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► **To cite this version:**

A. Bartolotta, Giuseppe Carini, Giovanna d'Angelo, G. Di Marco, Sergio La Rocca, et al.. Phase behaviour of thermoplastic interpenetrating polymer networks by thermal and mechanical measurements. *Philosophical Magazine*, 2007, 87 (3-5), pp.723-730. 10.1080/14786430600920821 . hal-00513754

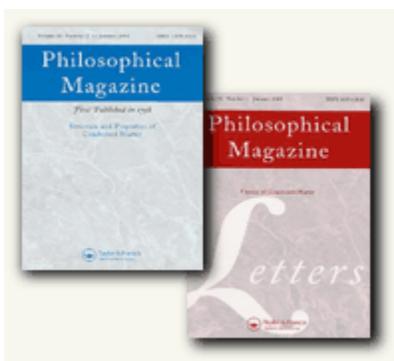
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Submitted on 1 Sep 2010

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Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-06-Apr-0125.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	12-Jul-2006
Complete List of Authors:	Bartolotta, A.; Istituto per i Processi Chimico-Fisici, CNR carini, giuseppe; University of Messina, Dept of Physics D'Angelo, Giovanna; university of messina, physics Di Marco, G.; Istituto per i Processi Chimico-Fisici, CNR La Rocca, Sergio; university of messina, physics Grigoryeva, O.P.; National Academy of Sciences of Ukraine, Institute of Macromolecular Chemistry Sergeeva, Ludmila; National Academy of Sciences of Ukraine, Institute of Macromolecular Chemistry Slisenko, Olga; National Academy of Sciences of Ukraine, Institute of Macromolecular Chemistry Starostenko, O.; National Academy of Sciences of Ukraine, Institute of Macromolecular Chemistry Tripodo, Gaspare; university of messina, physics
Keywords:	amorphous solids, mechanical properties, polymers, thermal properties
Keywords (user supplied):	



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Phase behaviour of thermoplastic interpenetrating polymer networks by thermal and mechanical measurements

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ABSTRACT

31 The phase behaviour of thermoplastic interpenetrating polymer networks based on semi-crystalline
32 polyurethane and a styrene/acrylic acid block-copolymer has been investigated by experiments of
33 differential scanning calorimetry and dynamic mechanical spectroscopy. Distinct calorimetric and
34 mechanical transitions point to an inherent heterogeneity characterizing the structure of
35 thermoplastic networks, mainly due to a weak affinity of the two components. At variance with
36 these observations, deviations from a simple additive law are revealed from the composition
37 behaviour of the melting endotherms associated to polyurethane component and of the γ - and α_a -
38 relaxation strengths. **The quantitative analysis of the low temperature γ -relaxation indicates that the
39 fraction of amorphous chains of polyurethane is enhanced on blending, this result being in close
40 agreement with calorimetric results. All these findings suggest the formation of a mixed amorphous
41 microphase as a consequence of specific weak interactions (H-bonds) between the functional groups
42 of the two components.**

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PACS INDEX: 61.40 km or 62.40+i

§ 1. INTRODUCTION

Thermoplastic interpenetrating polymer networks (*t*-IPNs) are multicomponent polymeric systems and can be considered as hybrid materials between linear polymer blends and classical IPNs whose structure is constructed by physical crosslinks rather than chemical cross-links [1,2]. Their components (semicrystalline polymers, block copolymer and polymer with ionic groups) are characterized by mutual penetration giving rise to a complex morphology: regions mainly built on by segments of one component are matched to regions based on the second component, substantial network interpenetration occurring at the interface. As a consequence, the mechanical properties and the molecular mobility of the whole network is strongly influenced by the domain and interface sizes. Thus *t*-IPNs are cross-linked and behave like IPNs at relatively low temperatures, while at elevated temperatures they show viscoelastic behaviour similar to that of thermoplastics. From this point of view the analysis of the relaxation dynamics represents an appropriate and unequivocal tool to study the coupling mechanism of the polymeric components and to evaluate their thermodynamic compatibility as opposite to some kind of microscopic or nanoscopic inhomogeneity.

Now *t*-IPNs obtained by the introduction of a second reactive polymer, such as block copolymers and/or polymers with ionic groups, to polyurethane (PU) permit to improve its mechanical characteristics which are inappropriate for technological applications as a consequence of the low rigidity and the high thermal expansion coefficient of PU [3]. A recent study [4] concerning the thermal and mechanical properties of one *t*-IPN sample, a blend of 80 wt% of semicrystalline polyurethane (cPU) and 20 wt% of poly(styrene-*b*-potassium acrylate) block copolymer (S-*b*-AK), gave indications about significant deviations of the measured properties from a simple dilution effect, leading to assume the existence of a weak miscibility of the two polymeric components.

In the present work, the structure-property relationships of *t*-IPNs based on blends of cPU and S-*b*-AK have been more widely investigated by extending the interval of compositions examined. The totality of observations, obtained by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA), show and confirm the existence of deviations from a simple additive law which have been associated to a weak, even if limited, compatibility of the individual components.

§ 2. EXPERIMENTAL DETAILS

The crystallisable polyurethane (cPU), the poly(styrene-*b*-acrylic acid) copolymer (S-*b*-AA, acid form) and the poly(styrene-*b*-potassium acrylate) ionomer (S-*b*-AK, salt form) were prepared following the same specific procedure elsewhere described [4,5]. Films of thermoplastic

composites, having compositions $\frac{cPU(wt\%)}{S-b-AK(wt\%)} = \frac{90}{10}, \frac{10}{90}$ and $\frac{5}{95}$ and referred to as *t*-IPNs

[1,6,7], were prepared at several compositions by casting from 20%-solutions in dioxane onto Teflon plates and subsequent evacuation to constant weight. In order to avoid undesirable effects due to contamination from absorbed water moisture [4], the samples were dried at about 330 K under vacuum of 10^{-4} mbar for ~12 h before each run of measurements and then analysed by maintaining the experimental chamber under a controlled atmosphere of nitrogen. Thermograms were determined by using a Perkin-Elmer Pyris1 differential scanning calorimeter (DSC), calibrated with indium and zinc standards. All DSC curves, obtained at a heating rate of 40 Kmin^{-1} , are baseline subtracted and normalized to 1 mg of sample.

Dynamic mechanical thermal properties (storage modulus E' and loss modulus E'') were investigated in the 120÷450 K temperature and 0.3-30 Hz frequency range at heating rate of 2 K/min, using a dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories.

§ 3. RESULTS

3.1 Thermal transitions

DSC traces of *t*-IPNs containing 90, 10 and 5 wt % of cPU (cPU/S-b-AK=90/10, 10/90 and 5/95) are compared in figure 1 to those of pure semi-crystalline cPU, pure amorphous S-b-AK and cPU/S-b-AK=80/20, already reported and discussed [4]. The 90/10 *t*-IPN exhibits a small jump at $T_g \cong 233 \pm 2 \text{ K}$ corresponding to the glass transition of the amorphous regions and a further jump at about 300 K, which overlaps to the distinct endothermic peak at $T_m = 330 \text{ K}$ (heat of melting $\Delta H_m^* = 50 \pm 3 \text{ J g}^{-1}$) associated to the melting of oligomeric butylene adipate glycol (BAG) microcrystals of cPU [4]. *t*-IPNs having weight fractions of 10/90 and 5/95 show sudden, well defined jumps at $T_g \cong 343 \pm 2 \text{ K}$ and $T_g \cong 357 \pm 2 \text{ K}$, corresponding to the glass transition of the S-b-AK component.

3.2. Mechanical transitions

The experimental results for the loss modulus $E''(T)$ at 3 Hz for the 90/10 sample are compared to those previously reported [4] of pure cPU and cPU/S-b-AK=80/20 in figure 2a, while those for the samples with low cPU contents (10/90 and 5/95) are compared to the one of pure S-b-AK [4] in figure 2b. As the temperature is increased from 120 K to 200 K, $E''(T)$ of 90/10 sample (figure 2a) increases and passes through the γ -relaxation peak, located at about the same temperature (158 K at 3 Hz) of the γ -peaks revealed in both pure cPU and 80/20 sample. In the same temperature range the storage modulus $E'(T)$ (figure 2c) shows the corresponding inflexions, whose magnitude increases with decreasing cPU content. Above 200 K, $E''(T)$ shows the large α_a -relaxation peak paralleled by

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3 corresponding drops in $E'(T)$ (figure 2c), which is associated to the primary relaxation due to the
4 cooperative segmental motions of amorphous chains at the glass transition. All the relaxation peaks
5 shift to higher temperatures as the mechanical driving frequency is increased (see the behaviours
6 reported in figure 2d as typical).
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10 The mechanical spectrum of pure S-b-AK exhibits the β -relaxation at about 186 K (at 3 Hz) and the
11 α_a -relaxation at about 360 K (at 3 Hz) [4]. The addition of relatively small amounts of cPU to S-b-
12 AK (cPU/S-b-AK=5/95 and 10/90) leads to a significant suppression of both the β - and α_a -
13 relaxations, whose strengths deviate markedly from a linear concentration behaviour showing a
14 faster decrease with decreasing S-b-AK content, figure 2b. The same considerations also result from
15 the analysis of $E'(T)$, the drop associated to the α_a -relaxation in pure S-b-AK being more than twice
16 as large as the one observed in the 10/90 sample, figure 2c. A further relaxation peak is revealed at
17 about 248 K (at 3 Hz) in both the samples having a ratio equal to 5/95 and 10/90. This peak, not
18 observed in pure S-b-AK, shows an increasing strength with increasing cPU content and a T_{peak}
19 very close to those of the α_a -relaxation peaks in pure cPU and in *t*-IPNs with high concentrations of
20 cPU (figure 2a). As explained in the following, this transition should be associated to an α_a -
21 relaxation process within a cPU/S-b-AK mixed amorphous phase.
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34 § 4. DISCUSSION

35 Prominent thermal features of *t*-IPNs, having the compositions cPU/S-b-AK=90/10 and 80/20, are
36 (i) the increase of T_g and of the corresponding jumps and (ii) the decrease of T_m and of the heat of
37 melting with decreasing cPU content. In particular the decrease of the heat of melting ΔH_m^* , from
38 74 Jg^{-1} in pure cPU [4], through 50 Jg^{-1} in 90/10, to 37 Jg^{-1} in 80/20 [4], is larger than that expected
39 from a simple dilution effect. The slight depression of T_m implies a reduction of the mean size of
40 BAG microcrystals in agreement with the modified Thomson equation [8] (Bershstein and Egorov
41 1994), $T_m = T_m^0 (1 - b / \langle D \rangle)$, where T_m^0 is the melting point of an ideal infinitely long crystal, b a
42 constant and D the mean size of a microcrystal. From the above results it follows a hindrance to the
43 crystallization of cPU in *t*-IPNs, probably due to a small but significant miscibility between BAG
44 and S-b-AK due to intermolecular hydrogen bonds between the functional groups of the two
45 components. This weak affinity between the two components is assumed to promote the formation
46 of a mixed amorphous phase, characterized by a higher T_g than that of pure cPU and coexisting with
47 microphases of pure crystalline BAG and of amorphous S-b-AK. The existence of the mixed phase
48 is also supported by the mechanical relaxation peaks observed around 250 K (figure 2b) in *t*-IPNs
49 with high concentrations of S-b-AK (cPU/S-b-AK=5/95 and 10/90) which exhibit an increasing
50 strength with growing cPU content. These observations lead to conclude that these latter *t*-IPNs,
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3 whose thermograms do not exhibit any melting endotherms, can be regarded as wholly amorphous
4 systems having a morphology based on the coexistence of microphases of essentially pure S-b-AK
5 and of mixed cPU/S-b-AK microphases. A further consideration concerns the absence of crystalline
6 BAG in the *t*-IPNs with high concentrations of S-b-AK which, as pointed out in Section 2, were
7 annealed at temperatures close to the melting temperature of BAG. This finding is apparently in
8 contrast with the results of a X-ray scattering study of as-cast *t*-IPNs based on cPU and S/AA
9 random copolymer (acid form) [9], which showed the existence of BAG crystals in the whole range
10 of compositions from pure cPU to pure S/AA. Besides the structural differences of one of the
11 component (S-b-AK is a block copolymer), this discrepancy is probably due to the annealing
12 procedure imposed on the present samples which is expected to favour the formation of the mixed
13 amorphous phase preventing BAG crystallization.

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23 Further support for the hindrance to the tendency of BAG to crystallise in *t*-IPNs and for the
24 existence of the mixed amorphous phase is given by the mechanical results. The following
25 considerations are offered:

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29 **(i) α_a -relaxations**

30 the strength of the α_a -relaxation, observed at about 250 K in pure cPU and in *t*-IPNs with a
31 weight ratio of 90/10 and 80/20 (figures 2a and 2c), increases with decreasing cPU content
32 as an evidence of a growing non-crystallinity degree. More interestingly, the relaxation peak
33 observed at about the same temperature in *t*-IPNs with weight ratios of 5/95 and 10/90
34 exhibits a increasing strength with increasing cPU content (figures 2b and 2c) which is
35 paralleled by a noticeable suppression of the α_a -relaxation ascribed to S-b-AK component. It
36 is believed that this peak arises from the cooperative relaxation motion of the amorphous
37 chains within cPU/S-b-AK mixed microphases, whose formation is favoured by thermal
38 annealing of *t*-IPNs at temperatures close to the BAG melting temperature.

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47 **(ii) γ -and β -relaxations**

48 the magnitude of the γ -relaxation peak, which is located at about the same temperature in
49 pure cPU and in *t*-IPNs with weight ratios of 90/10 and 80/20, increases with decreasing
50 cPU content (see figure 2a). In close agreement with the result previously obtained [4], an
51 average activation energy $E_\gamma=0.43 \pm 0.04$ eV is obtained for 90/10 *t*-IPN confirming the
52 assignment of this process to crankshaft motions of $(\text{CH}_2)_n$ segments within the amorphous
53 chains [9,10]. It is believed that, in *t*-IPNs, this process is due to the contributions of γ -
54 relaxation within cPU amorphous chains of the mixed phase, whose fraction is enhanced on
55 blending as also observed by the calorimetric results. In all the samples the γ -relaxation is
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unexplainable in terms of a single relaxation time and has been analysed by the symmetric double-well potential (SDWP) model. It schematizes the locally mobile relaxing particles in terms of symmetric double-well potentials having a broad distribution of the barrier height E , which accounts for random variations in the local environments of particles due to the topological disorder. A quantitative analysis was carried out by using a procedure elsewhere detailed [11,12]:

$$Q^{-1} = \frac{A}{T} \int \exp\left(-\frac{(E-E_m)^2}{2E_o^2}\right) \times \frac{\omega\tau(E)}{1+\omega^2\tau^2(E)} dE \quad (1)$$

where

$$A = \frac{NB^2}{\sqrt{32\pi}\rho\nu^2k_B E_o} \quad (2)$$

The relaxation time τ is given by the usual Arrhenius expression, $\tau = \tau_0 e^{E/k_B T}$. E_m and E_o represent the most probable activation energy and the width of the distribution, N is the number of relaxing molecular groups, B is an average deformation potential and the other symbols have the usual meanings. Numerical evaluation of the experimental curves by equation (1) gave the following values for the relaxation parameters: $E_m=0.34$ eV, $E_o=0.031$ eV, $NB^2=3.97*10^{-13}$ J²m⁻³ and $\tau_0^{-1}=1.11*10^{13}$ s⁻¹ for pure cPU; $E_m=0.35$ eV, $E_o=0.035$ eV, $NB^2=7.37*10^{-13}$ J²m⁻³ and $\tau_0^{-1}=1.49*10^{13}$ s⁻¹ for 80/20 *t*-IPN. The theoretical fits are shown by a solid line in the inset of figure 2a. An interesting feature of the results is that the product NB^2 involving the density of relaxing particles and the deformation potential increases with decreasing cPU concentration. Since no significant change for the deformation potential is expected by going from neat cPu to *t*-IPNs with weight ratios of 90/10 and 80/20, the quantity in NB^2 , which increases with increasing S-b-AK content, must be the number of relaxing particles. This result represents a further confirmation that the fraction of cPU amorphous chains of the mixed phase is enhanced on blending.

The β -relaxation, observed at about 186 K (at 3 Hz) in pure S-b-AK [4], is severely suppressed in *t*-IPNs with weight ratios of 5/95 and 10/90 preventing any kind of quantitative analysis in these polymers.

The totality of observations concerning the thermal characteristics and the relaxation dynamics of *t*-IPNs leads to conclude that these systems are characterized by a heterogeneous morphology, based on microphases of pure cPU (BAG crystals), pure amorphous S-b-AK and a cPU/S-b-AK amorphous complex. **The phase micro-segregation between cPU and S-b-AK takes place in all**

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3 cases, although a mixed amorphous microphase resulting from the participation of intermolecular
4 hydrogen bonds between the functional groups of the two components and having distinct physical
5 characteristics is formed.
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10 § 5. CONCLUSIONS

11 To gain an insight into the phase behaviour of *t*-IPNs based on semi-crystalline cPU and S-b-AK
12 block-copolymer, a comparative experimental study of differential scanning calorimetry and
13 dynamic mechanical spectroscopy has been made here in samples having different cPU/S-b-AK
14 weight ratios (90/10, 10/90 and 5/95). The purpose of making specific heat and mechanical
15 measurements on these systems was to investigate more accurately the weak affinity between the
16 two components, previously revealed in a sample (80/20) belonging to this class of interpenetrating
17 polymers. The heat of melting of the crystalline phase of cPU component shows a faster
18 suppression with decreasing cPU content than that expected from a simple dilution effect. This
19 finding has been interpreted as a hindrance to crystallization of cPU in *t*-IPNs, due to a small degree
20 of miscibility between BAG and S-b-AK arising from intermolecular hydrogen bonds between the
21 functional groups of the two components. The observation of distinct calorimetric and mechanical
22 transitions have been associated to the heterogeneous morphology of the thermoplastic networks,
23 where microphases of crystalline cPU (BAG crystals) and amorphous S-b-AK coexist with those of
24 a cPU/S-b-AK mixed amorphous complex. The thermodynamic compatibility of the components,
25 even if limited, promotes the formation of the mixed amorphous phase characterized by a higher T_g
26 than that of the amorphous phase of pure cPU. A further indication for the hindrance to
27 crystallizability of BAG on blending is offered by the quantitative analysis of the γ -relaxation in
28 terms of a symmetric double-well potential model: the amorphous fraction of polyurethane
29 increases with decreasing cPU content.
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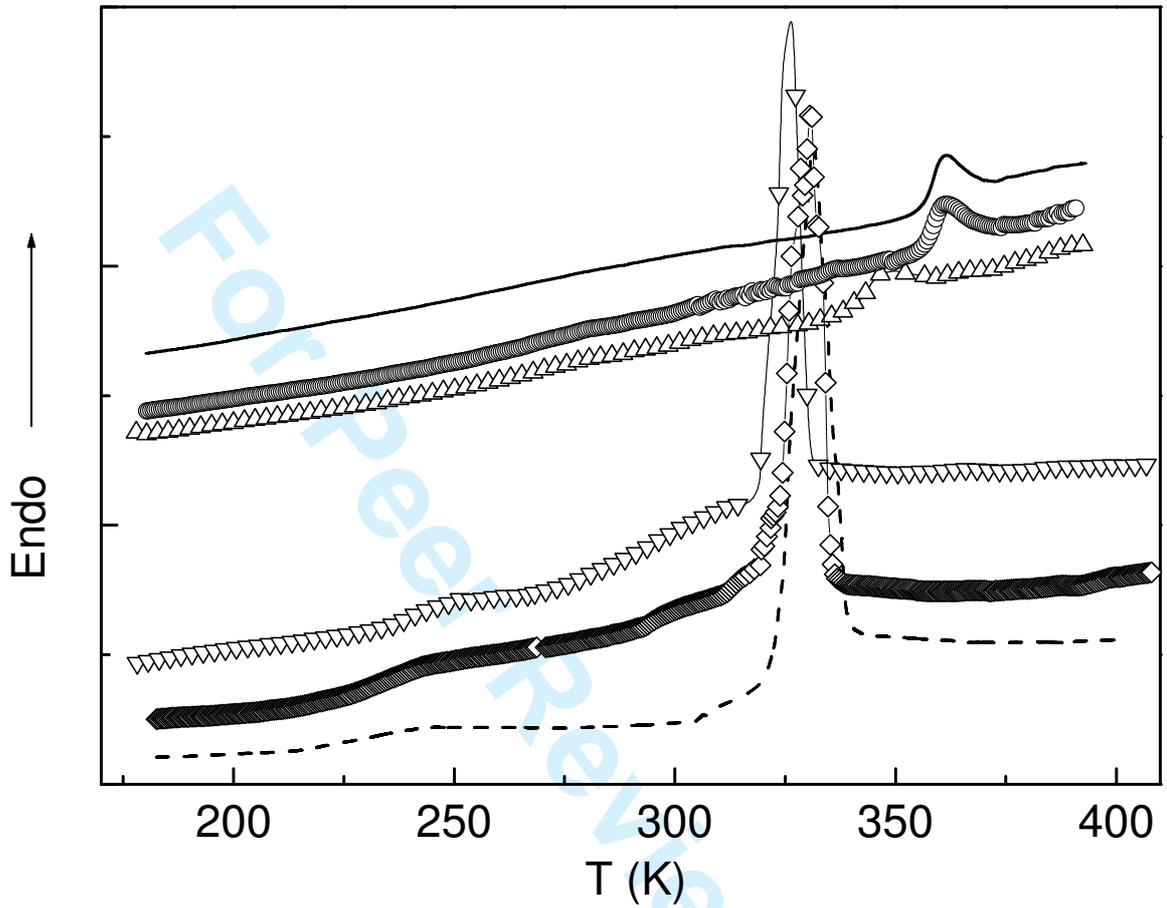
FIGURE CAPTIONS

Figure 1. DSC traces through the glass transition region for the neat cPU (dashed line) and S-b-AK (solid line) and for the *t*-IPNs having the following cPU/S-*b*-AK compositions: 90/10, (\diamond); 80/20, (∇); 10/90, (Δ); 5/95, (O). The curves have been duly shifted for easier comparison. The continuous lines are only guides for eyes.

Fig. 2. Comparison of the dynamical mechanical spectra of *t*-IPNs at a frequency of 3 Hz.

- (a) Temperature dependence of the loss modulus E'' in: pure cPU, dashed line; cPU/S-*b*-AK=90/10, (O); cPU/S-*b*-AK=80/20, (Δ). The inset reports the comparison between the experimental data for the internal friction at 30 Hz across the γ -relaxation peak and the theoretical fits by Eq. (1) in neat cPU (\bullet) and in *t*-IPN (Δ) with a weight ratio of 80/20.
- (b) Temperature dependence of the loss modulus E'' in: pure S-*b*-AK, solid line; cPU/S-*b*-AK=5/95, (+); cPU/S-*b*-AK=10/90, (∇).
- (c) Temperature dependence of the storage modulus E' in: pure cPU (dashed line) and S-*b*-AK (solid line); cPU/S-*b*-AK=90/10, (O); cPU/S-*b*-AK=80/20, (Δ); cPU/S-*b*-AK=10/90, (∇).
- (d) The effect of the driving frequency on the temperature dependence of E' in cPU/S-*b*-AK=10/90: 0.3 Hz, (O); 3 Hz, (+); 30 Hz, (Δ).

FIG. 1



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Fig. 2

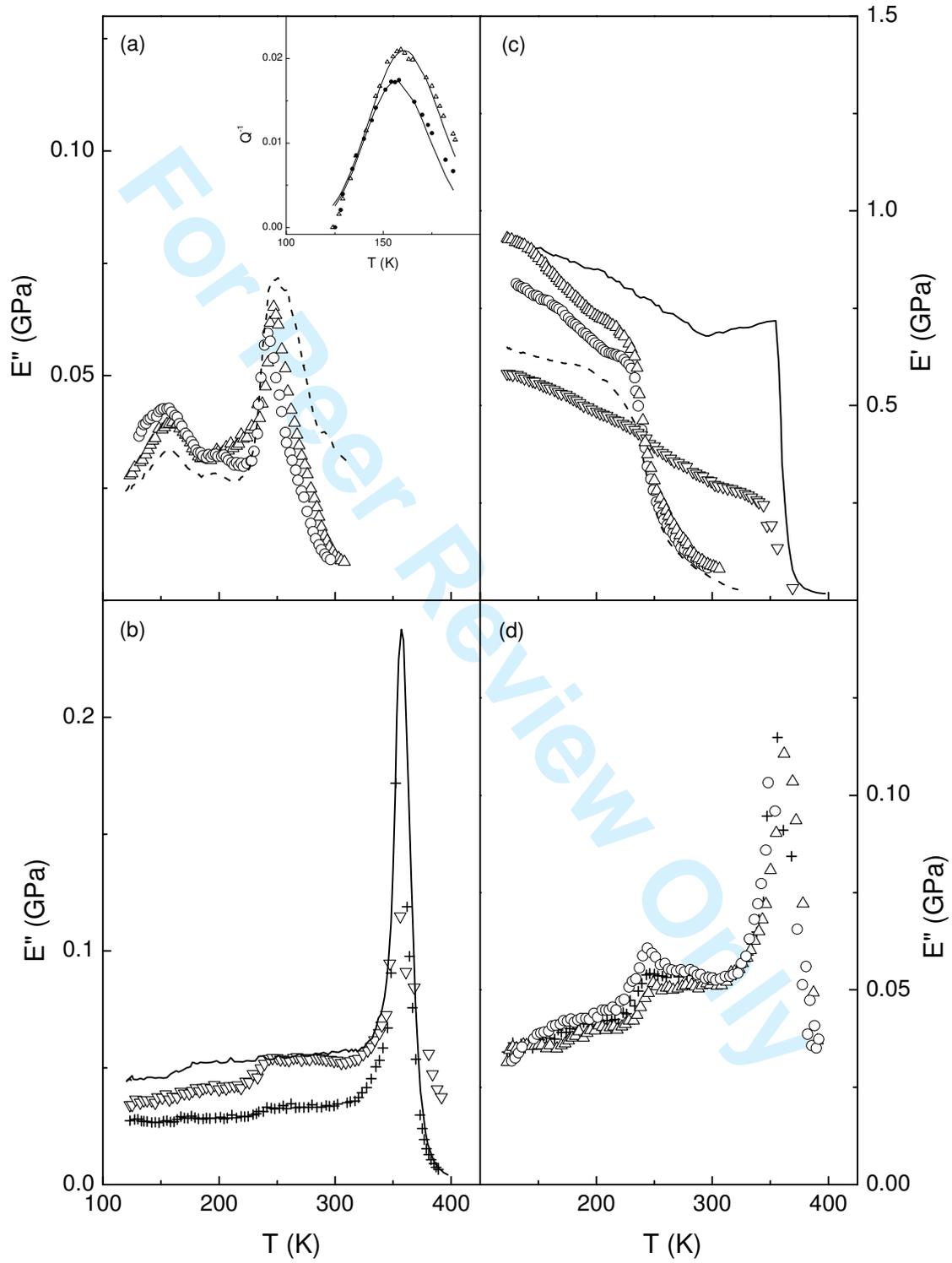
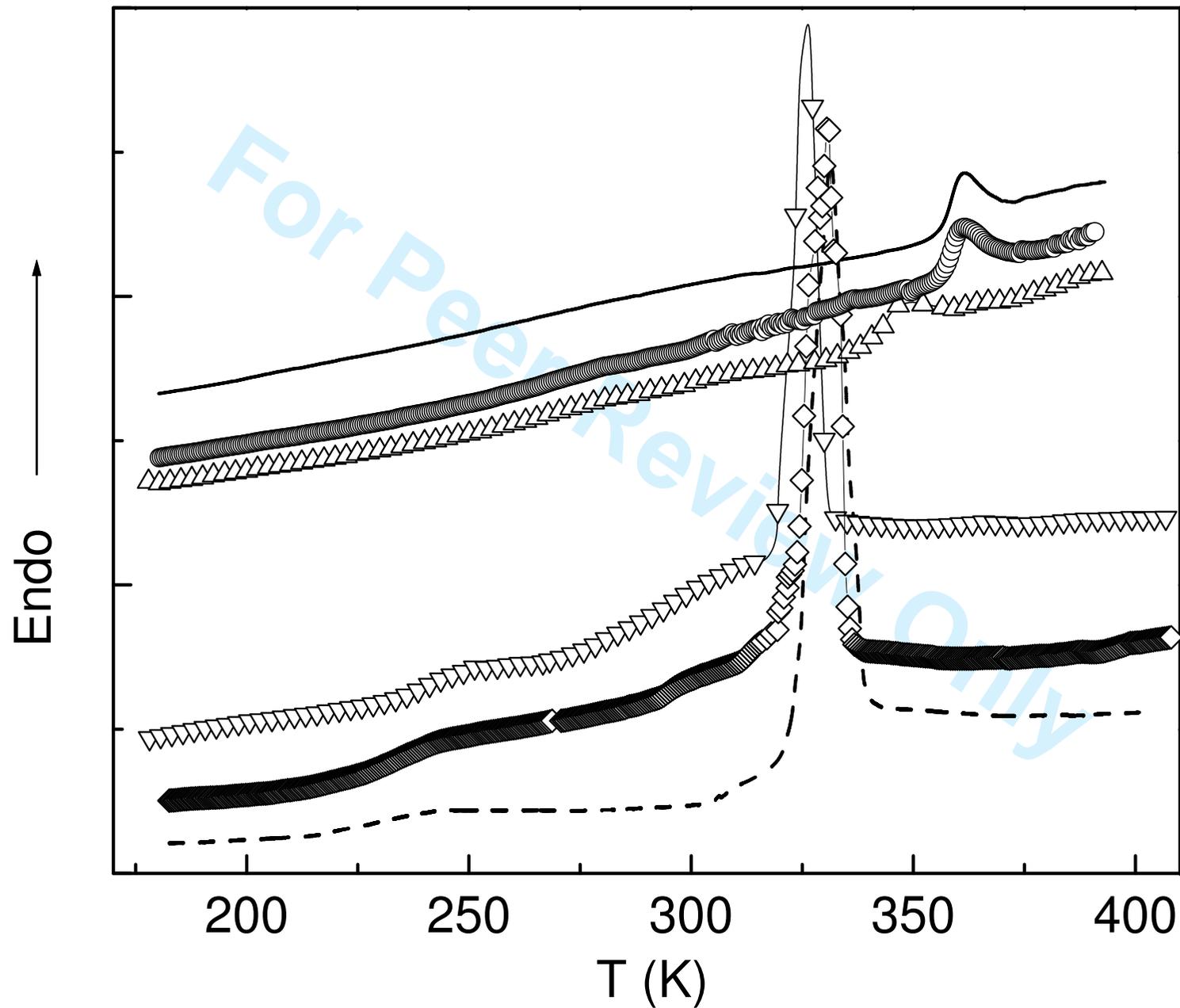


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Fig. 2

