Synthesis, Morphology, Component Distribution, and Mechanical Properties of Nitrocellulose/Gradient Poly(ethylene glycol dimethacrylate) Semi-IPN Material

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ABSTRACT: Nitrocellulose (NC), a rigid natural polymer, was modified by gradient interpenetrating polymer networks containing poly(ethylene glycol dimethacrylate) (PEGDMA) to obtain both high strength and large toughness across the thickness from surface to the core of samples. PEGDMA content decreased with distance from the surface to core of nitrocellulose with a gradient of poly(ethylene glycol dimethacrylate) (NC/grad. PEGDMA) determined by elemental chemical analysis. The distribution of the guest component across the NC/grad. PEGDMA semi-IPNs sample thickness was reciprocal function. SEM micrographs of NC/grad. PEGDMA semi-IPNs revealed that, when the content of guest component was about 23%, the gradient system showed almost single phase morphology. At the same time, the tensile test results showed that NC/grad. PEGDMA featured both higher tensile strength and larger toughness. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 510–514, 2007

Key words: nitrocellulose; poly(ethylene glycol dimethacrylate); gradient interpenetrating polymer networks

INTRODUCTION

Nitrocellulose (NC), a cellulose derivation, is a natural polymer composed of β-1, 4-anhydroglucose units. It has been long used both in protective and decorative lacquer coating for automobile and wood furniture and in military application for explosives and propellants.[1] A more recent application is a safety device for automobile; emergency seat belt fasteners are equipped with a gas generator in which a small amount of nitrocellulose serves as a gas-generating reagent. One of significant lacks of NC is its mechanic properties. Generally NC products are used at temperature range of about −40°C to +60°C. Since NC is rigid polymer, its glass transition temperature is higher (the range of its glass transition temperature is about 53–63°C) comparing with its temperature range during usage, and it is apt to be brittle at low temperature as well as room temperature. The shortcoming limits NC to wide application in industrial and other agriculture fields et al.

Although adding plasticizers to NC can decrease its glass transition temperature, mechanic strength of NC production maybe decrease once plasticizers are excessively used. So, much more research works are devoted to improvement of mechanic properties of NC by means of chemical modification. In lacquer coatings application of NC, polyurethane/NC,[2–6] polyurethane/poly(vinyl chloride-co-vinyl acetate)/NC interpenetrating polymer networks (IPNs)[7] were especially studied to improve the shortcomings of NC. The interpenetrated and entangled networks in IPNs can increase the phase stability and therefore enhance the properties of the resulting materials.[8,9]

Distinct from traditional IPNs, gradient IPNs have compositions which vary as a function of position in the sample.[10] Gradient IPNs exhibit significant advantage over ordinary IPNs and initial matrices in specific functional application field and thermal and mechanic properties as well.

A gradient semi-interpenetrating polymer networks of nitrocellulose and poly(ethylene glycol dimethacrylate) (NC/grad. PEGDMA semi-IPNs) has been studied in our lab. Firstly, the synthesis, compatibility, mechanic properties will be reported in this paper.

EXPERIMENTAL

Materials and synthesis

The nitrocellulose is a pressed thick sheet with thickness of 4 mm containing about 12.97% nitrogen by weight (denoted as N %). Ethylene glycol dimethacrylate is washed by 5% NaOH solutions to remove
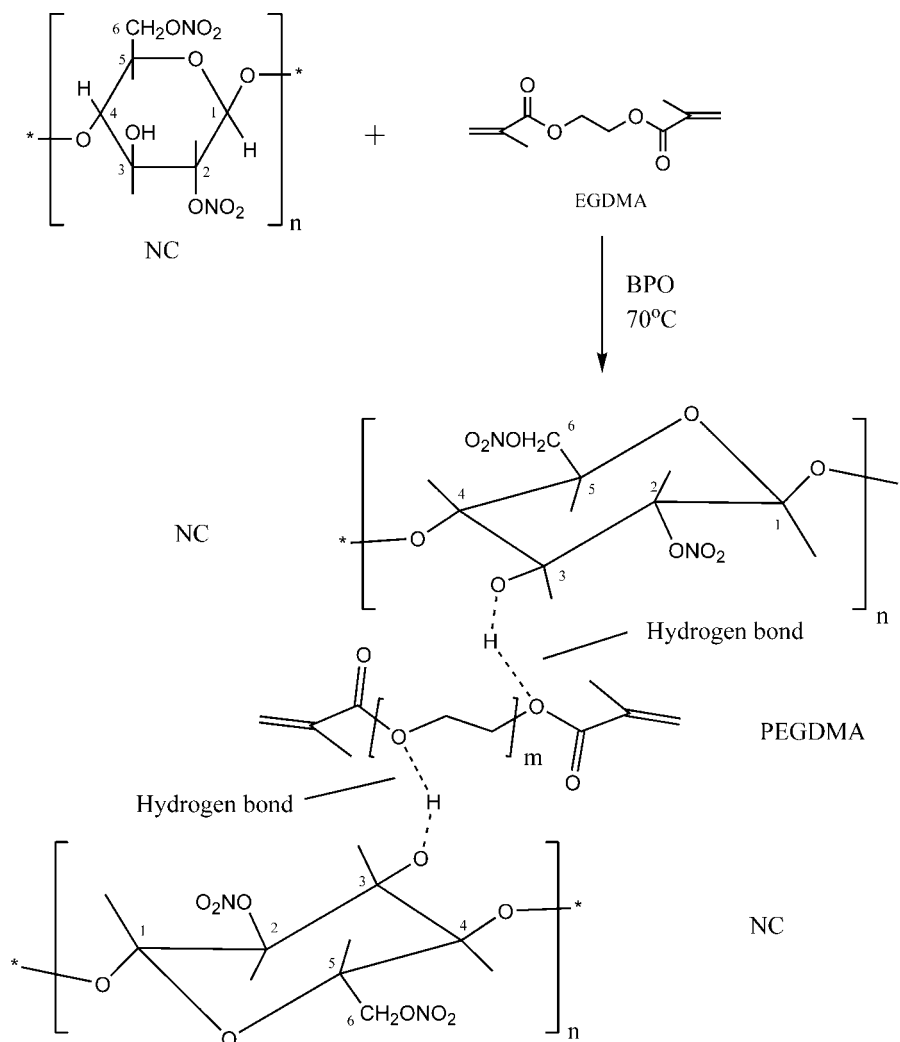
Scheme 1   Polymerization of EGDMA itself and crosslinks with NC by hydrogen bonding.

the inhibitor. Nitrocellulose and washed EGDMA was added to the flask, and the host polymer, nitrocellulose, was swollen in the monomers EGDMA forming the guest network for different time at 30°C. Benzoyl peroxide (BPO) was used as initiator in the polymerization reaction. It is soluble in monomer EGDMA which adsorbed and penetrated inside nitrocellulose matrix. The diffusion rate and contents of initiator BPO affect mainly polymerization rate and final structure of PEGDMA. Excess using of BPO will increase polymerization rate and is difficult to control reaction process. The initiator BPO was added to the reactor to initiate polymerization of EGDMA itself and crosslinks with NC by hydrogen bonding for three h at 70°C to obtain initial gradient semi-IPN samples with thickness of about 4.2 mm (Scheme 1). Hydrogen bond is formed between oxygen atoms of EGDMA and hydrogen of hydroxyl groups on the C3 position of NC whose complete nitration process are generally not reached because of steric hindrance.

To determine the gradient profile of the guest component, four approximately 0.2 mm thick section were cut using slitter perpendicular to the successive sections of gradient IPNs containing 10.72% (by mass) PEGDMA.

Measurement and characterization

Elementary chemical analysis was used to determine nitrogen content by combustion at CHN-O-Rapid, Foss Heraeus Analysensystem Gmbh.

By exploring the morphology of prepared system, a series of ordinary IPNs film containing the same components with gradient IPNs samples were gold coated and studied by electron microscopy X650, Hitachi, Japan.

Tensile strength and ultimate elongation are measured on a DMA Q800 tensile tester with extension rate of 300 mm/min at room temperature. The tensile test specimens were cut from the gradient IPN sheets in dumbbell shapes according to ASTM D638 specifi-
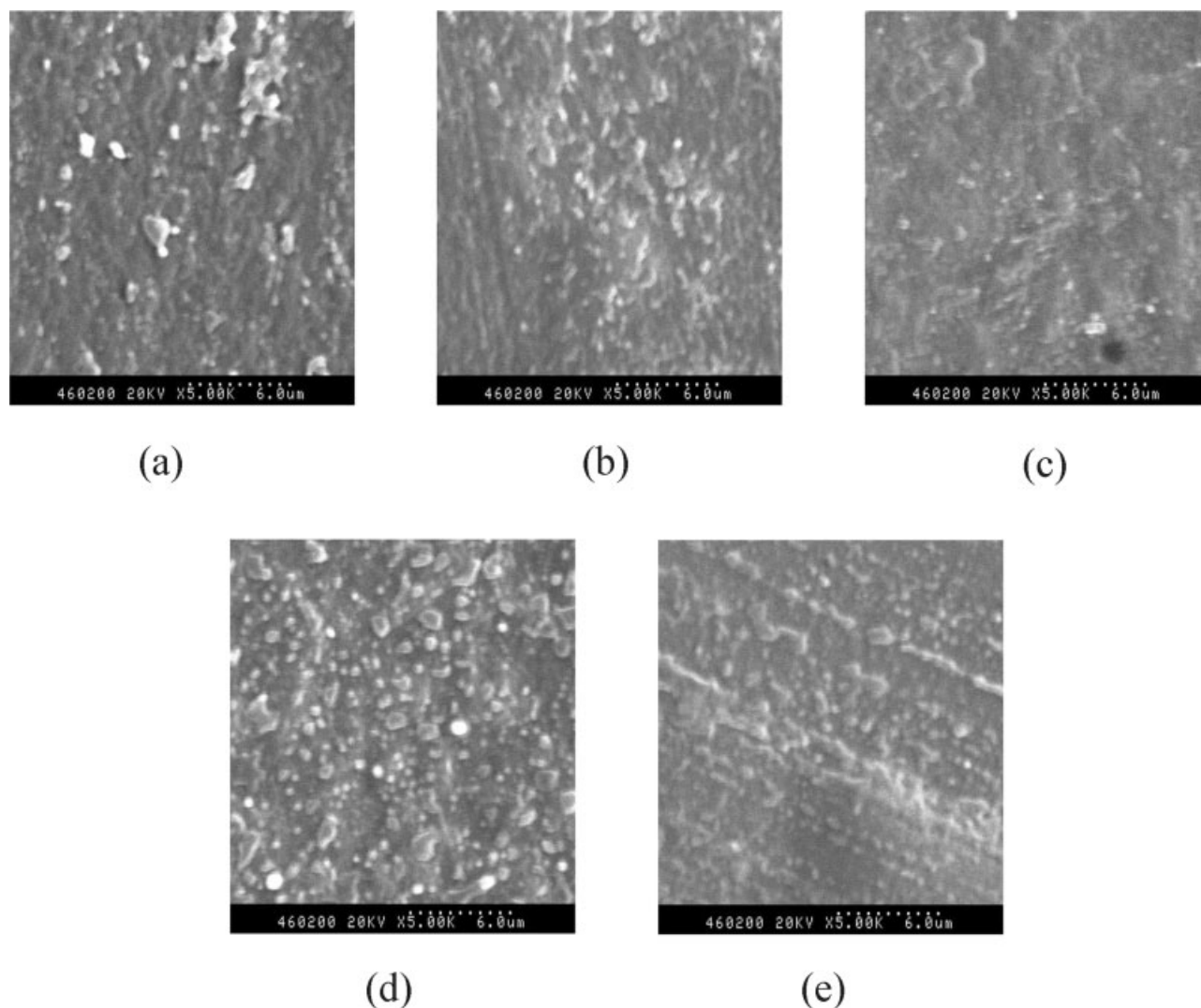
Figure 1 SEM photographs of NC/grad. PEGDMA semi-IPNs containing various guest component content: (a) 7.4%; (b) 16.7%; (c) 23.1%; (d) 28.6%; (e) 37.5%.

cations. All samples were of uniform thickness. All measurement were made at room temperature.

RESULTS AND DISCUSSION

The morphology of NC/grad. PEGDMA semi-IPNs containing various guest component contents are shown in Figure 1. The NC phase showed with black matrix is heterogeneous with white PEGDMA domain distributed inside. SEM micrographs of NC/grad. PEGDMA semi-IPNs reveal that, there are two distinct phases due to individual component network. Polymer NC is swollen in monomer EGDMA for different time; EGDMA monomer is adsorbed and penetrated with the NC network. The swelling is terminated at a certain stage and then polymerization of EGDMA is carried out to produce the guest network. SEM micrographs Figure 1(a) shows two-phase morphology when guest component content is only 7.4%. With the increase of guest component content, Figure 1(b) reflects the enhanced miscibility of gradient system. And when the content of guest component is 23.1%, the gradient system shows almost single phase morphology [Fig. 1(c)]. For the same gradient system, an increase in guest component content increases the crosslink density of the system thereby giving a more homogeneous phase. However, with further increase of guest component content, since redundant monomer EGDMA dissociate in polymer NC network, such a non homogeneous system shows poor miscibility [Fig. 1(d)]. Figure 1(e) reveals that the guest network begins to form continued phase.

The rate of diffusion of the monomer in the course of preparing gradient IPNs and the resulting distribution of the guest polymer throughout the host polymer are to a great extent dependent on the monomer concentration in solvent and swelling time. In NC/
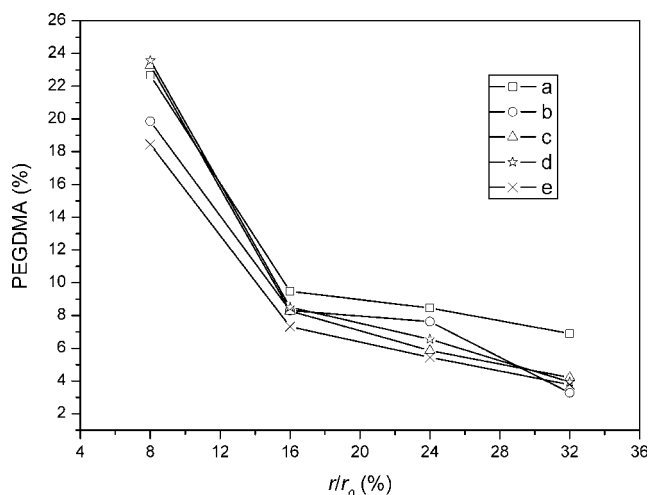
Figure 2 PEGDMA gradient profiles in NC/grad. PEGDMA semi-IPNs after different swelling time: (a) 90 min; (b) 60 min; (c) 45 min; (d) 30 min; (e) 10 min.

grad. PEGDMA semi-IPNs, PEGDMA concentrates mainly at the surface layers of the sample, penetrating up to 90 μm within NC matrix. A low content of PEFDMA at deeper than 90 μm and its complete absence in the core of the samples are observed. The gradient profiles are shown in Figure 2.

From Figure 2, the PEGDMA content decreases with distance from the surface to core of the samples. The distribution of the guest component across the sample thickness is reciprocal function. And the relation between guest component content and sample thickness can be expressed with following formula

$$xy = \text{const}$$

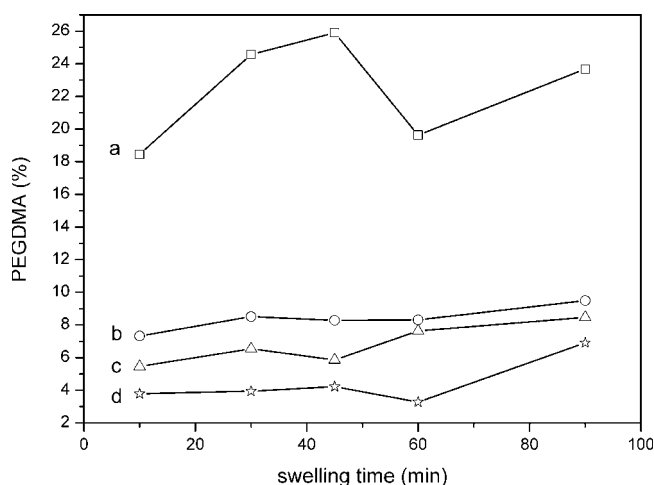where, x is guest component content, y is the sample thickness.

Figure 3 Dependence curves of PEGDMA content in various layers with different swelling time: (a) surface layer; (b) the second layer; (c) the third layer; (d) the fourth layer.

Figure 3 shows the dependence of PEGDMA content at the same deep into the sample with different swelling time. From Figure 3, the PEGDMA content in the first layer, i.e., the surface, significantly increase with the swelling time increase from 10 to 45 min, and reach to the maximum, and then decrease. However, the rest three layers exhibit a less significant one than the surface layer. When the NC is swollen in monomer EGDMA to 30–45 min, the equilibrium could be established.

Mechanic tests demonstrated that gradient IPNs offer higher fracture energy than homopolymers and ordinary IPNs. A number of hypotheses have been put forward to account for this phenomenon. One of them treats gradient IPNs as collections of an infinite number of layers whose compositions and elastic module change progressively. The tensile strength values of NC/grad. PEGDMA semi-IPNs containing various guest component content are given in Table I. As can be seen from the table, PEGDMA content increases to 23.41%, the break strength reaches to the maximum, and break elongation is larger than the control samples. When PEGDMA content increase further, the break strength dropped, but break elongation is still increase to the maximum. The obtained stress–strain curves for temperature at room temperature of NC/grad. PEGDMA semi-IPNs containing various guest component contents are demonstrated in Figure 4. Test results show that NC/grad. PEGDMA featured both higher tensile strength and larger toughness when PEGDMA content is about 23%. The area under the stress–strain curve at break point is also the evidence for the higher strength and larger toughness of surface treatment of NC with EGDMA swelling and gradient polymerization.

It is worth mentioning that the mechanical properties of plasticized nitrocellulose are weak and the plasticizers are easy to migrate between nitrocellulose chains. And gradient PEGDMA modified nitrocellulose can improve both the strength and toughness of NC.

A number of hypotheses have been put forward to account for reason that gradient structure in a polymeric material can markedly improve its mechanic

TABLE I
Effect of PEGDMA Content on Tensile Strength of the NC/grad PEGDMA Semi-IPNs

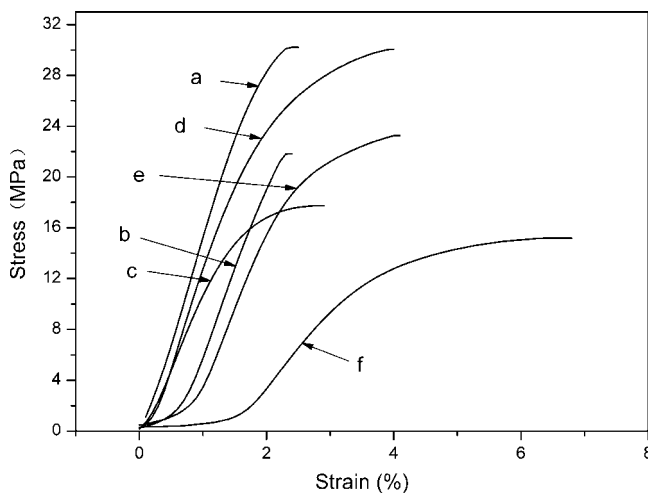| Sample	PEGDMA content (%)	Break strength (MPa)	Elongation at break (%)
a	0	30.42	2.343
b	7.4	21.32	2.221
c	16.7	17.73	2.704
d	23.1	30.05	3.996
e	28.6	23.25	3.996
f	37.5	15.15	6.234

Figure 4 Stress-strain curves of NC/grad. PEGDMA semi-IPNs containing various guest component content: (a) 0%; (b) 7.4%; (c) 16.7%; (d) 23.1%; (e) 28.6%; (f) 37.5%.

properties. However, ultimate advantages in the mechanical properties of gradient can be attained with the use of components sharply differing in properties, such as creating a hard gradient in a soft matrix or, conversely, a soft gradient in a hard matrix.

Radhakrishnan and coworkers[7] have ever indicated that the miscibility of prepared polyurethane-NC was related to the NCO/CO ratio, namely, cross density of whole system. IPNs with 25 and 30% NC showed an increase in tensile strength with increase NCO/CO ratio due to an increased crosslink density but those with 40% NC showed the reverse trend because the increase in crosslink density enhanced the rate of phase separation, thereby reducing the phase continuity, which results in a decrease in the tensile strength.

For NC/grad. PEGDMA semi-IPN material here, it is obvious that if the gradient system is conventionally divided into layers, the compositions of every such layer will differ from the average for the IPNs. Hence conditions for the microphase separation will differ from layer to layer, resulting in differences in morphology and properties.

Monomer ethylene glycol dimethacrylate have been penetrating into between nitrocellulose molecular chains, meanwhile, crosslinking with NC by hydrogen bonding. The functional groups of polymerization production of monomer ethylene glycol dimethacrylate itself and the hydrogen bonds be-

tween EGDMA and NC interact strongly in interpenetration networks. So mechanic strength can be increased over initial matrix.

In preceding part of this paper, we discussed the influence of the content of monomer and swelling time or diffusion rate on the distribution of the final materials. In fact, the rate of diffusion and content of the initiator of BPO will also affect the morphology and distribution of PEGDMA in NC matrix. This will be discussed in future work in detail.

CONCLUSIONS

Polymer NC is swollen in monomer EGDMA with different time to form NC/grad. PEGDMA semi-IPNs by polymerization and crosslinking of EGDMA itself and with NC. The distribution of the guest component across the semi-IPNs sample thickness was reciprocal function. When the NC is swollen in monomer EGDMA to 30–45 min, the equilibrium could be established. SEM micrographs of NC/grad. PEGDMA semi-IPNs revealed that, when the content of guest component was about 23%, the gradient system showed almost single phase morphology. At the same time, the tensile test results showed that NC/grad. PEGDMA featured both higher tensile strength and larger toughness. The reasons have been discussed according to the gradient structure and microphase separation.

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