazouz,*[a, c, *] *Huagui Zhang* [a, d]

[a] Université de Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, INSA Lyon, F-69621, Villeurbanne, France;

[b] Université de Lyon, CNRS, UMR 5259, LaMCoS, Laboratoire de Mécanique des Contacts et des Structures, INSA Lyon, F-69621, Villeurbanne, France;

[c] Hassan II Academy of Science and Technology, Rabat, Morocco;

[d] School of Chemical and Process Engineering, University of Leeds, LS2 9JT, Leeds, United Kingdom.

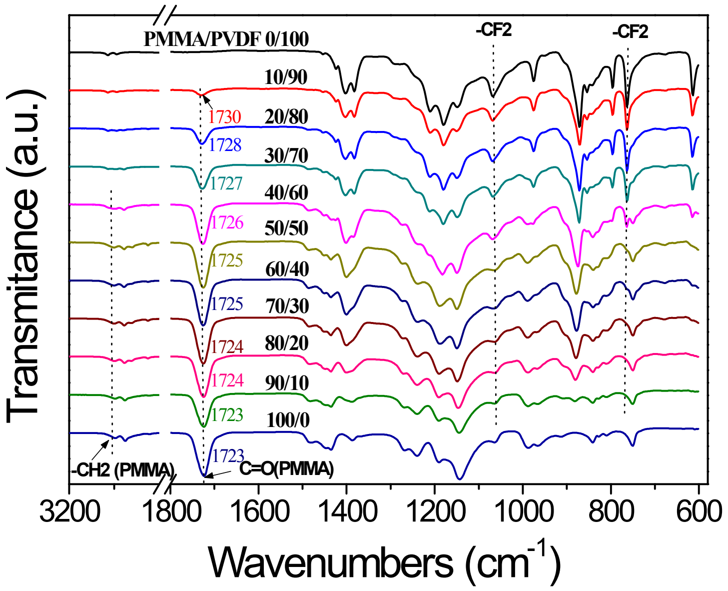

Fig. S1 FTIR spectrum of PMMA/PVDF blends with various compositions.

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[*] Corresponding authors:

khalid.lamnawar@insa-lyon.fr (K. Lamnawar);

abderrahim.maazouz@insa-lyon.fr (A. Maazouz)

Fig. S1 illustrates the FTIR spectra of PMMA/PVDF blends with various compositions. It is clear that the stretching frequency at 1723 cm^{-1}, which corresponds to the characteristic C=O of PMMA, is continuously shifted to higher wavenumbers with increasing PVDF fraction and reaches 1730 cm^{-1} in the PMMA/PVDF (10/90) blends. PVDF-rich blends show the greater shift, whereas blends with intermediate compositions display the moderate shift. This shift observed in the carbonyl stretching frequencies of blends compared to pure PMMA is due to specific interaction (*i.e.* hydrogen bonding) between carbonyl groups of PMMA and -CH_2 groups of PVDF and also indicates the formation of blends Meanwhile, PMMA –CH_2 stretching vibration at 2995 cm^{-1} is shifted to the higher wavenumbers, coupled with PVDF –CF_2 bending mode at 763 cm^{-1} and stretching vibration at 1068 cm^{-1} to the lower wavenumbers with the inclusion of PVDF, indicates the dipole-dipole interactions between -CH_2 of PMMA and -CF_2 in PVDF.

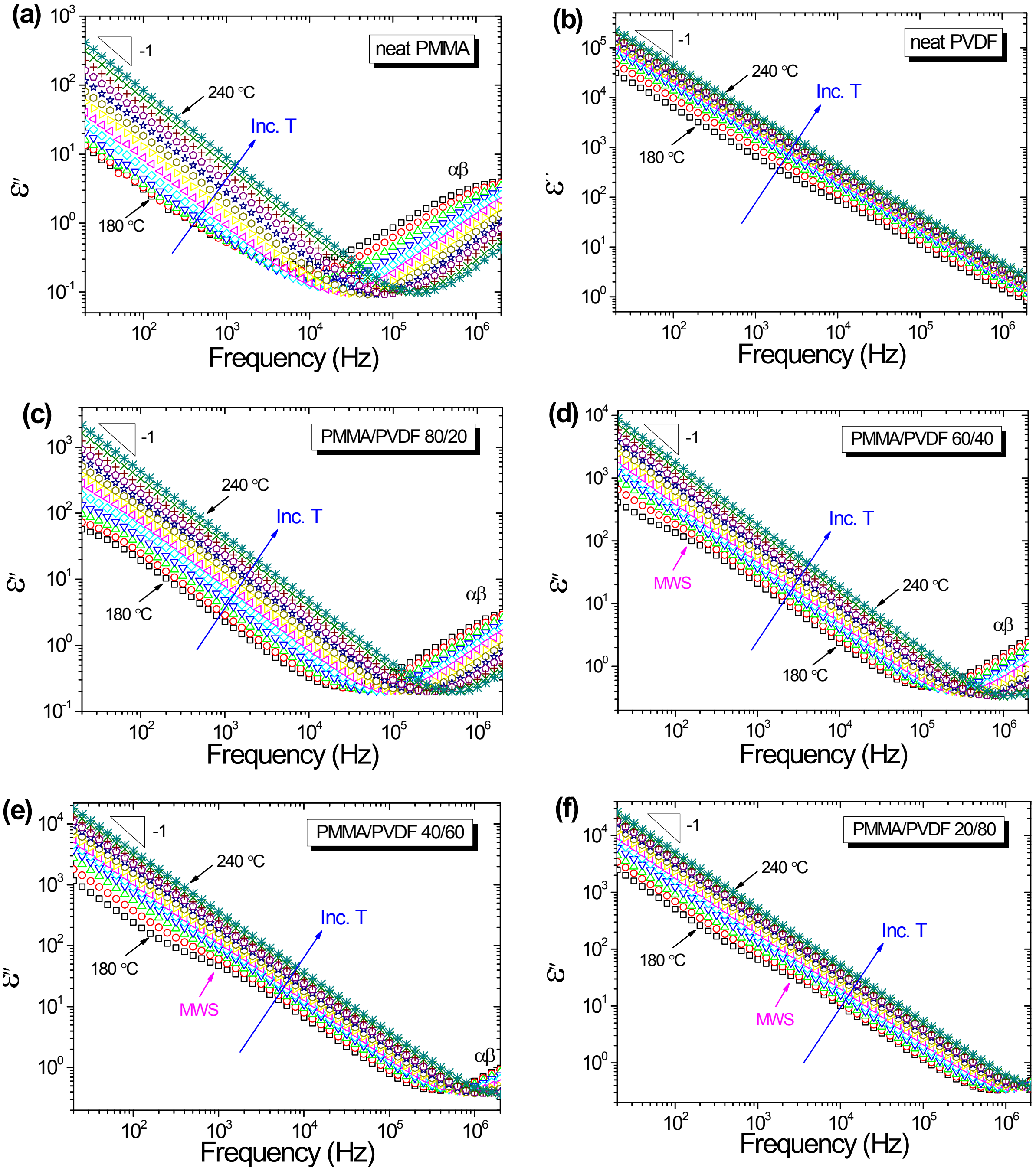

Fig S2. Dielectric loss ε'' as a function of frequency with temperature ranging from 180 °C to 240 °C (5 °C increment) for (a) neat PMMA; (b) neat PVDF; (c) PMMA/PVDF (80/20); (d) PMMA/PVDF (60/40); (e) PMMA/PVDF (40/60); (f) PMMA/PVDF (20/80)

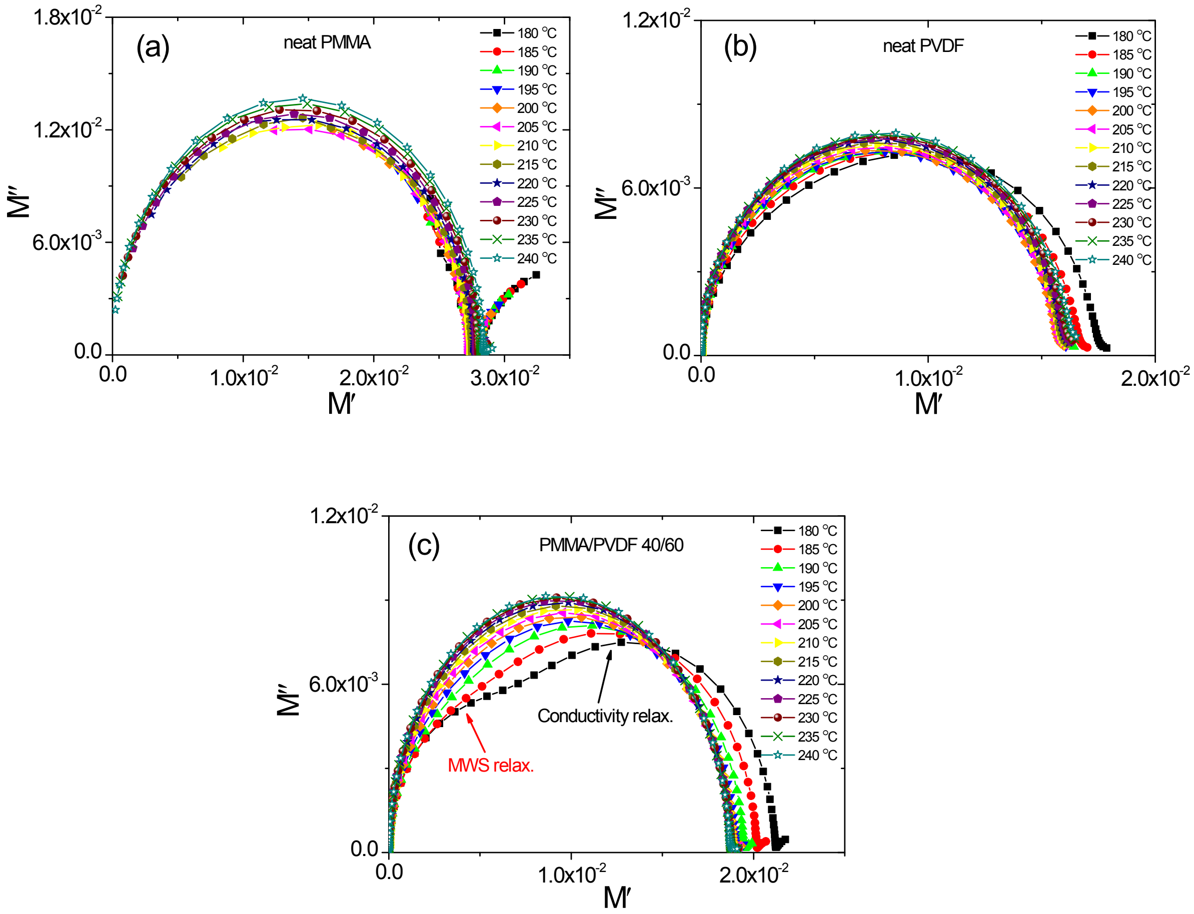

Fig. S3 Cole-Cole plots for neat PMMA (a), neat PVDF (b), and PMMA/PVDF 40/60 blend (c)

Fig. S3 maps the Cole-Cole plots of *M″ versus M′* in the frequency domain for neat PMMA, PVDF and PMMA/PVDF blends. Here, PMMA/PVDF (40/60) blend is representatively chosen to demonstrate the local heterogeneity. For neat PMMA at higher temperatures, a single semicircular arc in the Cole-Cole plots is complete and ceases at the origin, which is clearly the sign of DC conductivity. At comparatively low temperatures, the semicircle does not reach its origin and is accompanied by a small tail concerning *αβ* relaxation. For neat PVDF, the single semicircular arc is complete and ends at the origin. Whereas, in the case of the PMMA/PVDF (40/60) blend, two semicircles are obtained at low temperatures, manifesting a bimodal relaxation time distributions and therefore dynamic heterogeneity. The first for $0 < M' < 0.01$ is attributed to the MWS relaxation and second for $0.01 < M' < 0.02$ is related to the conductivity relaxation.

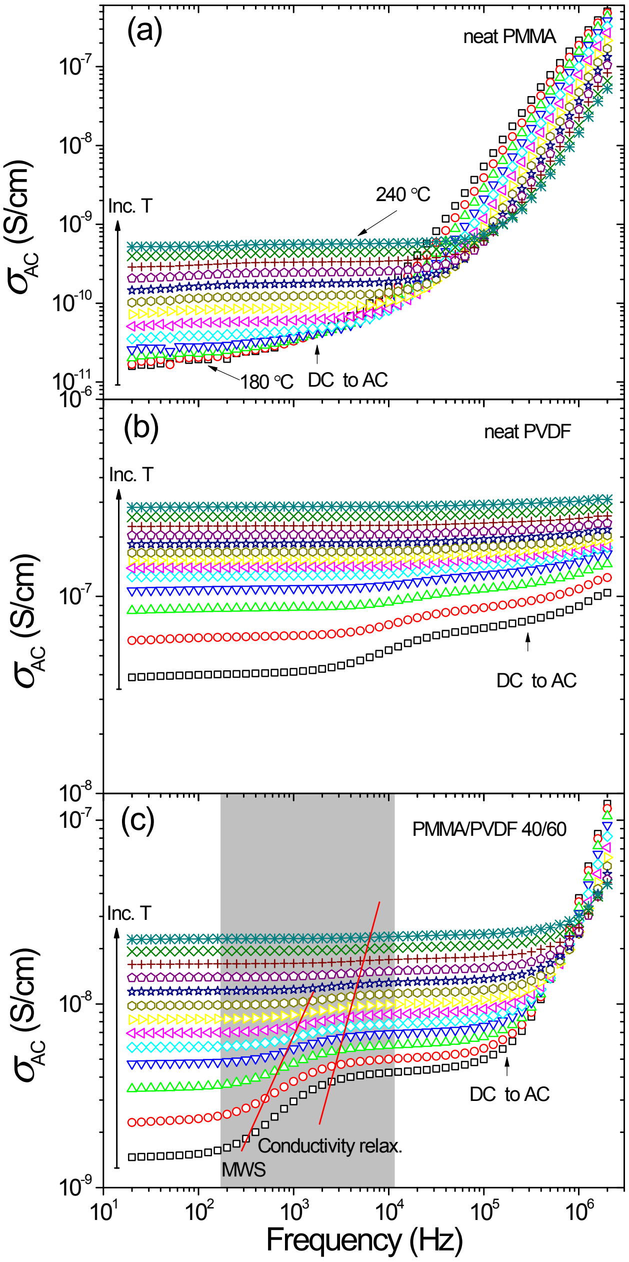

Fig. S4 Alternating current conductivity (σ_{AC}) as a function of frequency at different temperatures ranging from 180 °C to 240 °C (5 °C increment) for (a) neat PMMA, (b) neat PVDF, (c) PMMA/PVDF (40/60) blend

Fig. S4 depicts the alternating current conductivity (σ_{AC}) as a function of frequency at different temperatures for neat PMMA and PVDF, and PMMA/PVDF (40/60) blends. It can be noticed that for neat polymers σ_{AC} exhibit a nearly frequency independent plateau at low frequencies, corresponding to the typical DC conductivity region. It suggests that the high degree of ε'' at lower frequency is mainly ascribed to the long-range migration of charge carriers (DC conductivity). It is also apparent that this DC conductivity effect increases and shifts to the higher frequencies when increasing temperature. The DC conductivity is observed to gradually decrease and AC conductivity becomes prominent at higher frequencies due to the trapping of free charges to potential wells. The transition region from DC frequency-independent to AC frequency-dependent conductivity shifts to higher frequencies with increasing temperature. By contrast, the DC-to-AC transition for PMMA/PVDF (40/60) blend occurs at higher frequency regions. Aside from the DC-to-AC transition, PMMA/PVDF (40/60) blend also demonstrates a broader dispersion step at lower frequency regions, which is more pronounced at lower temperatures (the gray frame). The emerged dispersion step cannot be resolved only at temperatures above 220 ^{o}C. It is easily understood that the onset of the step is related to the accumulation of charge carriers and their local motion at the interfaces (MWS), and the end of the step indicates the transition from long-range to short range hopping of charge carriers in the bulk (conductivity relaxation); the plateaus on the left and right side of the step are assigned to the long-range migration of charge carriers, respectively. The decoupled charge carrier transports, including the hopping of charge carriers at the interface and the bulk, lead to the bimodal loss peak in the electric loss modulus.

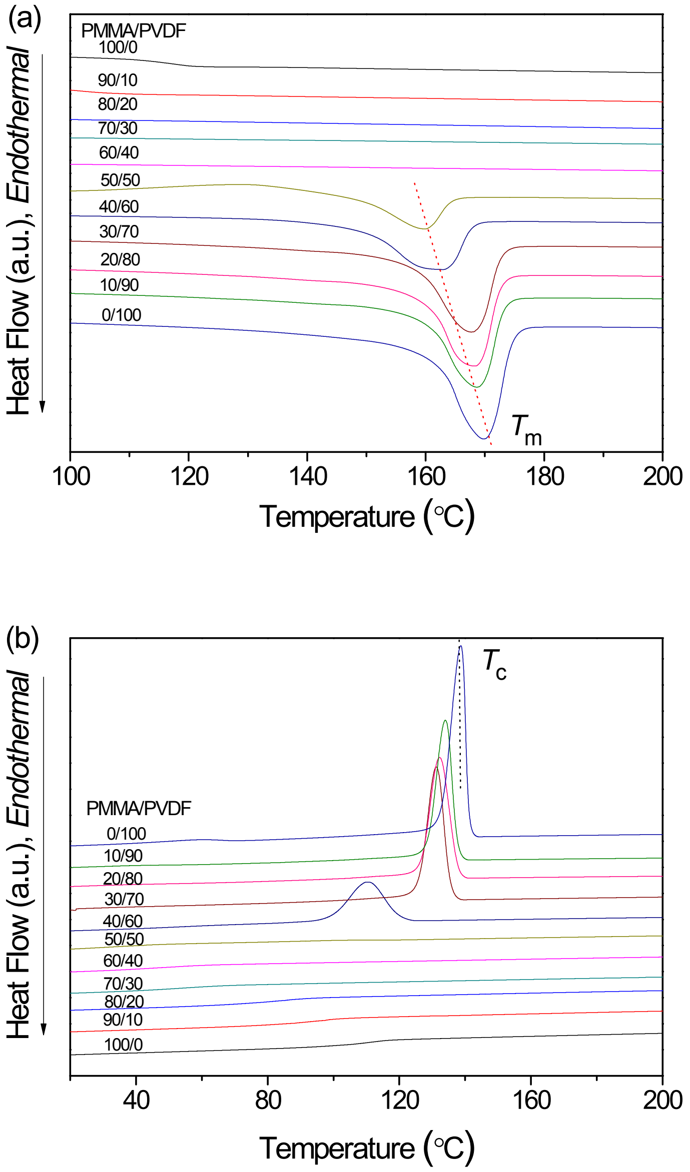

Fig. S5 DSC thermograms for PMMA/PVDF blends with various compositions. (a) Heating scan; (b) cooling scan.

Table S1 Melting temperatures, crystallization temperatures, and crystallinity of PMMA/PVDF blends calculated from DSC scans

PMMA/PVDF (v/v)	T_m (°C) [a]	T_c (°C) [c]	X_c (%) [c]
100/0	-	-	-
90/10	-	-	-
80/20	-	-	-
70/30	-	-	-
60/40	-	-	-
50/50	159.81	-	8
40/60	162.97	110.92	44
30/70	167.72	131.23	51
20/80	168.24	132.25	54
10/90	168.65	133.97	57
0/100	169.80	138.68	59

[a] Melting temperatures (T_m) was taken from the second heating scan, crystallization temperatures (T_c) taken from exothermal peak in the cooling run, respectively.

[b] Crystallinity was calculated according to: $X_c(\%) = \Delta H_m / w \Delta H_m^0$, where ΔH_m is the experimental enthalpy of fusion, w is the weight content of PVDF in blends, ΔH_m^0 is the standard heat of fusion for 100% crystalline PVDF (*i.e.* 104.6 J/g).