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Self-organized cross-linked phenolic thermosets: thermal and dynamic mechanical properties of novolac/block copolymer blends

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Abstract

We have recently demonstrated a concept to prepare self-organized spherical, cylindrical and lamellar nanostructures of phenolic thermosets by blending novolac and poly(2-vinylpyridine)-*block*-poly(isoprene), i.e. P2VP-*block*-PI, followed by thermal curing by hexamethyltetramine (HMTA) [Macromolecules 34 (2001) 3046]. In the present work, hydrogen bonding, dynamic mechanical properties and glass transition temperatures are investigated using Fourier transform infrared spectroscopy (FTIR), dynamic mechanical spectroscopy (DMA) and differential scanning calorimetry (DSC). Even after curing, FTIR shifts indicate hydrogen bonding between the hydroxyl groups of novolac and nitrogens of P2VP, thus promoting the self-organization. DMA shows that the storage E' and loss moduli E'' do not change considerably as PI forms the spherical or cylindrical phases. A slightly larger drop takes place in the lamellar phase. In agreement with the self-organization, a separate glass transition temperature of PI is observed at ca. −62°C. Based on hydrogen bonds that tolerate the thermal curing and the possibility to tailor the self-organized morphologies, it is suggested that the properties of phenolic thermosets might be tailored in a systematic way, upon blending with proper block copolymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phenolic resin; Block copolymer; Cross-linking

1. Introduction

During the recent years, there has been considerable effort to obtain nanostructured polymeric materials based on self-organization, i.e. due to competing interactions. A classic example consists of block copolymers [1,2] where the repulsive blocks are covalently connected within a polymer backbone. In diblock copolymers, lamellar, gyroid, cylindrical, spherical, and disordered phases are observed. A recent trend is to incorporate more blocks to form complicated architectures, as well as to combine mesogenic moieties, in which case a rich phase behavior is obtained [3–7]. Covalent connection between the repulsive blocks within the block copolymer chains can be replaced by weaker physical bonds, for example by ionic interactions [8–10], coordination [11], and hydrogen bonds [12–15], which also allow a facile route to hierarchical order and functional materials [16,17]. The self-organizing entities in the latter case are formed due to matching physical interactions, and can thus be regarded as supramolecules [18].

In the field of polymer networks and thermosets, there have been related trends in order to modify the mechanical and other properties. Liquid crystalline thermosets and elastomers containing mesogenic groups have been studied [19–22]. Interesting functional properties were already early suggested if cross-linking could be performed in a liquid crystalline state [23,24]. Self-organization in thermosets is not straightforward, as the chemical curing reaction can impede the relatively small physical energies related to self-organization and the structures may not tolerate the curing. Systematic work on self-organization has been reported in amine cured epoxy resin/block copolymer blends [25–27], as well as in hexamethyltetramine (HMTA) cured novolac/block copolymer blends [28].

Mechanical properties of thermoplastic block copolymers are largely dominated by the continuous phase, but the microphase separated morphology, block copolymer architecture, deformation mechanism, phase behavior, and especially the interface structure and strength are important for modification of the properties [29–34]. It is difficult to improve all the mechanical properties (strength, toughness, and stiffness) simultaneously to achieve synergistic properties. However, in some cases, synergistic properties have been found in a small composition range for diblock copolymers having a large interface width [31].

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Also blends of block copolymers and thermoplastic homopolymers can form self-organized structures. In blends of block copolymer A-*block*-B and homopolymer A, there is an interplay between a macrophase and a microphase separation [2,35]. Homopolymers of sufficiently low molecular weight can be selectively dissolved within the microphase separated domains. Increased molecular weight of the homopolymer increases the tendency of their segregation to the center of the microphase separated domains. Finally, when the molecular weight of a homopolymer is greater than that of the corresponding block of the block copolymer, macrophase separation is expected to take place [2]. More generally, the phase behavior of a blend of A-*block*-B and homopolymer C reminds that of A-*block*-B and homopolymer A when the Flory–Huggins interaction parameters χ_{AB} and χ_{BC} are much larger than χ_{AC} [2].

Phenolic thermosets belong to the most common thermosets [36]. Mesophases have been observed by polymerizing phenol–formaldehyde in the presence of cationic surfactants [37]. Self-organized lamellar, cylindrical and spherical phases of cross-linked phenolic thermosets have been demonstrated by transmission electron microscopy (TEM) using blends of HMTA cured novolac and poly(2-vinylpyridine)-*block*-poly(isoprene), i.e. P2VP-*block*-PI [28]. The phenolic hydroxyls of novolac are hydrogen bonding donors. Without cross-linking, novolac is miscible in several polymers containing hydrogen bonding acceptors, such as poly(ε-caprolactone), polyethylene oxide and polymethylmethacrylate, and partial miscibility is observed even upon HMTA curing, taken that the weight fraction of novolac in the blend is sufficiently large [38–42]. However, thermal curing at the elevated temperatures tends to cause phase separation also due to reduced hydrogen bonds, in addition to the entropy penalty upon forming the network. In this paper, hydrogen bonding between novolac and the P2VP block of P2VP-*block*-PI is investigated using FTIR. Effects of the morphology on the dynamic mechanical properties and the glass transition temperatures are determined using DMA and DSC.

2. Experimental

2.1. Materials

P2VP-*block*-PI diblock copolymer was provided by Polymer Source Ltd and was used without further purification. Molecular weights of the blocks were $M_{n,\mathrm{P2VP}} = 21\,000$ g/mol and $M_{n,\mathrm{PI}} = 71\,000$ g/mol and polydispersity was 1.04. Novolac was supplied by Bayer Ltd (Vulcadur A),and was used without further purification. Molecular weight of novolac was about 2000 g/mol. Vulcadur A contains 10 wt% of a cross-linking agent HMTA. Tetrahydrofuran (THF) was provided by Riedel-de-Häen (99.9%).

2.2. Sample preparation

We used different weight fractions (w_{PI}) of PI in the cured blends. The studies were limited to the minor amounts of PI, i.e. $w_{\mathrm{PI}} = 0$, 0.05, 0.10, 0.20, 0.30 and 0.40 as our interest was to modify the dynamic mechanical properties of cross-linked novolac.

Novolac (containing HMTA) and P2VP-*block*-PI were added into THF. The mixtures were stirred for one day at room temperature and finally for 30 min at 60°C, followed by evaporation of THF at 60°C. Samples were subsequently dried in a vacuum oven (ca. 10^{-2} mbar) at 60°C for 10 min. Curing of the samples was performed in a compression press using the pressure 7 MPa at 100°C for 2 h at 150°C for 1 h, and finally at 190°C for 30 min.

2.3. Infrared spectroscopy

Infrared spectra were obtained on a FTIR spectrometer (Nicolet 730 FTIR). In all cases, 64 scans with a resolution of 2 cm^{-1} were averaged. Samples were prepared by applying a few drops of the solutions onto potassium bromide crystals. Solvent was evaporated in a vacuum oven at a temperature of 25°C for 3 h. Curing was performed in a sealed container under analytical nitrogen atmosphere (AGA 99.999%) using the same temperature profile as in the compression press. Pressure at the room temperature was 2 bar.

2.4. Dynamic mechanical spectroscopy

The response of the self-organized structures on a small strain mechanical deformation was measured as a function of temperature using Perkin–Elmer dynamic mechanical analyzer (DMA7) in a three-point bending mode. The span between the supports was 15 mm and sample length, width and height were 18, 5 and 1 mm, respectively. The measurements were carried out under helium atmosphere using frequency of 1 Hz, a static stress 1.76 MPa, a dynamic stress 1.6 MPa, and the heating rate of 4°C/min. The storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta$) were determined in the temperature range from -90 to 90°C. The glass transition temperature was recorded as a peak in the $\tan\delta$ curve.

2.5. Differential scanning calorimetry

Glass transition temperatures were measured using Perkin–Elmer differential scanning calorimeter (DSC7) under nitrogen atmosphere. Cured samples were scanned from -90 to 90°C using a heating rate of 10°C/min. Weight of samples was typically 25 mg. The glass transition temperatures (T_g) were taken as a midpoint of the transition.

3. Results and discussion

Self-organized nanostructures of blends of block copolymer

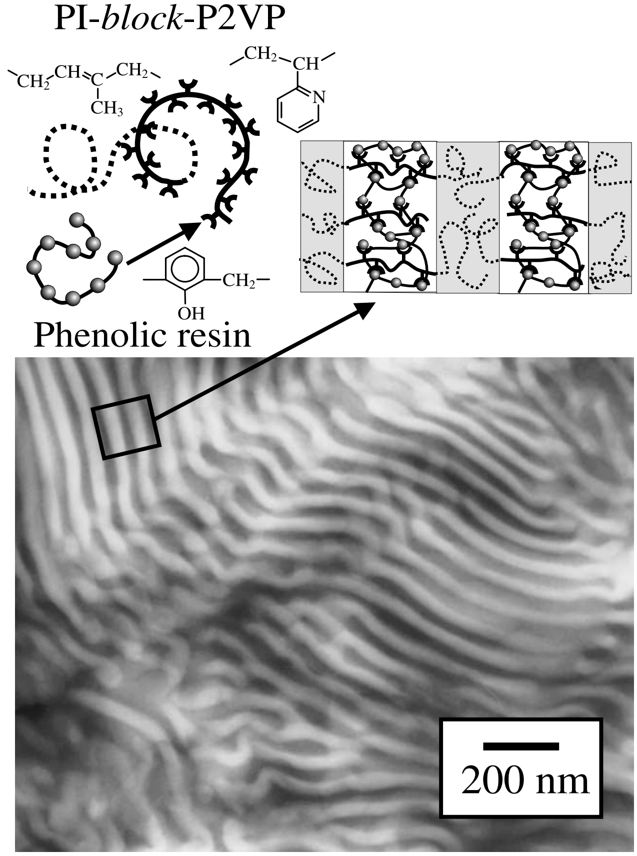

Fig. 1. Schematics of the cross-linked lamellar structure of blends of novolac and P2VP-*block*-PI. The hydrogen bonding between novolac and P2VP is also indicated. Transmission electron micrograph of the HMTA cured lamellar structure is also shown [28]. The weight fraction of PI in the final blend is $w_{PI} = 0.40$. Cylindrical morphology is observed for $w_{PI} = 0.30$ and spherical morphology for $w_{PI} = 0.05, 0.10, 0.15, 0.20$ [28].

A-*block*-B and homopolymer C can be obtained if the polymers, their interactions, and their molecular weights are well chosen. Using TEM, we recently reported that HMTA cured self-organized structures of novolac can be obtained by blending with P2VP-*block*-PI [28]. As an example, Fig. 1 shows schematically the lamellar structure and a TEM micrograph. The polar microphase separated lamellae consist of cross-linked mixtures of novolac and P2VP, and the nonpolar lamellae consist of PI. The morphology can be tailored by using different weight fractions of PI in the blends: For example keeping the present molecular weights of the P2VP and PI blocks and novolac, lamellar morphology is illustrated when the PI weight fraction in the blend is $w_{PI} = 0.40$ (as shown in Fig. 1), cylindrical morphology for $w_{PI} = 0.30$, and spherical morphology for $w_{PI} = 0.05, 0.10, 0.15, 0.20$ [28].

FTIR indicates that phenols form relatively strong hydrogen bonds with poly(vinylpyridine)s and that the amount of hydrogen bonding decreases when the temperature is increased (see e.g. [13,14]). Phenolic resins can form miscible blends with homopolymers but curing increases the tendency of phase separation [39–42]. An essential question is to understand the level of hydrogen bonding which remains upon curing at the elevated temperatures, i.e. whether the hydrogen bonds are still formed in the cured sample or whether the macrophase separation between novolac and P2VP-*block*-PI has been purely 'topologically' prohibited due to the formation of the cross-linked network. Such factors may play a role in determining the interface structure of the self-organized structures, which, in turn, may reflect in the mechanical properties.

Hydrogen bonding between P2VP and novolac was investigated using FTIR. Fig. 2 shows the FTIR spectra of novolac, P2VP-*block*-PI and their blend with $w_{PI} = 0.40$ at room temperature after thermal curing. Such a high concentration of PI in the blend is used as an illustrative example because the weight fraction of P2VP is relatively high [$w_{P2VP} = 0.118$) in this case and the corresponding changes in the FTIR-signal due to hydrogen bonding are therefore quite pronounced. In the other compositions, the weight fraction of P2VP is smaller and, therefore, the effects in FTIR are smaller but qualitatively similar. Fig. 2a shows the spectra in the region from 970 to 1030 cm^{-1}. A characteristic absorption peak of the free P2VP is at 993 cm^{-1} and due to hydrogen bonding it is shifted to 1008 cm^{-1}. As shown in Fig. 2b, a ring stretching band of free P2VP is at 1589 cm^{-1} and it is shifted to 1597 cm^{-1} upon hydrogen bonding. Fig. 2c shows the spectra in the stretching region of the novolac hydroxyl group. For pure novolac, two absorption bands are observed: one is a broad phenol–phenol hydrogen bonding band at ca. 3365 cm^{-1} and the other is a shoulder band due to free hydroxyl groups at about 3500 cm^{-1}. No peaks of P2VP-*block*-PI are observed in this region, thus simplifying the interpretation. In the cured blends the free hydroxyl group band remains roughly constant at about 3500 cm^{-1}, and the hydrogen bonding band has been shifted to ca. 3344 cm^{-1}. Furthermore, it seems that the relative fraction of hydrogen bonded hydroxyl groups increases slightly in the cross-linked blends compared to pure novolac. All these observations indicate that there exists hydrogen bonding between hydroxyl groups of novolac and nitrogen of P2VP even after the thermal curing. Note also that there was not a large difference in the amount of hydrogen bonding before and after curing which is likely due to the moderate first curing temperature. P2VP chains are then partly locked to the novolac rich phase due to cross-linked chains and they cannot phase separate at the still higher final curing temperature even if hydrogen bonds would break.

Phenolic thermosets are strong, hard and brittle thermosets and tailoring of their mechanical properties by blending with thermoplastic homopolymers [39,41] or rubbers is difficult because the morphologies, sizes of structures and interface widths are difficult to control. Self-organization allows one to control the sizes and the shapes of the rubbery domains, and next, we studied how the soft PI domains affect the dynamic mechanical properties of the cured blends. In Fig. 3a, tan δ is presented as a function of temperature. The glass transition temperature of the PI domains can be observed at ca. -62°C and it does not change much when the weight fraction of PI is increased. In Fig. 3b, the storage modulus E' is plotted as a function of temperature. Below the glass transition temperature of PI, the magnitudes of E' of all samples are almost equal, independent on the morphology (note that, for clarity, the traces corresponding to different compositions have been shifted by multiplication factors indicated in the figure). However, above the glass transition temperature of PI, E' decreases as a function of PI concentration, due to the softness of the latter polymer. Fig. 3c shows that the decrease of E' and E'' upon adding PI is not large as long as PI forms spherical or cylindrical structures within the hard cross-linked phenolic matrix. However, a larger drop is observed for the lamellar phase where the hard phenolic phase and the rubbery PI phase form alternating layers in parallel.

Glass transition temperatures were also measured using DSC and Fig. 4 shows that T_g of PI does not change notably as a function of the composition. The enthalpy change increases as a function of the weight fraction of PI. The glass transition temperatures based on DMA and DCS are compared in Table 1. It can be concluded that the glass transition temperatures were ca. -62°C in all cases and the morphology of samples did not have a pronounced effect on T_g.

In the literature dealing with rubber toughening of thermoplastic polymer composites, block copolymers allow a natural means to achieve high interfacial strength between the glassy and the rubbery phases as well as structural control of the size and shape of the rubber phase [30–34]. However, it has actually turned out to be untrivial to achieve toughening based on block copolymers, as it depends on a complicated interplay between many parameters, such as the block copolymer segregation state, interface widths, microphase separated morphology, block copolymer architecture (diblock, triblock, or more complicated architecture), molecular weights, and deformation mechanism. Interestingly, even in diblock copolymers of poly(styrene)-*block*-poly(butyl methacrylate) (PS-*block*-PBMA), toughened phases can be observed if the molecular weight is high and the PS volume fraction is proper, i.e. slightly in excess of ca. 70% [31,34]. In this case, a combination of lamellar and cylindrical morphology is obtained. Note that PS and PBMA are partially miscible, thus leading to broadened interface widths.

In the present case dealing with the self-organized phenolic thermosets, it becomes difficult to achieve well-annealed

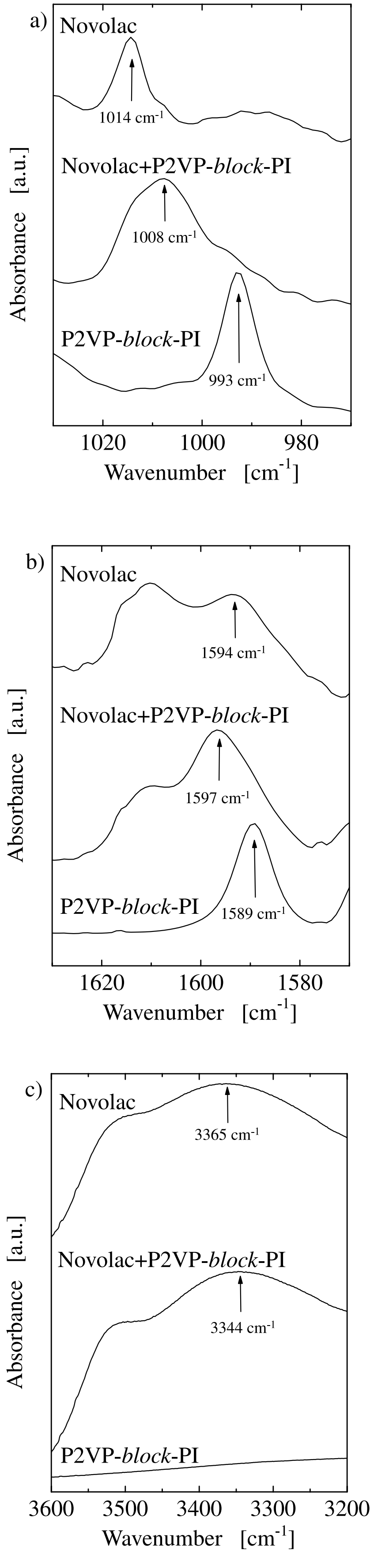

Fig. 2. FTIR spectra of novolac, P2VP-*block*-PI, and their blend containing 40 wt% of PI after curing. The blend is the same as shown in Fig. 1. Hydrogen bonding between P2VP and phenol causes shifts in FTIR bands: (a) a characterictic band of P2VP shifts from 993 to 1008 cm^{-1}, (b) a ring stretching band of P2VP shifts from 1589 to 1597 cm^{-1} and (c) a hydroxyl stretching band of hydrogen bonded novolac shifts from ca. 3365 to 3344 cm^{-1}. The shoulder at ca. 3500 cm^{-1} is due to free hydroxyl groups and it is slightly reduced in the cured blends.

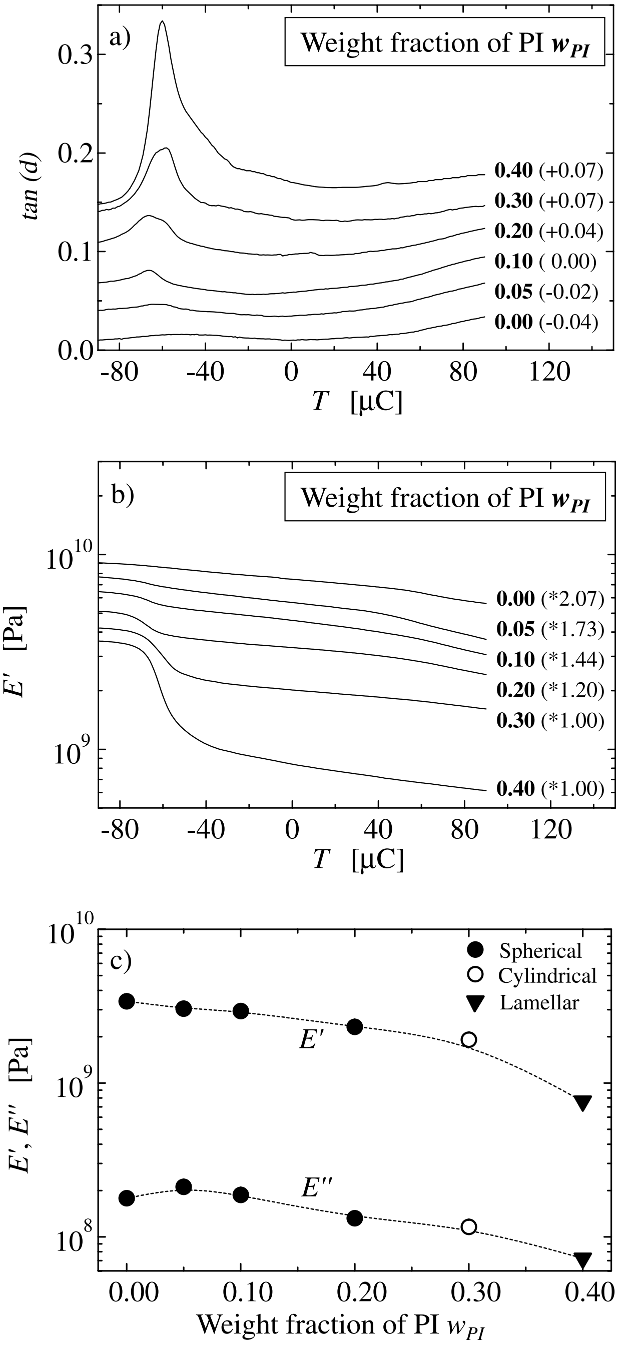

Fig. 3. The DMA data of HMTA cured novolac/P2VP-*block*-PI blends: (a) The loss tangent tan δ as a function of temperature. The weight fraction of PI in the cured blend (w_{PI}) is indicated. The curves have been shifted for clarity, the amounts of which have been indicated; (b) The storage moduli E' as a function of temperature. The curves have been shifted for clarity by multiplication factors, the amounts of which are also indicated; (c) E' and E'' as a function of the weight fraction of PI at the room temperature.

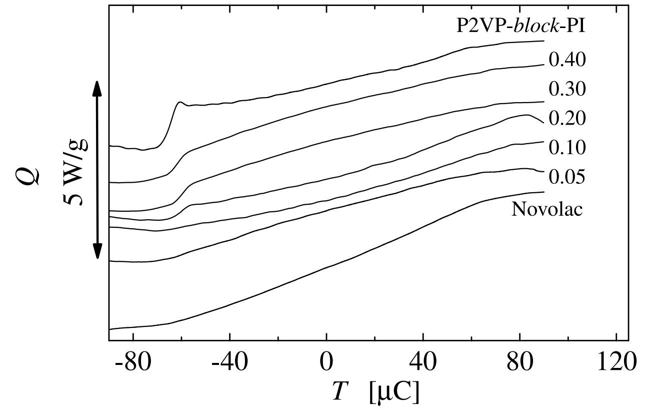

Fig. 4. DSC traces of HMTA cured novolac/P2VP-*block*-PI blends. The weight fraction of PI in the cured blend (w_{PI}) is indicated.

and defect-free samples due to the concurrent thermal cross-linking in the compression mold. Therefore, so far we did not achieve sufficiently defect-free samples whose strength and toughness could have been measured reliably. However, indirect indications can be made based on DMA and DSC. The glass transition temperatures of the PI domains do not much change upon blending, which points towards rather strong segregation state. This suggests that the interfaces might be rather narrow. However, broad interfaces seem to be more feasible to achieve improved mechanical properties, based on the previous work on thermoplastic block copolymers [31,34].

In conclusion, improvement of mechanical properties could be expected in cured blends of novolac even when diblock copolymers are used if proper compositions are identified [31,34]. Use of triblock copolymers P2VP-*block*-PI-*block*-P2VP could allow a wider range of feasible compositions. Perhaps more importantly, PI might be replaced by a less repulsive elastomeric polymer, thus potentially leading to a state of weaker segregation and broader interfaces.

4. Conclusions

Glassy thermoplastic polymers are typically brittle under deformation and more ductile polymer compounds have been previously obtained using self-organization. It is therefore feasible to consider tailoring of also thermosets based on self-organization, which allows a means to control the morphologies of multiphase materials in detail. In cured phenolic thermosets, the hydrogen bonding between the P2VP-*block*-PI and novolac in combination with the

Table 1

Weight fraction of PI w_{PI}	Glass transition temperature T_g (°C)	
	DMA	DSC
0.00	–	–
0.05	−64	–
0.10	−66	−60
0.20	−66	−60
0.30	−60	−60
0.40	−60	−62
P2VP-*block*-PI	–	−65

repulsion due to PI allows to construct different nanoscale soft domains in a systematic manner based on self-organization [28]. In this work, we show that substantial hydrogen bonding takes place between P2VP and novolac even after curing at the elevated temperatures. The storage moduli E' did not significantly change upon increasing the weight fraction of PI when it formed the spherical or cylindrical phases. A slightly larger drop takes place in the lamellar phase. Glass transition temperatures of the PI domains were around −62°C in all samples and it did not much depend on the morphology. Construction of controlled rubbery nanoscale domains of characteristic sizes of ca. 300 Å using diblock copolymers did not, however, suggest essentially improved mechanical properties based in dynamic mechanical spectroscopy when polyisoprene was used. However, the shown concept based on blending hydrogen bonding block copolymer is fairly easy and general and may ultimately allow synergistic material properties due to structural control, when block copolymers of different architectures and different rubbery blocks are identified.

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