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Research Article

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Effects of Molecular Weight of Dextran on Dynamic Mechanical Properties in Functional Polymer Blend Systems

Fonksiyonel Polimer Karışım Sistemlerinde Dekstran Molekül Kütlesinin Dinamik Mekanik Özellikler Üzerindeki Etkileri

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ABSTRACT

Blending of natural/synthetic polymers is one of the most practical way to obtain a new material with desired properties such as thermal, mechanical and dynamic mechanical properties. Dynamic mechanical analysis (DMA) is a strong method to investigate the mechanical/viscoelastic properties, thermal transitions and compatibility in these polymer blend systems. In this study, biocompatible T10 and T40 dextran (DEX) and polymethacrylamide (PMAM) blend systems were prepared by solution casting method. Variations of dynamic mechanical properties including storage modulus (SM), loss modulus (LM) and tan δ of the DEX/PMAM blends were investigated for all samples at a specific fixed frequency of dynamic mechanical loading in a certain temperature range. The SM of the pristine polymers increased in the following order: PMAM<DEX10<DEX40. Thermal transitions and α-relaxations were observed from results of DMA measurements. In general, a single glass transition temperature was observed in binary blend systems. Glass transition temperatures increased with increasing molecular weight of DEX in 50/50 wt.% blend systems. It was found that temperature dependence of dynamic mechanical properties and curves exhibit typical behaviors and strongly depended on the molecular weight, intra- and intermolecular interactions due to the hydrogen bonding in these blend systems.

Key Words

Dextran, polymethacrylamide, polymer blends, DMA.

ÖZ

Doğal/sentetik polimerlerin karıştırılması termal, mekanik ve dinamik mekanik özellikler gibi istenilen özelliklere sahip yeni bir malzeme elde etmenin en pratik yöntemlerden biridir. Dinamik Mekanik Analiz (DMA), bu polimer karışım sistemlerindeki mekanik/viskoelastik özellikleri, termal geçişleri ve uyumluluğu araştırmak için güçlü bir yöntemdir. Bu çalışmada, biyouyumlu T10 ve T40 dekstran (DEX) ve polimetakrilamit (PMAM) karışım sistemleri çözücü uzaklaştırılması yöntemiyle hazırlanmıştır. DEX/PMAM karışımlarının depolama modülü (SM), kayıp modül (LM) ve tan δ parametrelerini içeren dinamik mekanik özelliklerinin değişimleri tüm örnekler için belirli sabit bir frekansta dinamik mekanik yükleme ile belirli bir sıcaklık aralığında analiz edilmiştir. Saf polimerlerin SM'leri şu sırayla artmıştır: PMAM<DEX10zDEX40. DMA ölçümleri sonucunda termal geçişler ve α-relaksasyonları gözlenmiştir. Genel olarak ikili karışım sistemlerinde tek bir camsı geçiş sıcaklığı gözlenmiştir. Camsı geçiş sıcaklıkları DEX'ın molekül kütlesinin artmasıyla 50/50 wt.% karışım sistemlerinde artmıştır. Dinamik mekanik özelliklerin ve eğrilerinin sıcaklığa bağlılığının tipik davranışlar gösterdiği ve bu karışım sistemlerindeki molekül kütlesine, hidrojen bağına bağlı molekül içi ve moleküller arası etkileşimlere önemli ölçüde bağlı olduğu bulunmuştur.

Anahtar Kelimeler

Dekstran, polimetakrilamit, polimer karışımları, DMA.

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INTRODUCTION

Nowadays, there has been a growing interest in new functional polymeric materials based on the mixtures of two or more functional synthetic/natural polymer or copolymer. Novel polymeric blend materials are more substantial and specific material than their components due to the advanced mechanical/rheological properties and biocompatible character. These advanced materials can be obtained by the blending of synthetic and natural polymers. Such materials obtained by blending natural and synthetic polymers must also be biocompatible and having improved thermal, mechanical and rheological properties, especially for use as biomaterials in bioengineering areas [1]. Blending is also used for the modification/improvement of the miscibility-structure or impact strength-structure properties of the known polymers [2].

Biocompatibility and phase separation investigations of certain polysaccharides and their synthetic polymer blends are of great interest as intramolecular and intermolecular interactions allow the obtain novel polymeric materials especially in biomedical applications [3,4]. Dextran (DEX) is a water soluble and naturally occurring polysaccharide having perfect biocompatible and biodegradable characteristics and also exhibit antithrombotic and anti-inflammatory properties. Dextrans are used for the rheological bettering of artificial tears and plasma volume expanders with these important properties [5]. Dextrans have shown to be a potential material for use in a variety of drug formulation and gene delivery systems. Due to the great number of functional hydroxyl groups, dextran polymer is useful for chemical conjugation with different materials as well as modification and/or crosslinking. Due to its potential advantages, dextran, modified dextrans and dextran derivatives allow the possibility for the design and preparation of new desired biomaterials. Methacrylamide is another important environmentally friendly, biodegradable and less expensive water-soluble monomer than other vinyl synthetic material and it is estimated that methacrylamide has low bioaccumulation potential [6-8]. Because of the water-soluble character, reactivity and highly polar side groups, polymethacrylamide (PMAM) and its derivatives are used in different applications in construction, texture industries and biological applications. Copolymers of PMAM have also been used in oral drug delivery systems, catalytic antibody-polymer conjugate systems [9-11]. Besides, hydroxypropyl derivatives of methacrylamide polymers or copolymers have been synthesized, characterized and investigated. They have been used in drug delivery systems as drug carriers and polymer-drug conjugates, as well as gene delivery carriers due to their hydrophilic and non-immunogenic characteristics. The efficacy and biocompatible properties of these polymers have also been reported [12-22].

The molecular weight of polymers is an effective parameter that affects the properties and usage areas of the polymeric material. Many studies have been reported on the investigation of the molecular weight effect of polymers so far. Influence of glass transition temperatures and molecular weight of different dextran and poly(vinylpyrrolidone) (PVP) on drug amorphization kinetics [23]; composition and molecular weight effects on the miscibility behavior of dextran/PVP blends [24]; different molecular weights of dextran for freeze-drying and storage stability of the model protein and product quality attributes [25, 26]; miscibility of carbohydrate polymers in different dextran systems by thermal analysis [27]; effect of molecular weight of dextran on the biodegradable hydrogel with oil and quality of wheat sourdough breads [28,29] were investigated. Thermal/mechanical/rheological properties are considered to most important of all properties of polymeric materials in many applications. Especially rheological, mechanical and viscoelastic properties of potential biocompatible polymeric biomaterials significantly affect their clinical effectiveness. In polymeric blend system, dynamic mechanical analysis (DMA) is one of the most proven techniques for investigating viscoelastic properties, type of thermal transitions, intra-/intermolecular interactions and miscibility/phase separation-structure-property relationships to utilize all potentials of blending using especially measurements of storage modulus (SM), loss modulus (LM) and loss factor (tan δ) which represents the internal friction or damping at a specific fixed frequency or frequency range over a range of temperatures. All these important parameters derived from dynamic mechanical analysis are related to the molecular motions under applied stress and therefore provide important information about the chain structure and viscoelastic properties of the polymeric material. In addition, DMA also provides information about the secondary and tertiary transition as well as the main transition, which is not easily distinguishable by other common techniques [30].

The objective of this study is to investigate and analyze dynamic mechanical properties, type of transitions, intra- and intermolecular interactions and compatibility/phase separation-structure-property relationships of the blends of DEX with certain molecular weights and PMAM. Dynamic mechanical behavior and thermal transitions of polymers and blends were described by SM, LM and tan δ with increasing temperature. Dynamic mechanical properties and glass transition temperatures were discussed for the neat polymers and their blends due to the intramolecular/intermolecular interactions and hydrogen bonding as a function of the molecular weight and composition.

MATERIALS and METHODS

Materials

Dextran T10 and T40 with molecular weights 10000 (DEX10) and 40000 (DEX40) polymer samples studied in this work was provided from Pharmacia Fine Chemicals (Sweden). Polymethacrylamide (PMAM) polymer sample used in this study supplied from Polysciences, Inc. (Warrington, PA). Polymers used without further purification. Double-distilled water was used for the preparation of solutions.

Preparation of Polymer Blends

DEX and PMAM polymers were dissolved in water to the total concentrations of 1.0 g dL^{-1} and each solution was stored overnight to ensure complete dissolution. Certain polymeric blend systems were then prepared and by mixing the stock solutions of each polymer, identical to the resulting weight ratios of the polymers 50/50, 30/70 and 70/30 wt.%. The mixtures were stirred for 1 hour to obtain the homogeneous solutions and then polymeric samples obtained by solution casting at room temperature and finally samples were dried under vacuum at 50°C. All samples were kept under dry condition.

Dynamic Mechanical Analysis (DMA)

The dynamic mechanical properties of neat polymer and polymer blend materials were investigated using Dynamic Mechanical Analyzer (DMA, TA Instruments, Q800, USA). Polymers and blend samples were mixed with Al_2O_3 (50:50 wt.%) and loaded into the powder holder which consist of upper and lower tray of stainless steel used in conjunction with the standard dual cantilever clamps. The temperature was increased at a heating rate of 3 °C/min over a temperature range of 25 °C to 250 °C at a 1 Hz constant frequency. All necessary calibrations of the instrument were performed before the analysis according to the TA operation manual.

RESULTS and DISCUSSION

The dynamic mechanical properties of most of polymers show a significant dependence on temperature and rate of deformation because these polymers are viscoelastic in nature [31]. The mechanical, thermal and viscoelastic behavior of polymer blends depends on the properties and composition of each component and the interaction between the polymer chains in the system. DMA is one of the leading tools to investigate the dynamic mechanical properties, viscoelasticity of polymeric materials and it can be used to identify the thermal transitions, glass transitions and other relaxations, miscibility, physicochemical and rheological properties of the polymer components in the blend systems. Compatibility can be evaluated using DMA by monitoring the homogeneity resulting from the intermolecular interactions. Compatible blends may show a single transition, but incompatible blends may show characteristics of both types. In DMA technique, stiffness and damping properties of a polymeric materials are measured. Important parameters such as storage modulus, loss modulus and tan δ can be obtained. These parameters are specific to the polymeric material and are also related to the molecular motions under stress, and all parameters depend on the material’s structure and history, as well as on the experimental conditions. Dynamic mechanical and viscoelastic properties were obtained in temperature scans at a constant frequency from DMA measurements for all transition regions of the polymers and polymeric blend samples.

All thermal transitions of pristine PMAM, DEX10 and DEX40 polymers were shown in storage modulus, loss modulus and tan δ *vs*. temperature curves in Figure 1a-c. The storage modulus provides the elastic response of the polymeric material during deformation and measures the stored energy. The SM values also indicates the strength of the polymeric materials. At any constant deformation rate, the temperature at which the value of storage modulus begins to decrease quickly, point out the glass transition temperature [31,32]. This process of decreasing SM as with an increasing temperature in polymeric system occurs due to increased chain mobility and flexibility of polymer sample. The loss modulus refers to a viscous part and signifies the energy dissipates. Another important parameter loss factor,

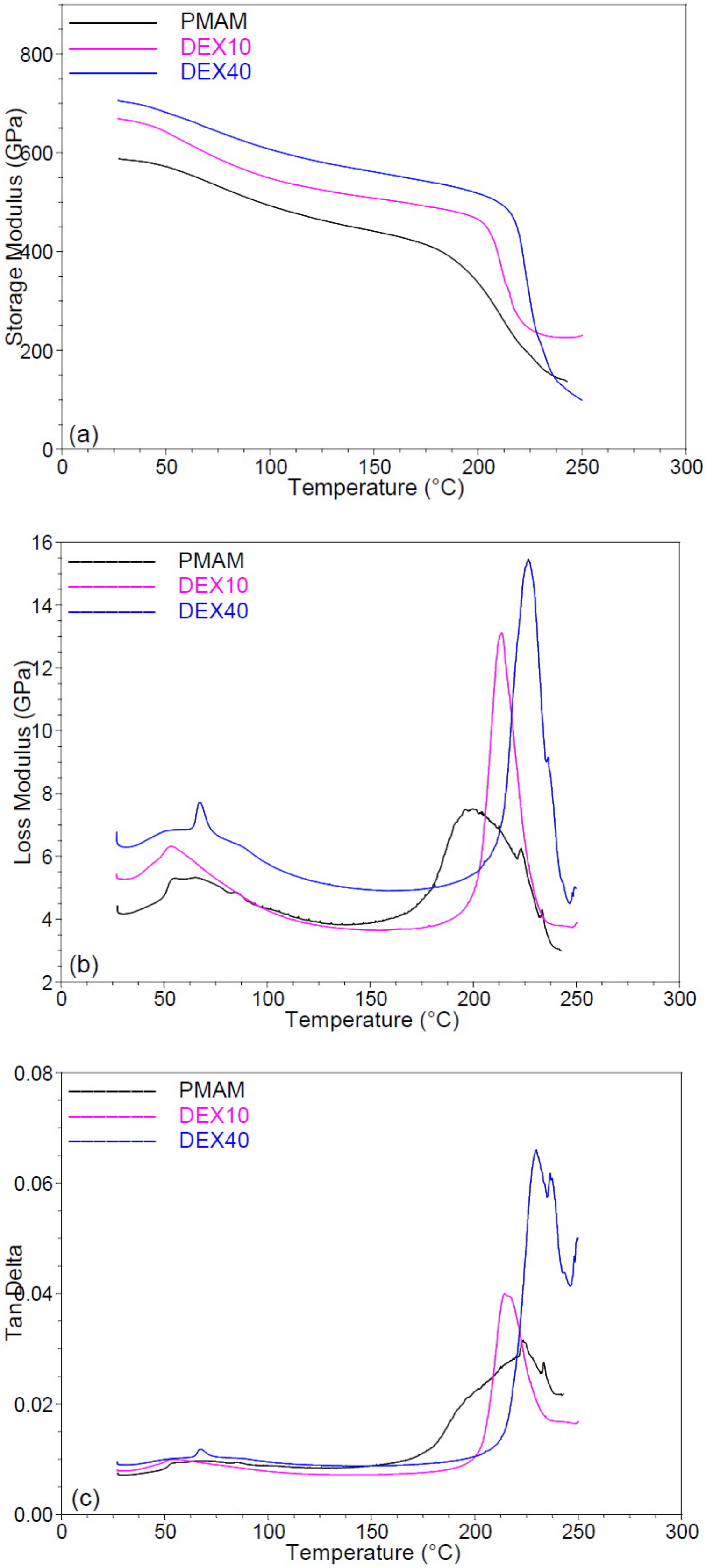

Figure 1. SM (a), LM (b) and tan δ (c) curves of PMAM, DEX10 and DEX40 as a function of temperature.

tan δ is defined as the ratio between the loss modulus to storage modulus (δ is the phase angle) and measure of damping property of the polymeric material [30]. All samples had a main transition, glass transition, T_g, occurring with an increasing temperature as a response of polymers from all measured DMA parameters and can be shown in DMA curves. PMAM showed a main transition at 65.1°C from tan δ curve corresponds to glass transition and exhibited degradation at above 200°C. DEX10 and DEX40 exhibited glass transitions at 53.6°C and 67.3°C from tan δ curves. In the tan δ curves, degradation was observed for DEX10 at 214.3°C, while degradation was observed for DEX40 at 229.2°C and 236.4°C (Table 1).

It was observed that the glass transition temperature was higher for DEX40 as expected. It can be said that the results are consistent with the literature [27]. In general, the glass transition temperatures of polymers increase with increasing molecular weight until they have long polymer chains, and then a region characterized by a low increase in glass transition temperature can be observed. It has been described in the literature that at higher molecular weights, a less dependence of the glass transition temperature dependent state may occur due to entanglement coupling resulting in an infinite molecular weight dependent network [26,27]. It has been reported previously that dextran reaches entangled coupling molecular weight in the range of about 11000 to 43000 [27,33,34].

Figure 2 shows the storage modulus and derivative storage modulus-temperature curves of 50/50 blend systems for two molecular weights of dextran with PMAM. In this figure, typical storage modulus-temperature behaviors were observed for the blend samples. Storage modulus values gradually decreased with increasing temperature. The first transitions can be interpreted as a softening of the polymeric material and these transitions result from the primary α-transition or glass transition. In the glassy region, blends showed high modulus. Glassy high modulus region that restricted segmental mobility decreased by the increasing temperature to the rubbery plateau with the loss of ri-

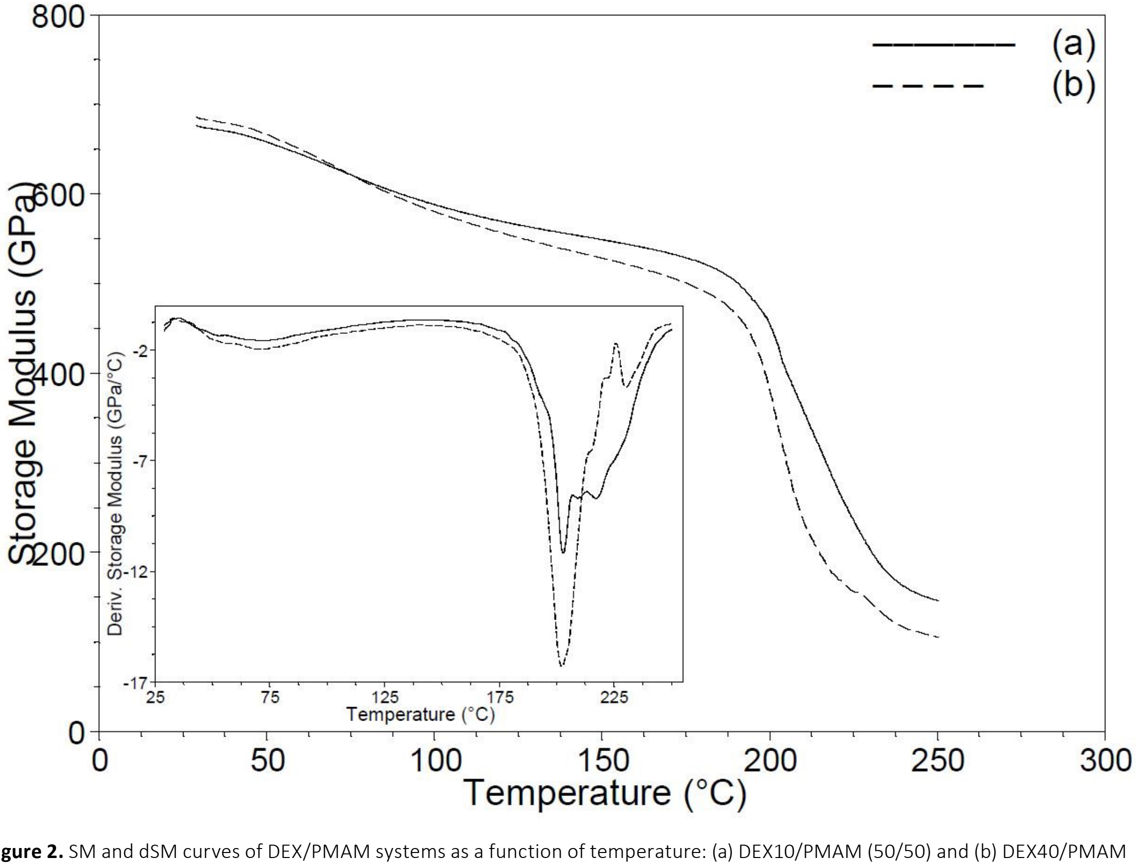

Figure 2. SM and dSM curves of DEX/PMAM systems as a function of temperature: (a) DEX10/PMAM (50/50) and (b) DEX40/PMAM (50/50).

gid solid structure of polymer chains. Storage modulus exhibited higher values for the DEX10/PMAM systems after nearly glass transition. The second sharp decrease (T_2) observed in the storage modulus and derivative storage modulus curves at higher temperatures can be interpreted as the pseudo-melting behavior of the hydrogen bonding units. This sharp decrease can also be caused by degradation or decomposition of organic moieties and breaking of the main chains [35]. SM values of DEX10/PMAM (50/50) system were higher than pure polymers due to the intermolecular interactions in this blend system. Higher modulus values of blend may also be attributed to the presence of intermolecular interactions via hydrogen bonding in between amide groups of PMAM and hydroxyl groups of DEX component in blend systems. In the DEX40/PMAM (50/50) system, SM values were observed in between pure polymers.

According to loss modulus and tan δ curves (Figure 3), two transitions were observed due to the same molecular motions and interactions. Loss modulus and tan δvalues increased to a maximum at isothermal condition because of the increased chain mobility. The first peak of loss modulus and tan δ associated with molecular process of glass transition (Table 1). After a maximum, decreasing tendency were observed and this may come from free movement of the polymer chains [36]. The variations of tan δ with temperature were similar to variation of the loss modulus with temperature. Generally, broadened low temperature transitions were observed at 60.8°C and 69.0°C due to the glass transition for DEX10/PMAM and DEX40/PMAM blend systems of 50/50 wt.% from tan δ curves, respectively. At relatively higher temperatures other peak maximums were observed at 211.1°C, 238.8°C from tan δ curves for the DEX40/PMAM blend system of 50/50 wt.%.

DEX-PMAM compatibility can be interpreted by DMA results, especially from the α-transition/glass transition parameter. Generally, miscible/compatible blends typically exhibit only one glass transition that lies between the pure polymer components depending on the composition and they have a single, combined tan δ maximum [37]. For the immiscible/incompatible blends, original glass transitions and relaxations are observed. Where a limited or partial miscibility/compatibility is observed, shifting or broadening of the glass transition regions in one or more components may be observed. Shifts in glass transition regions and broadening of the transition for DEX10/PMAM blends for 30/70 composition can be observed from the DMA curves for the corresponding DMA parameters. T_g values of the blend samples were observed at higher temperatures that of pure polymers depending on the blend composition for the 30/70 ratio. T_g values increased by increasing PMAM weight fraction. Higher SM values also observed for the higher PMAM composition (Figure 4). In dextran, there are 3 different hydroxyl groups and intra- and intermolecular interactions can occur via hydrogen bonding with these groups. In the presence of PMAM, molecular interactions take place through the amide and carbonyl groups of PMAM and hydroxyl groups of DEX by intermolecular hydrogen bonding in these blend systems. PMAM also forms both intermolecular and intramolecular hydrogen bonding with hydrogen bond donor and acceptor groups because it has -N-H and -C=O groups. However, dextran forms both intramolecular and intermolecular hydrogen bonds due to the hydroxyl groups on the structure.

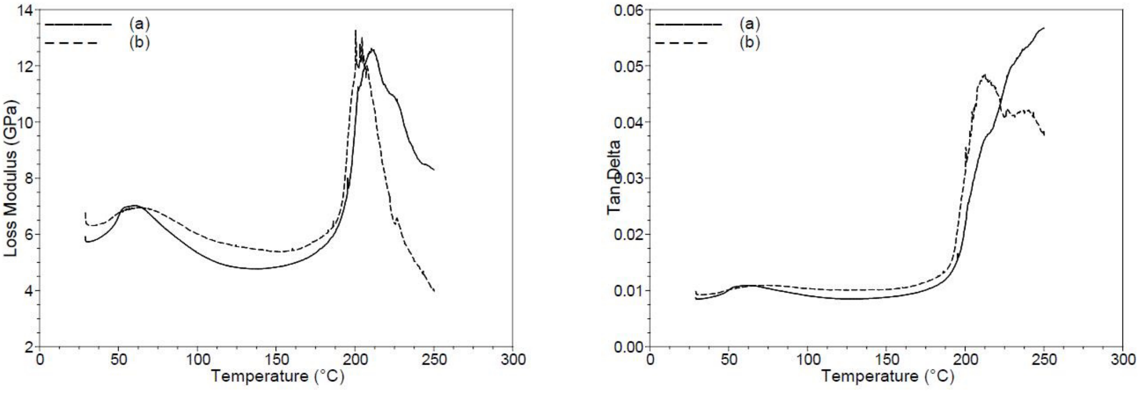

Figure 3. LM and tan δ curves of DEX/PMAM systems as a function of temperature: (a) DEX10/PMAM (50/50) and (b) DEX40/PMAM (50/50).

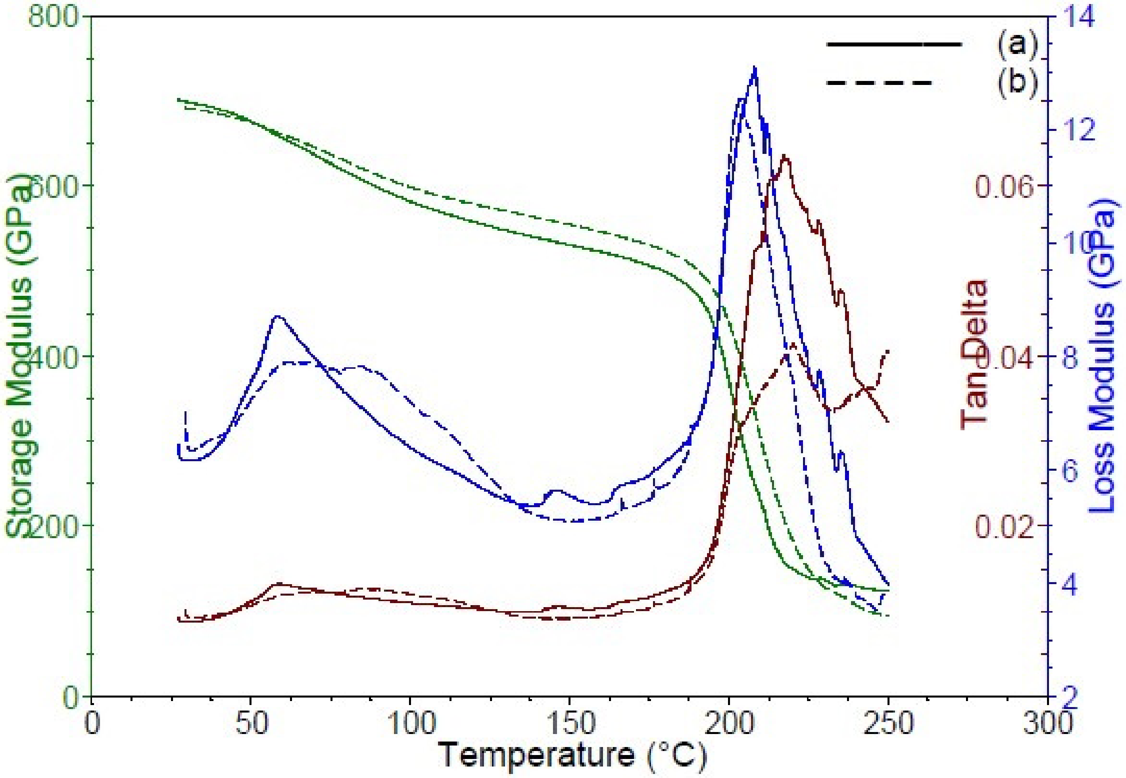

Figure 4. DMA curves as a function of temperature: (a) DEX10/PMAM (70/30), (b) DEX10/PMAM (30/70).

Table 1. DMA parameters of DEX/PMAM blend systems.

Sample	DMA parameters[a]: T_1 and T_2 (°C)					
	$T_{1,o}$ (SM)	T_2 (SM)	T_1 (LM)	T_2 (LM)	T_1 (tan δ)	T_2 (tan δ)
PMAM	50.1	211.3	65.1	199.5	65.1	223.4
DEX10	43.3	211.1	53.6	213.7	53.6	214.3
DEX40	46.4	222.1	67.3	226.7	67.3	229.2 236.4
DEX10/PMAM (30/70 wt.%)	51.3	208.9	84.1	204.1	84.1	220.1
DEX10/PMAM (50/50 wt.%)	50.1	202.9	60.8	210.4	60.8	N.O.
DEX10/PMAM (70/30 wt.%)	46.2	201.4	58.6	208.0	58.7	217.2
DEX40/PMAM (50/50 wt.%)	49.5	201.7	63.5	200.4	69.0	211.1 238.8

[a]SM, storage modulus; LM, loss modulus; tan δ, tan delta; o, onset; N.O., not observed.

CONCLUSION

At the first part of this study, DEX/PMAM blends were prepared at different molecular weight of DEX and compositions by solution casting method. In the second part, dynamic mechanical properties of polymer components and blends were investigated in detail with DMA. Results were then given depending on the molecular weight and blend composition. The effects of molecular weight and composition on the transitions and dynamic mechanical properties were determined by known DMA parameters. In addition, compatibility behavior and intra- and intermolecular interactions by hydrogen bonding were interpreted from especially observed transitions and modulus values. Hydrogen bonding forms in between the amide and carbonyl groups of PMAM and the hydroxyl groups of DEX as expected. However, it can be said that intramolecular interactions are still strong in polymers because of stronger/higher number of hydrogen bonding donor and/or hydrogen bonding acceptor character. Because, PMAM and DEX contain -C=O, -N-H and -O-H units, respectively. In these blend systems, it has been observed from the DMA properties that polymers form compatible mixtures. Generally, compatible blends exhibited one glass transitions between or close to the glass transitions of those of the pure polymer components. Blend with high molecular weight of DEX in 50/50 wt.% displayed high glass transition temperature. DMA parameters of DEX/PMAM blend systems were in good agreement with each other.

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