 

Figure SD1. A comparison between the imaginary parts of (a) dielectric permittivity and (b) electric modulus, as a function of frequency at varying temperatures for the PE\_30 sample.



Figure SD2. The imaginary part of electric modulus as a function of frequency varying temperature for the PE\_30 sample. The dots represent the experimental data while the lines are the superposition of the Havriliak-Negami fits.

Table SD1. All the parameters used for the Havriliak-Negami function model in the form of complex electric modulus (Figures 4).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| T (oC) | Process | $$M\_{\infty }$$ | $$M\_{s}$$ | $$τ$$ | *β* | *γ* |
| 50 | γ2- | 0.05990 | 0.04235 | 1.67E-05 | 0.815 | 0.190 |
| γ1- | 0.04500 | 0.04235 | 6.72E-05 | 1.000 | 0.658 |
| αc- | 0.04437 | 0.04235 | 1.11E-02 | 0.871 | 1.000 |
| βdis- | 0.04330 | 0.04234 | 8.14E-02 | 0.761 | 1.000 |
| βent- | 0.04234 | 0.04234 | - | - | - |
| IP- | 0.04234 | 0.04234 | - | - | - |
| 60 | γ2- | 0.05960 | 0.04235 | 1.32E-05 | 0.815 | 0.210 |
| γ1- | 0.04410 | 0.04235 | 4.42E-05 | 1.000 | 0.658 |
| αc- | 0.04445 | 0.04235 | 5.57E-03 | 0.871 | 1.000 |
| βdis- | 0.04350 | 0.04234 | 5.45E-02 | 0.761 | 1.000 |
| βent- | 0.04234 | 0.04234 | - | - | - |
| IP- | 0.04234 | 0.04234 | - | - | - |
| 70 | γ2- | 0.05900 | 0.04235 | 8.65E-06 | 0.815 | 0.220 |
| γ1- | 0.04350 | 0.04235 | 1.38E-05 | 1.000 | 0.658 |
| αc- | 0.04415 | 0.04235 | 1.28E-03 | 0.945 | 1.000 |
| βdis- | 0.04420 | 0.04244 | 1.28E-02 | 0.761 | 1.000 |
| βent- | 0.04300 | 0.04200 | 4.07E-01 | 0.761 | 1.000 |
| IP- | 0.04234 | 0.04234 | - | - | - |
| 80 | γ2- | 0.05820 | 0.04235 | 4.29E-06 | 0.815 | 0.230 |
| γ1- | 0.04330 | 0.04235 | 7.67E-06 | 1.000 | 0.658 |
| αc- | 0.04430 | 0.04235 | 4.50E-04 | 0.965 | 1.000 |
| βdis- | 0.04490 | 0.04244 | 5.61E-03 | 0.761 | 1.000 |
| βent- | 0.04354 | 0.04254 | 1.63E-01 | 0.761 | 1.000 |
| IP- | 0.04234 | 0.04234 | - | - | - |
| 90 | γ2- | 0.05610 | 0.04235 | 2.09E-06 | 0.815 | 0.240 |
| γ1- | 0.04320 | 0.04235 | 3.45E-06 | 1.000 | 0.658 |
| αc- | 0.04450 | 0.04235 | 1.56E-04 | 0.948 | 1.000 |
| βdis- | 0.04585 | 0.04244 | 2.42E-03 | 0.625 | 1.000 |
| βent- | 0.04460 | 0.04254 | 1.52E-01 | 0.715 | 1.000 |
| IP- | 0.04220 | 0.03900 | 2.46E+00 | 1.000 | 1.000 |
| 100 | γ2- | 0.05420 | 0.04235 | 7.25E-07 | 0.815 | 0.260 |
| γ1- | 0.04330 | 0.04235 | 1.80E-06 | 1.000 | 0.658 |
| αc- | 0.04430 | 0.04235 | 5.25E-05 | 0.953 | 1.000 |
| βdis- | 0.04780 | 0.04244 | 8.62E-04 | 0.561 | 1.000 |
| βent- | 0.04540 | 0.04254 | 1.13E-01 | 0.791 | 1.000 |
| IP- | 0.04200 | 0.03850 | 1.74E+00 | 1.000 | 1.000 |
| 110 | γ2- | 0.05370 | 0.04235 | 2.85E-07 | 0.802 | 0.260 |
| γ1- | 0.04320 | 0.04235 | 7.64E-07 | 1.000 | 0.658 |
| αc- | 0.04470 | 0.04235 | 2.36E-05 | 0.965 | 1.000 |
| βdis- | 0.04880 | 0.04244 | 4.21E-04 | 0.542 | 1.000 |
| βent- | 0.04660 | 0.04254 | 7.26E-02 | 0.742 | 1.000 |
| IP- | 0.04190 | 0.03790 | 1.26E+00 | 1.000 | 1.000 |
| 120 | γ2- | 0.05370 | 0.04235 | 4.43E-08 | 0.802 | 0.260 |
| γ1- | 0.04320 | 0.04235 | 3.10E-07 | 1.000 | 0.658 |
| αc- | 0.04495 | 0.04235 | 1.08E-05 | 0.935 | 1.000 |
| βdis- | 0.05020 | 0.04244 | 1.98E-04 | 0.487 | 1.000 |
| βent- | 0.04790 | 0.04254 | 5.12E-02 | 0.647 | 1.000 |
| IP- | 0.04150 | 0.03650 | 1.01E+00 | 1.000 | 1.000 |
| 130 | γ2- | 0.04235 | 0.04235 | - | - | - |
| γ1- | 0.04235 | 0.04235 | - | - | - |
| αc- | 0.04510 | 0.04235 | 5.86E-06 | 0.905 | 1.000 |
| βdis- | 0.05150 | 0.04244 | 8.43E-05 | 0.457 | 1.000 |
| βent- | 0.04780 | 0.04254 | 2.75E-02 | 0.657 | 1.000 |
| IP- | 0.04650 | 0.04150 | 8.11E-01 | 1.000 | 1.000 |
| 140 | γ2- | 0.04948 | 0.04948 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05160 | 0.04948 | 1.71E-06 | 0.885 | 1.000 |
| βdis- | 0.05832 | 0.04956 | 1.66E-05 | 0.478 | 1.000 |
| βent- | 0.05152 | 0.04967 | 8.25E-03 | 0.647 | 1.000 |
| IP- | 0.05403 | 0.04863 | 5.05E-01 | 1.000 | 1.000 |
| 150 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04748 | 0.04748 | - | - | - |
| αc- | 0.05110 | 0.04948 | 1.55E-06 | 0.885 | 1.000 |
| βdis- | 0.05832 | 0.04956 | 2.08E-05 | 0.418 | 1.000 |
| βent- | 0.05200 | 0.04967 | 3.70E-03 | 0.586 | 1.000 |
| IP- | 0.05463 | 0.04863 | 3.25E-01 | 1.000 | 1.000 |
| 160 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04748 | 0.04748 | - | - | - |
| αc- | 0.05100 | 0.04948 | 1.48E-06 | 0.765 | 1.000 |
| βdis- | 0.05790 | 0.04956 | 2.07E-05 | 0.418 | 1.000 |
| βent- | 0.05225 | 0.04967 | 2.23E-03 | 0.556 | 1.000 |
| IP- | 0.05463 | 0.04163 | 5.64E-01 | 1.000 | 1.000 |

Table SD2. The R2 from the Arrhenius fittings (Figure 5).

|  |  |
| --- | --- |
| Relaxation | R2 |
| βent-process | 0.93035 |
| βdis-process | 0.98589 |
| αc-process | 0.99634 |
| γ1-process | 0.98660 |
| γ2-process | 0.90763 |

Table SD3. All the parameters used for the Havriliak-Negami function model in the form of complex electric modulus (Figure 6). The same computational approach has been employed to develop the analysis shown in Figure 7 where 21 frequency sweeps were applied at 5 different temperatures.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| n | Process | $$M\_{\infty }$$ | $$M\_{s}$$ | $$τ$$ | *β* | *γ* |
| 1 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05100 | 0.04948 | 1.48E-06 | 0.765 | 1.000 |
| βdis- | 0.05790 | 0.04956 | 2.07E-05 | 0.418 | 1.000 |
| βent- | 0.05225 | 0.04967 | 2.23E-03 | 0.556 | 1.000 |
| IP- | 0.05463 | 0.04163 | 5.64E-01 | 1.000 | 1.000 |
| 2 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05760 | 0.04956 | 2.00E-05 | 0.439 | 1.000 |
| βent- | 0.05325 | 0.04967 | 5.33E-03 | 0.515 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 3 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05760 | 0.04956 | 2.42E-05 | 0.447 | 1.000 |
| βent- | 0.05325 | 0.04967 | 5.33E-03 | 0.541 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 4 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05770 | 0.04956 | 2.79E-05 | 0.457 | 1.000 |
| βent- | 0.05325 | 0.04967 | 5.33E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 5 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 3.09E-05 | 0.461 | 1.000 |
| βent- | 0.05325 | 0.04967 | 5.33E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 6 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 3.50E-05 | 0.461 | 1.000 |
| βent- | 0.05340 | 0.04967 | 5.35E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 7 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 3.79E-05 | 0.461 | 1.000 |
| βent- | 0.05340 | 0.04967 | 5.35E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 8 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 3.99E-05 | 0.461 | 1.000 |
| βent- | 0.05355 | 0.04967 | 5.36E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 9 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 4.70E-05 | 0.478 | 1.000 |
| βent- | 0.05355 | 0.04967 | 5.36E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 10 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 1.86E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 5.09E-05 | 0.478 | 1.000 |
| βent- | 0.05355 | 0.04967 | 5.36E-03 | 0.565 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.35E-01 | 1.000 | 1.000 |
| 11 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.12E-06 | 0.835 | 1.000 |
| βdis- | 0.05780 | 0.04956 | 5.54E-05 | 0.478 | 1.000 |
| βent- | 0.05355 | 0.04967 | 5.36E-03 | 0.582 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 12 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.30E-06 | 0.835 | 1.000 |
| βdis- | 0.05795 | 0.04956 | 5.91E-05 | 0.478 | 1.000 |
| βent- | 0.05350 | 0.04967 | 5.36E-03 | 0.582 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 13 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.37E-06 | 0.835 | 1.000 |
| βdis- | 0.05805 | 0.04956 | 6.32E-05 | 0.478 | 1.000 |
| βent- | 0.05350 | 0.04967 | 5.36E-03 | 0.582 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 14 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.48E-06 | 0.835 | 1.000 |
| βdis- | 0.05815 | 0.04956 | 6.79E-05 | 0.478 | 1.000 |
| βent- | 0.05350 | 0.04967 | 5.36E-03 | 0.582 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 15 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.64E-06 | 0.835 | 1.000 |
| βdis- | 0.05823 | 0.04956 | 7.06E-05 | 0.478 | 1.000 |
| βent- | 0.05350 | 0.04967 | 5.36E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 16 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.73E-06 | 0.835 | 1.000 |
| βdis- | 0.05830 | 0.04956 | 7.97E-05 | 0.478 | 1.000 |
| βent- | 0.05350 | 0.04967 | 5.36E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 17 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 2.73E-06 | 0.835 | 1.000 |
| βdis- | 0.05850 | 0.04956 | 8.35E-05 | 0.478 | 1.000 |
| βent- | 0.05345 | 0.04967 | 5.35E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 18 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 3.27E-06 | 0.835 | 1.000 |
| βdis- | 0.05850 | 0.04956 | 9.16E-05 | 0.478 | 1.000 |
| βent- | 0.05345 | 0.04967 | 5.91E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 19 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 3.64E-06 | 0.835 | 1.000 |
| βdis- | 0.05850 | 0.04956 | 1.02E-04 | 0.478 | 1.000 |
| βent- | 0.05345 | 0.04967 | 5.91E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 20 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 3.99E-06 | 0.835 | 1.000 |
| βdis- | 0.05850 | 0.04956 | 1.11E-04 | 0.478 | 1.000 |
| βent- | 0.05345 | 0.04967 | 5.91E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |
| 21 | γ2- | 0.04798 | 0.04798 | - | - | - |
| γ1- | 0.04948 | 0.04948 | - | - | - |
| αc- | 0.05080 | 0.04948 | 3.99E-06 | 0.835 | 1.000 |
| βdis- | 0.05850 | 0.04956 | 1.18E-04 | 0.478 | 1.000 |
| βent- | 0.05345 | 0.04967 | 5.91E-03 | 0.586 | 1.000 |
| IP- | 0.05407 | 0.04107 | 6.16E-01 | 1.000 | 1.000 |

Table SD4. The R2 employing the linear model of isothermal entanglement formation fittings (Figure 7a).

|  |  |
| --- | --- |
| Temperature (oC) | R2 |
| 80 | 0.98751 |
| 100 | 0.97558 |
| 120 | 0.98198 |
| 140 | 0.98997 |
| 160 | 0.98925 |