J Mater Sci (2010) 45:1315–1320
DOI 10.1007/s10853-009-4084-5

Properties of polymer networks prepared by blending polyester urethane acrylate with acrylated epoxidized soybean oil

S. Oprea

Received: 17 September 2009 / Accepted: 24 November 2009 / Published online: 3 December 2009

Abstract Polyurethane network films were prepared using polyester urethane acrylate (PUA) having terminal double-bond functional groups and acrylated epoxidized soybean oil (AESO). PUA elastomers were prepared by reacting polyester diol with diisocyanates, hexamethylene diamine, and acrylic acid. PUA/AESO network blends are synthesized by a simultaneous thermal polymerization process. The physical and thermal properties of the polymer networks obtained from the blend of AESO and polyester urethane urea acrylate were studied using FTIR-ATR, the thermal degradation behavior was studied by thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, and tensile properties measurements being applied. The measurements were compared to the results for elastomers made from the PUA. The weight ratios of PUA/AESO affected the thermal and mechanical properties. With an increase in AESO content, the glass-transition temperature of the networks decreased from 40 to −4.8 °C, tensile strength increased from 1.7 to 9.8 MPa, and elongation at break decreased from 470 to 70%.

Introduction

Polyurethanes (PU) are polymeric materials with wide properties and applications, which can vary from linear polymers to thermosetting plastics [1–4].

In order to protect the environment and to reduce the dependence on fossil fuels, because oil resources are diminishing and thus becoming expensive to produce, research effort was devoted to the development of innovative technologies using renewable resources [5–10].

Vegetable oils are one of the most abundant biological sources and important raw materials for the production of biobased polyurethanes due to the presence of functional groups such as hydroxyl, epoxy, carboxyl, or vinyl groups into the chains of the vegetable oils. Vegetable oils produce polyurethanes that have excellent chemical and physical properties such as enhanced hydrolytic tendencies, high tensile strength and elongation, and thermal stability doubled by other advantages such as low toxicity, inherent biodegradability, and high purity [11–17].

Acrylated urethane materials can potentially combine the properties of polyurethanes (high abrasion-resistance, toughness, tear strength, and good properties at low temperatures) with those of polyacrylates (good optical properties and weatherability) [18].

There has recently been considerable attention granted to polymer-blends obtained from the mixture of two or more distinctly cross-linked polymers. This can be explained by the fact that it creates polymer network materials which have improved properties [11, 19–21].

Functionalized vegetable oils have been used as constituent component materials to prepare polymer network materials. These materials can also be obtained by vinyl polymerization of the double bonds within the fatty acid chains of these vegetable oils [22–25]. The properties of resin samples obtained from AESO with varying amounts of styrene that were cured at room temperature were studied [26].

In this study, the blending technique applied utilizes the polymer networks of the two prepolymer components. The aim of this article is the development of novel flexible network polymers from small-weight prepolymers by free-

---

S. Oprea (✉)
“Petru Poni” Institute of Macromolecular Chemistry, Aleea
Grigore Ghica Voda No. 41-A, 700487 Iasi, Romania
e-mail: stefop@icmpp.ro

radical multivinyl crosslinking polymerization with potential for industrial relevance. After crosslinking, the network biopolymer became a smooth and very flexible film.

Experimental

Materials

The polyester, poly(butane adipate)diols ($M_n = 1000$), 4,4′-diphenylmethane diisocyanate (MDI), acrylated epoxidized soybean oil (AESO), and acrylic acid (AA) were purchased from Aldrich. 1,6-hexamethylene diamine, obtained from Merck, was used without further purification and dimethylformamide (DMF) was purified and dried by vacuum distillation. 4,4′-diphenyl methane diisocyanate, obtained from Merck, was purified by vacuum distillation and acrylic acid was distilled at reduced pressure and the middle portions were stored at 0–4 °C until being used.

Synthesis of polyester urethane acrylate

Polyester urethane acrylate (PUA) was synthesized as described in previous study [27]. Polyester diols were introduced in the flask and melted in an oil bath at 120–130 °C and dehydrated for 2 h at 2 mmHg. In the first step, MDI was poured into a glass reactor together with polyester at 80 °C and kept maintained for 2 h, resulting in a molecular structure carrying an isocyanate at both ends. The NCO/OH ratio of all formulations was 1.03–1.05. In the second step, the obtained prepolymer diisocyanate was added slowly, while mechanically stirring, over 2 mol of 1,6-hexamethylene diamine in a 100-mL DMF solution. The reaction mixture was stirred for another 2 h. In the third step, 2 mol of acrylic acid was poured into the reactor at room temperature while being mechanically stirred. The result is a product which created a reactive vinyl group to the molecular chain ends as polymerizable groups. Films from the synthesized polymers have been obtained on cleaned glass plates by thermal treatment at 80 °C for 2 h.

Preparation of PUA/AESO blend films

A series of PUA/AESO prepolymer blends were prepared by changing the weight ratio of PUA to AESO. The prepolymers used in the blend networks have approximately equal weights. For the mixtures of polymers, PUA was used immediately after synthesis.

AESO dissolved in 50-mL DMF at room temperature was poured over the PUA prepolymer in the flask. The mixture was stirred at room temperature for 20 min to form a homogeneous solution. The resulting mixture was given a solid content of about 15 wt% by adding DMF and then it was cast onto cleaned glass plates. The obtained blends were cured at 80 °C for 2 h to obtain PUA/AESO network films. The PUA/AESO blends' formulations for the various weight ratios and the nomenclature used for these network polymers are shown in Table 1.

Table 1 Formulations of the obtained network polyurethanes blends

Designation samples	PUA content (wt%)	AESO content (wt%)
IPA 1	100	–
IPA 2	85	15
IPA 3	70	30
IPA 4	55	45
IPA 5	40	60
IPA 6	25	75
IPA 7	10	90

Measurements

FTIR spectra were recorded on a Bruker VERTEX 70 Instruments equipped with a Golden Gate single-reflection ATR accessory. The spectra were recorded in the range of 600–4000 cm^{-1} with a nominal resolution of 4 cm^{-1}.

The *thermal stability* of polyurethanes was tested in an air atmosphere through thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of TGA scans was of 10 °C/min. The initial weight of the samples was of about 50 mg and the temperature range 30–700 °C.

A *differential scanning calorimeter* (DSC) type DSC-7 Perkin-Elmer was used for thermal analysis and was operated at a heating rate of 10 °C/min. The thermal transition behavior was studied in a temperature range of −100–60 °C. Tests were conducted on samples of about 10 mg that were gradually heated to observe the glassy transition temperature (T_g).

Dynamic mechanical analysis (DMA) was performed using a Perkin Elmer Diamond DMA to determine the storage modulus (E') and the loss factor (tan δ). All samples were scanned at a constant heating rate of 2 °C per min, within a temperature range of −100–250 °C. The resulting plots for E' and tan δ are displayed as a function of temperature and at 1-Hz frequency.

Stress–strain measurements were performed on dumbbell-shaped samples cut from the obtained polyurethane network sheets. The tests were performed at room temperature using a Shymadzu EZTest (Japan), equipped with a 5-kN load cell. The used cross-head speed was of 50 mm/min.

Contact Angle Measurements (CA) were performed using deionized water and ethylene glycol droplets of 5 μL in volume applied onto the neat surface of the different polyurethanes using a Dataphysics Contact Angle System KSV Instruments LTD, Finland. Water contact angle measurements were acquired using the sessile drop method [28]. The contact angle was measured within 45–60 s of the addition of the liquid drop with an accuracy of ±1°. Measurements were repeated 6–10 times with different test pieces of the same sample to check for accuracy.

Results and discussion

FTIR spectroscopy was used to investigate the structural differences of PUA/AESO networks with various weight ratio formulations. The FTIR spectra of the PUA/AESO films as a function of the AESO content are shown in Fig. 1.

For characterization of the hydrogen bonding state of the polyurethanes, two principal vibration regions were generally used: the N–H stretching vibration (3200–3500 cm^{-1}) and the carbonyl C=O stretching vibration in the amide I region (1690–1730 cm^{-1}). Polyurethanes are capable of forming several kinds of hydrogen bonds, either hard segment–hard segment or hard segment–soft segment bonds [13, 29].

The peak at 1720 cm^{-1} is the assigned frequency for the absorption of the free-bonded C=O stretching [30, 31].

The intensity of the characteristic absorption peak in the region of 3200–3500 cm^{-1}—which corresponds to N–H stretching—decreases when the AESO content increases in the network blends. This is due to a steric hindrance effect caused by the large amount of dangling chains generated by the usage of AESO, which block the formation of hydrogen bonds [12]. Also, the infrared absorption frequency for N–H group shifts from 3380 to 3320 cm^{-1} with the increase of AESO content. This reveals changes in the strength of the intermolecular interactions with the increase of AESO content. They are due to the formation of intermolecular cross-linkage structures which disperse in the network films [32–34]. This is deemed to improve the mechanical properties of the cross-linked polyurethane elastomers.

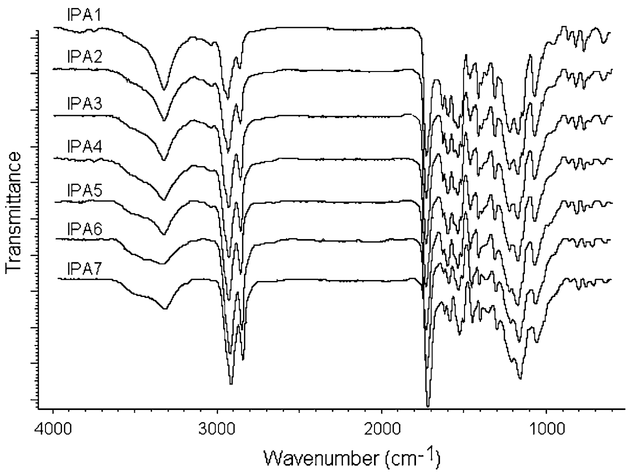

Fig. 1 FTIR spectra of network blend films

Thermal behavior

Polyurethanes have relatively low thermal stability, mainly because of the presence of urethane bonds.

TGA curves of the PUA/AESO elastomers with various blend ratios are shown in Fig. 2. There were three distinct stages of decomposition in the curves. In the first stage, polyurethane elastomers decomposed slowly until 200–300 °C, which accounted for the first 3–5% of the weight loss. The initial decomposition temperatures of these network blends' films are higher than those of the PUA film and increased with the increase of AESO content. The weight loss of the PUA in first decomposition stage takes place at a lower temperature when compared to the PUA/AESO weight loss temperature. This can be explained through the existence of a higher amount of weaker urethane bonds (in the PUA) [12, 35]. High cross-linked molecular structures are more thermal-resistant and that indicates a lower rate of diffusion of the degraded products within the matrix.

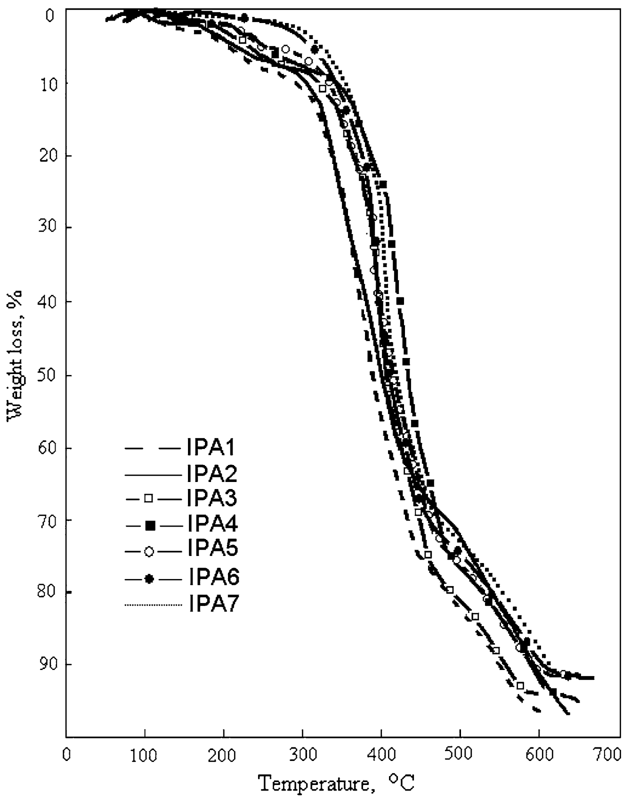

Fig. 2 TG curves of network blend films

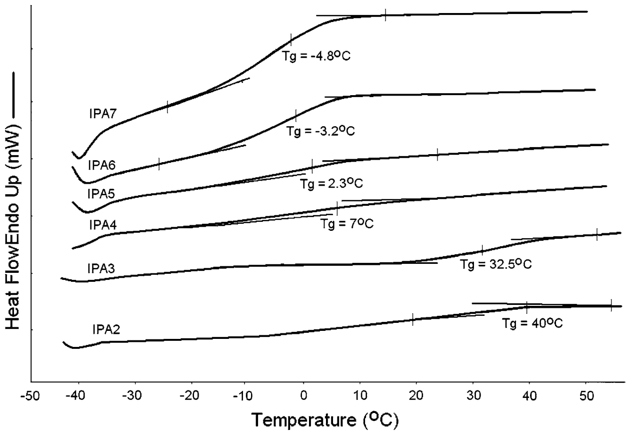

Fig. 3 The DSC scan plots for network polyurethanes films

The weight loss is very rapid in the temperature range of 300–500 °C and samples of PUA/AESO have similar degradation behavior above 400 °C.

The DSC curves of the PUA/AESO elastomer sheets with different component weight ratios are shown in Fig. 3.

The glass transition of a polymer network is affected by the cross-linking density and amount of dangling chains. The increase of AESO content leads to higher cross-linked networks, yet it causes the T_g to have a decreasing trend. This could be explained by the high amount of dangling chains which act as plasticizers which reduce the polymer rigidity and increase the flexibility, resulting in lower T_g as well. The T_g transition may be related to the motion of the backbone chain of the short groups of the fatty acid chains.

The dynamic mechanical properties, storage modulus (E') and mechanical loss factor (tan δ), for the PUA and PUA/AESO blend films (as a function of temperature at a frequency of 1 Hz) are shown in Figs. 4 and 5.

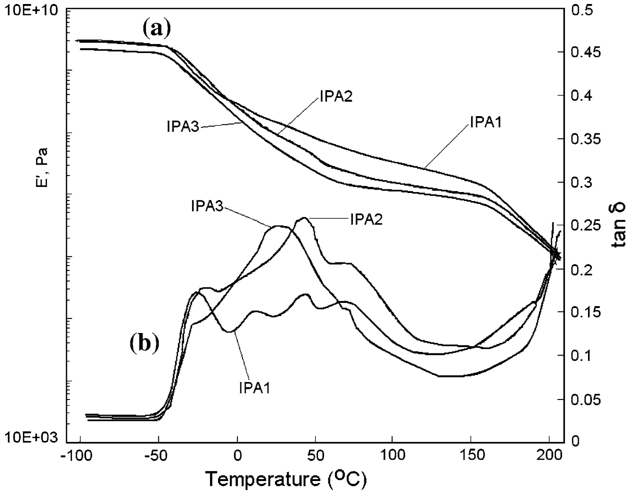

Fig. 4 The dependences of storage modulus (E') (*a*) and tan δ (*b*) on temperature for polymer networks with different PUA and AESO content

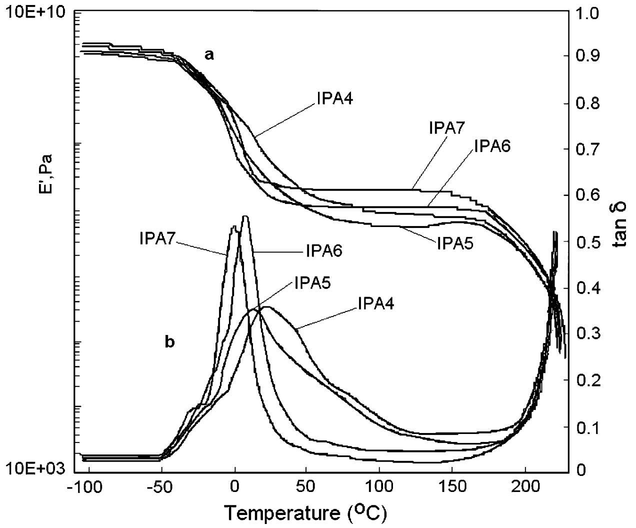

Fig. 5 The dependences of storage modulus (E') (*a*) and tan δ (*b*) on temperature for polymer networks with different PUA and AESO content

For PUA elastomers, the storage modulus decreased gradually, then decreased relatively fast around −20–0 °C followed by another large gradual decrease. The storage modulus of the PUA/AESO blends decreases slowly with the increase in temperature, yet in the glass-transition region, it is characterized by abrupt drops determined by the increase of AESO content.

For PUA/AESO blends, the storage modulus curve shows a plateau, which indicates the existence of an increase in size of the inter-connectivity of molecular chains, resulting in a significant structural reinforcement. This plateau is more extensive and clear for network polymer blends with high content of AESO, which is a result of the formation of more continuous phase morphology.

The network homogeneity for each network sample was analyzed by comparing the widths of the glass-transition peaks of the mechanical loss factor (tan δ) curves [36]. The width of the tan δ peak for network blends decreases with the increase of AESO content. Also, the maximum peaks for tan δ move from 45 °C (IPA2 with lower AESO content) to 0 °C (IPA7 that have the highest AESO content). The wide peak of the tan δ for network blends with lower AESO content shows a large distribution of the heterogeneities within the network structures [23]. The network polymers with the highest cross-linking density (highest AESO content) have a single sharp loss peak that indicates that the polymers' network had a homogeneous phase [26].

Mechanical properties

The mechanical behavior of the polyurethane network films is dependent on the intermolecular interactions between the molecular chains of these elastomers. The

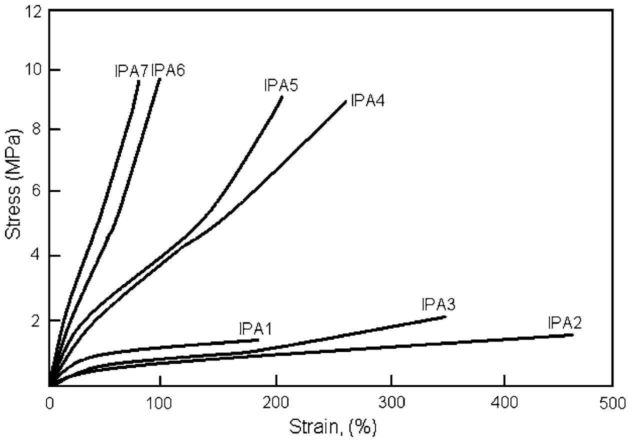

Fig. 6 Stress versus strain curves for the network films

stress versus strain curves for the network blends with various AESO content (which were uniaxially deformed until breaking) are shown in Fig. 6.

The best stress–strain properties were obtained from IPA4 network elastomers based on a 55% PUA and 45% AESO content, which have a tensile strength at break of 9 MPa but also present an elongation of 270%. The network sheet with a weight ratio of 10/90 for the PUA/AESO blend is more rigid, having a tensile strength of 9.5 MPa but only a 70% elongation at break. We could explain this behavior in terms of the three-dimensional cross-linked structure of the polymeric matrix imposed by the AESO monomer.

When the AESO content was more than 50 wt%, the tensile strenght at break-point only showed a slight increase, fact that can be explained as a result of the large amount of dangling chains that are present, which represent imperfections in the final polymer network [12, 37, 38].

The hydrophobicity or hydrophilicity of the PUA/AESO network films' surface is characterized by contact angle. The drop of liquid forming an angle may be considered as resting in equilibrium, which is enabled through the balancing of the following three forces: the interfacial tensions between solid and liquid SL, those between solid and vapor SV, and those between liquid and vapor LV. The angle within the liquid phase is known as the contact angle or wetting angle. Low surface wettability (high hydrophobicity) is a common surface characteristic of many polymers. Hydrophobicity reflects the surface energy of a substrate and influences the adsorption of proteins by materials surfaces [39, 40] and this is known to directly influence the behavior of cells grown on the substrate [39, 41]. Hydrophobic surfaces are known to inhibit the proliferation and increase of the rate of apoptosis of anchorage-dependent osteoblastic cells when compared to cells grown on hydrophilic surfaces [39, 41].

Table 2 Contact angle (θ) and work of adhesion (W_a) values of the network film surfaces

Sample	Water		Ethylene glycol	
	θ (°)	Wa (mN/m)	θ (°)	W_a (mN/m)
IPA 1	81.7	83.2	42.5	83.4
IPA 2	79.8	85.6	75.8	59.7
IPA 3	77.5	88.5	76.7	59
IPA 4	77.3	88.8	73.2	61.9
IPA 5	73	93.9	73.3	61.8
IPA 6	84	79.3	72.3	62.6
IPA 7	84.8	80.2	73.8	61.4

The wettability of PUA/AESO network blends was examined by CA measurements using two probe liquids, water and ethylene glycol. The contact angle (θ) and work of adhesion (W_a) values of the different PUA/AESO blend films' surfaces are tabulated in Table 2.

The work of adhesion, W_a, was calculated using the following equation:

$$W_a = \gamma_{lv}(1 + \cos\theta) \quad (1)$$

where γ_{lv} is the surface tension of the liquid used for the contact angle measurement.

The contact angles for the PUA/AESO films' surfaces show a decreasing trend when AESO content is increased up to 60%. At high values of AESO content the contact angles increases, which is due to the replacement of the PUA component on the film's surface by the AESO component.

All surfaces are hydrophobic in nature, with the mention that the surfaces that display the lowest contact angles are the ones that have an AESO content of maximum 60%.

The interfacial tension for a solid–liquid system (γ_{sl}) was calculated using the following equation [42]:

$$\gamma_{sl} = \left(\sqrt{\gamma_{lv}^{p}} - \sqrt{\gamma_{sv}^{p}}\right)^2 + \left(\sqrt{\gamma_{lv}^{d}} - \sqrt{\gamma_{sv}^{d}}\right)^2 \quad (2)$$

The resulting interfacial tensions are listed in Table 3.

Table 3 Interfacial tension for a solid–liquid system (γ_{sl}) network films obtained

Sample	λ_{sv}^{p} (mN/m)	λ_{sv}^{d} (mN/m)	γ_{sl} (mN/m)	
			Water	Ethylene glycol
IPA 1	2.6	41.2	33.4	8.5
IPA 2	25.3	2.2	16.6	15.7
IPA 3	30.8	0.9	16	20.8
IPA 4	27.3	2.3	13.6	15.7
IPA 5	36	0.8	15	22.9
IPA 6	13.9	7.8	15.15	7.1
IPA 7	16.1	5.9	15.7	8.7

p polar, *d* disperse

From Table 3, we can see that the values of the interfacial tension of the polymer blends decrease as the AESO content rises to a maximum of 50%, then being followed by an increase (with the increase of AESO content above 50%). The variation of the AESO content in the polymer matrix may have also affected the surface properties.

Conclusions

Polyurethane acrylate was blended with AESO and was cast on a DMF solvent system leading to the creation of new network blend films. These two components are compatible for a large distribution of ratio as a result of the chemical cross-linking existing in these network blends.

For the network blends containing more than 50-wt% AESO, the tensile strenght increases very little, while the elongation at break decreases greatly.

With the increase of AESO content in the network blend, thermal stability presents a moderate increase and T_g decreases due to the effect of the dangling chains present in the triglyceride structures, chains that act as plasticizers. The properties of PU films were mainly governed by the stoichiometric balance of the components in the reaction and the degree of cross-linking.

This study provides an alternative way of utilizing renewable resources to prepare network blend films with high performance for various applications.

Acknowledgement The author gratefully acknowledges Dr. Mariana Cristea for her assistance with the DMA measurements.

References

1. Hepburn C (1991) Polyurethane elastomers, 2nd edn. Elsevier, London
2. Kong X, Yue J, Narine SS (2007) Biomacromolecules 8:3584
3. Velankar S, Cooper SL (2000) Macromolecules 33:382
4. Chun BC, Cho TK, Chong MH, Chung YC (2007) J Mater Sci 42:9045. doi:10.1007/s10853-007-1824-2
5. Kong X, Narine SS (2007) Biomacromolecules 8:2203
6. Guo A, Zhang W, Petrovic ZS (2006) J Mater Sci 41:4914. doi:10.1007/s10853-006-0310-6
7. Li F, Hanson MV, Larock RC (2001) Polymer 42:1567
8. Petrovic ZS, Cevallos MJ, Javni I, Schaefer DW, Justice R (2005) J Polym Sci B 43:3178
9. Petrovic ZS, Zhang W, Javni I (2005) Biomacromolecules 6:713
10. Zlatanic A, Petrovic ZS, Dusek K (2002) Biomacromolecules 3:1048
11. Kong X, Narine SS (2008) Biomacromolecules 9:1424
12. Narine SS, Kong X, Bouzidi L, Sporns P (2007) J Am Oil Chem Soc 84:55
13. Lligadas G, Ronda JC, Galia M, Cadiz V (2007) Biomacromolecules 8:1858
14. Latere Dwanisa JP, Mohanty AK, Misra M, Drzal LT, Kazemizadeh M (2004) J Mater Sci 39:2081. doi:10.1023/B:JMSC.0000017770.55430.fb
15. Guner FS, Yagci Y, Erciyes T (2006) Prog Polym Sci 31:633
16. Zlatanic A, Lava C, Zhang W, Petrovic ZS (2004) J Polym Sci B 42:809
17. Yeganeh H, Mehdizadeh MR (2004) Eur Polym J 40:1233
18. Oprea S, Vlad S, Stanciu A, Ciobanu C, Macoveanu M (1999) Eur Polym J 35:1269
19. Athawale V, Kolekar S, Raut S (2003) J Macromol Sci Polym Rev 43:1
20. Duskova-Smrckova M, Dusek K (2002) J Mater Sci 37:4733. doi:10.1023/A:1020843020379
21. Begum M, Siddaramaiah (2004) J Mater Sci 39:4615. doi:10.1023/B:JMSC.0000034156.29967.82
22. Pattnaik T, Nayak PL, Lenka S, Mohanty S, Rao KK (1994) Thermochim Acta 240:235
23. Kong X, Narine SS (2008) Biomacromolecules 9:2221
24. Patel M, Suthar B (1987) J Appl Polym Sci 34:2037
25. Lu YS, Larock RC (2007) Biomacromolecules 8:3108
26. Sharma V, Kundu PP (2006) Prog Polym Sci 31:983
27. Oprea S, Vlad S, Stanciu A (2001) Polymer 42:7257
28. Erbil H (1997) Surface tension of polymers in handbook of surface and colloid chemistry. CRC Press, New York
29. Papadimtrakopoulos F, Sawa E, MacKnight WJ (1992) Macromolecules 25:4682
30. Queiroz DP, Pinho MN, Dias C (2003) Macromolecules 36:4195
31. Coleman MM, Lee KH, Skrovanek DJ, Painter PC (1986) Macromolecules 19:2149
32. Tsai MH, Huang SL, Chang PH, Chen CJ (2007) J Appl Polym Sci 106:4277
33. Coleman MM, Skrovanek DJ, Painter PC (1988) Macromolecules 21:59
34. Tanaka K, Yoon TS, Takahara A, Kajiyama T (1995) Macromolecules 28:934
35. Javni I, Petrovic ZS, Guo A, Fuller R (2000) J Appl Polym Sci 77:1723
36. Son TW, Lee DW, Lim SK (1999) Polym J 31:563
37. Fedderly JJ, Lee GF, Lee JD, Hartmann B, Dusek K, Duskova-Smrckova M, Sÿomvarsky J (2000) J Rheol 44:961
38. Lee YL, Sung PH, Liu HT, Chou LC, Ku WH (1993) J Appl Polym Sci 49:1013
39. Keen I, Raggatt LJ, Cool SM, Nurcombe V, Fredericks P, Trau M, Grøndahl L (2007) J Biomat Sci Polym Edi 18:1101
40. Tamada Y, Ikada Y (1994) J Biomed Mater Res 28:783
41. Chang EJ, Kim HH, Huh JE, Kim IA, Seung KJ, Chung CP, Kim HM (2005) Exp Cell Res 303:197
42. Erbil H (2006) Surface chemistry of solid and liquid interfaces. Blackwell Publishing, Oxford