Blends of thermoreversible gels of polyaniline with thermoplastic elastomers: Co-continuous melt processible polymer structures

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Abstract

Elastic electrically conducting network structures of acid doped polyaniline (PANI) within a solvent medium can be formed where heating to elevated temperatures causes melting with liquid-like flow. An example is provided by specific concentrations of PANI dissolved in dodecyl benzene sulphonic acid (DBSA). Such conducting thermoreversible gels are melt processible and allow conductive polymer blends with thermoplastic elastomers and other thermoplastic polymers as well, provided that the solvent, such as DBSA, is surface active to the matrix polymer.

Keywords: polyaniline, bi-continuous polymer network interfaces

1. Introduction

Feasible applications are suggested for conducting polyaniline (PANI) in polymer blends where the conductivity is achieved due to co-continuous networks at low concentrations. Percolative networks in blends have been demonstrated using solution processing upon evaporation of the solvent [1]. In melt blending, finding of plasticizers to allow fusibility of conducting PANI has proved to be untrivial: Specific plasticizers based on molecular recognition or coordination complexation have been introduced to have sufficient attraction with PANI [2, 3]. If the plasticizers are additionally surface active to commodity polymers, melt processible blends are achieved with low percolation threshold [4]. However, general scheme to achieve network structures remains a challenging problem: It has been claimed that the percolating networks will ultimately be composed of dispersed particles [5]. Arguments have been provided for co-continuous blends using block copolymers [6]. Here we demonstrate a scheme where an elastic fusible PANI network is first created within the plasticizer to yield thermoreversible gel [7]. Such networks are next embedded in a commodity polymer to form a co-continuous polymer blend. Thermoreversible gels are formed due to various types of *physical* crosslinks, instead of permanent *chemical* crosslinks and have attracted much attention recently in other branches of polymer science [8]. The elastic nature of PANI thermoreversible gels [7] allows particularly fascinating properties in combination with equally elastic matrix materials, such as thermoplastic elastomers (although the concept is not limited to them) if suitable surface activity is additionally incorporated. A particular example is demonstrated in the following.

2. Experimental

Emeraldine base (M_n=25.000 g/mol) has been polymerized at Neste Chemicals and dried at 60 °C in vacuum for at least 1 day. Dodecyl benzene sulphonic acid (DBSA) was acquired from Tokyo Kasei. Complexation of emeraldine base and DBSA to form PANI(DBSA)$_x$ was performed in dilute solution of formic acid (purity 99 %, Riedel & Haen) [7]. Formic acid was removed by vacuum drying and heating. The molar amount of DBSA in relation to EB repeat unit ranges from x=0.5 to 2.5. Polystyrene-*block*-poly(ethylene/butylene)-*block*-polystyrene triblock copolymer (Kraton G 1651 by Shell) is denoted as SEBS. Its physical crosslinks are formed due to glassy spherical microphase separated polystyrene domains and it is thus thermoplastic elastomer. PANI(DBSA)$_x$ was melt blended with SEBS using 3.5 g conical counter-rotating twin screw extruder (DACA Instruments) at 190 °C using 100 rpm and residence time 5 minutes.

3. Results and Discussion

Different mole fractions x lead to drastically different physical forms of PANI(DBSA)$_x$: *Regime 1) Infusible powder.* Selection of x=0.5 corresponds to the case when all the iminic nitrogens are nominally fully protonated but PANI(DBSA)$_{0.5}$ remains infusible powder with a conductivity of ca 4 S/cm. Fig. 1 shows that 10 %-wt of PANI(DBA)$_{0.5}$ does not lead to appreciable conductivity in blends, whereas 20 or 30 %-wt suffice to yield σ in the range 10^{-6} S/cm. *Regime 2) Thermoreversible gel.* If one increases x to be 1.5-2.0, PANI(DBSA)$_x$ becomes rubber-like elastic solid which melts at elevated temperature, i.e. thermoreversible gel [7]. In blends with SEBS, even 10 %-wt of PANI(DBSA)$_{2.0}$ leads to reasonable $\sigma \approx 10^{-4}$ S/cm. In this case the weight fraction of PANI(DBSA)$_{0.5}$

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is only 3.4 %-wt. Note that at first sight this seems paradoxical because the amount of fully protonated $PANI(DBS)_{0.5}$ has been *reduced* in comparison with Regime 1, thus showing the importance of the physical form of PANI(DBSA) for the conductivity. *Regime 3) Viscous fluid.* Still higher x leads to the case where $PANI(DBSA)_x$ behaves as a viscous fluid without a clear network formation and the conductivity in blends is again reduced, see Fig. 1.
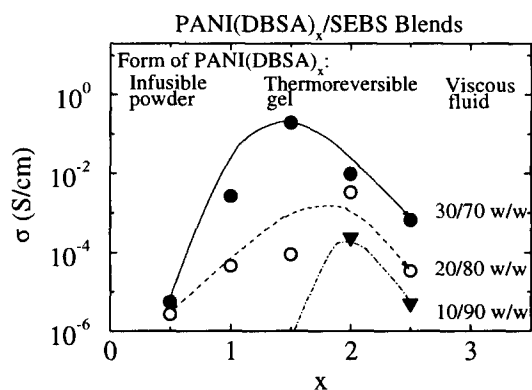

Fig. 1. Electrical conductivity of blends of $PANI(DBSA)_x$ with SEBS as a function of x = total amount of moles of DBSA vs moles of emeraldine base PhN repeat units.

Therefore, there exists an optimum value for the blend conductivity, near x=1.5-2.0, which corresponds to the thermoreversible gel regime. Because in the thermoreversible gel the protonated PANI chains, i.e. $PANI(DBSA)_{0.5}$, form a fusible network within the additional DBSA medium, it would be natural to expect that the network is formed also within the SEBS matrix. This hypothesis is studied in two ways. Firstly, if the conducting path within SEBS would be formed only due to percolation of solid conducting filler particles that that are infusible, such as in the case of $PANI(DBSA)_{0.5}$, one expects that the percolation paths will be disrupted upon mechanical extension of the blend. Indeed, even at a high weight fraction of 30 %-wt of $PANI(DBSA)_{0.5}$ within SEBS, a small extension suffices to reduce σ drastically due to reduced contacts between the dispersed $PANI(DBSA)_{0.5}$ particles, see Fig. 2. By contrast, for $PANI(DBSA)_{2.0}$ in the thermoreversible gel regime, conductivity remains nearly at the original value even when the material has been stretched to 250 % of the original length, suggesting "continuous" network. Such behavior is preliminarily supported also by electron microscopy [9].
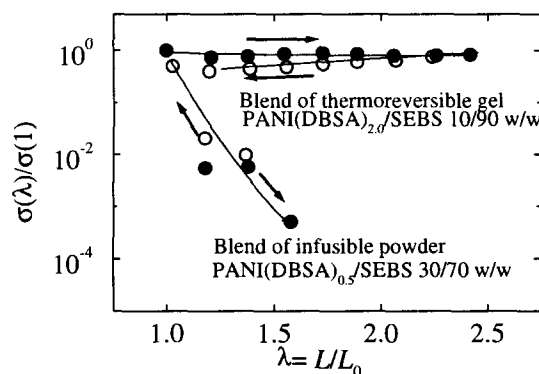

Fig. 2. Electrical conductivity under elongation $\sigma(\lambda)$ scaled by the unstretched value as a function of draw ratio λ=length L/original length L_0.

5. References

[1] C.Y. Yang, Y. Cao, P. Smith, A.J. Heeger, Synth. Met. 53 (1993) 293.

[2] T. Kärnä, J. Laakso, T. Niemi, H. Ruohonen, E. Savolainen, H. Lindström, E. Virtanen, O. Ikkala, A. Andreatta, U.S. Patent No. 5,340,499 (1994).

[3] O.T. Ikkala, L.-O. Pietilä, P.J. Passiniemi, T. Vikki, H. Österholm, L. Ahjopalo, J.-E. Österholm, Synth. Met. 84 (1997) 55.

[4] O.T. Ikkala, J. Laakso, K. Väkiparta, E. Virtanen, H. Ruohonen, H. Järvinen, T. Taka, P. Passiniemi, J.-E. Österholm, Y. Cao, A. Andreatta, P. Smith, A.J. Heeger, Synth. Met. 69 (1995) 97.

[5] B. Wessling, Synth. Met. 45 (1991) 119.

[6] G.H. Fredrickson, F.S. Bates, J. Polym. Sci., Polym. Phys. Ed. 35 (1997) 2775.

[7] T. Vikki, J. Ruokolainen, O.T. Ikkala, P. Passiniemi, H. Isotalo, M. Torkkeli, R. Serimaa, Macromolecules 30 (1997) 4046.

[8] K. te Nijenhuis, Adv. in Polym. Sci. 130 (1997) 1.

[9] To be published.