Synthesis and Characterization of a Novel Aqueous Glycidyl Azide Polymer Emulsion

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ABSTRACT: The current domestic and foreign research on azide polymers such as glycidyl azide polymers (GAP) mainly focuses on the design, synthesis, modification, and performance of elastomers; it is difficult to prepare the GAP/NC (nitrocellulose) blends, and they have poor mechanical properties. Here, we developed a green and safe strategy for the blending and compounding of azide binder and NC by blending the emulsion with NC in water and demulsifying. Considering the structural characteristics of GAP, a novel energetic aqueous GAP-E (energetic elastomer) emulsion was prepared by anionic self-emulsion polymerization using 2,2-dimethylol propionic acid as the hydrophilic chain extender, 1,4-butanediol as the chain extender, and triethylamine as a neutralizer. Furthermore, the GAP-E emulsion/triethylene glycol dinitrate/nitrocellulose blends (GAP-E/TEGN/NC) with different proportions were prepared in aqueous phase by the precipitation method. The related properties of the emulsion were studied by gel permeation chromatography, Fourier transform infrared, universal material testing machine, dynamic mechanical analyzer, thermogravimetric analysis, and scanning electron microscopy (SEM). Our results indicated the emulsion exhibited good stability with the number average molecular weight of 76,600. The GAP-E film showed a tensile strength of 17.8 MPa, elongation at break of 415%, glass transition temperature of $-28.5\,^\circ\text{C}$, and initial degradation temperature of 242 $^\circ\text{C}$. The GAP-E emulsion and TEGN/NC can be blended in the aqueous phase by the demulsification method to prepare a homogeneous GAP-E/TEGN/NC blend. Fourier transform infrared spectroscopy (FTIR) showed that there was a certain hydrogen bond interaction between GAP-E and TEGN/NC molecules, which was conducive to the improvement of the mechanical properties. The results of SEM indicated that GAP-E could obviously soften the rigid fiber structure of TEGN/GN, and the blends were well mixed with good interfacial compatibility between the GAP-E (5%) and TEGN/NC. When the mass fraction of GAP-E was 5%, the tensile strength and the elongation at break of the blend reached up to 32.1 MPa and 54.4%, which were improved by 33 and 46% compared to those of the TEGN/NC blend system, respectively. The transition temperature remained at $-21.6\,^\circ\text{C}$ with obvious enhancement on the mechanical properties.

1. INTRODUCTION

The glycidyl azide polymer (GAP) is a hydroxy-terminated polyether with azide groups in the side chain, which is also a linear energetic prepolymer with a polyether structure in the main chain. It has obvious advantages such as positive heat formation, high density, low mechanical sensitivity, and so on. Thus, it has good application prospects. The most intensive application of the GAP, as shown in the current study, is to replace the traditional inert adhesive with GAP-based energetic elastomer adhesive from the reaction of the GAP with isocyanate or click reaction. Ampleman et al. synthesized a series of GAP-based thermoplastic energetic elastomers by using different...
ent molecular weights of the GAP and different chain extenders. Thereafter, based on the synthesis of GAP-based elastomers, Liu et al. studied the effect of the catalyst, the addition method of the chain extenders, and the synthesis process on the performance of the elastomer. Zhang et al. developed a GAP-based high-energy thermoplastic elastomer with a bonding function by using a mixed chain extender. Noh et al. studied the thermal decomposition properties of GAP-based ETPE and calculated the thermal decomposition activation energy by simulation. However, due to the presence of the large \(-\text{CH}_2\text{N}_3\) side group in the GAP molecular structure and the inadequate number of atoms in the main chain, the intermolecular force is small and the secondary cross-linking in the system is insufficient. Therefore, the number of atoms in the main chain is inadequate, and the hindering effect on the chain rotation is obvious, which leads to poor flexibility of the chain and poor mechanical properties of the prepared elastomer.11

In order to improve the mechanical properties, a large amount of research work has been reported through the strategies of blending, copolymerization, grafting, and so on. Min et al. adopted the blending method by mixing polyethylene glycol, polycaprolactone, and GAP together, which were then cured with multifunctional isocyanate or isophorone disocyanate to obtain a blending-modified elastomer. The results showed that the addition of the variety of prepolymers improved the mechanical brittleness of GAP-based elastomers. Abdelhafiz and Elbeih successfully prepared a low-moisture GAP using a modified two-step method, where epichlorohydrin was polymerized into polypeichlorohydrin and subjected afterward to the azidation step using sodium azide. Besides, it is also reported that the linear GAP can be modified to the branched GAP with a lower viscosity than that of the linear GAP, which was then cross-linked with the curing agent to prepare thermosetting energetic elastomers.15 The results showed the branched GAP exhibits superior performance with a more rigid network structure when compared with the linear GAP and is expected to produce higher energy during combustion. However, the current domestic and foreign research on azide polymers mainly focuses on the design, synthesis, modification, and performance of elastomers; it is difficult to prepare the GAP/NC (nitrocellulose) blends, and they have poor mechanical properties.

In this study, the anionic self-emulsification method was adopted to synthesize GAP-based polyurethane emulsion by designing the content and \(R\) value of the hydrophilic chain extender. By referring to the manufacturing process of the absorbent cotton, a new green and safe way for the blending and extending the emulsion with NC in water and demulsifying. The overall factors include the \(R\) value, DMPA content, and crosslink agent trimethylolpropane (TMP), which play important roles in the mechanical properties of the blends, which were comprehensively studied. To the best of our knowledge, the fabrication of the azide polymer emulsion and the further blending strategy with NC in aqueous phase have not been reported.

2. RESULTS AND DISCUSSION

2.1. Preparation Method of the GAP-E Emulsion.

2.1.1. Influence of Reaction Time on GAP-E Polymerization.

In order to determine whether the terminal hydroxyl group of the soft segment completely reacted during the prepolymerization reaction stage, the di-\(n\)-butylamine method was adopted to measure the isocyanate content. The \(R\) value (the molar ratio of \(-\text{NCO}/-\text{OH}\)) was set to 3.5, and the samples were taken at 1, 2, 3, and 4 h respectively for titration, as shown in Figure 1.

It can be seen that the percentage of \(-\text{NCO}\) decreases slowly after the prepolymerization reaction for 1.5 h. This is mainly because the relative molecular mass of the prepolymer gradually increases as the reaction progresses, resulting in the reduction of the reaction rate with \(-\text{NCO}\). After 2 h of reaction, the percentage of \(-\text{NCO}\) generally reaches the theoretical value (3.58%); it can be considered that the prepolymerization reaction has reached the end point. Therefore, the prepolymerization reaction time was selected as 2 h in this paper.

2.1.2. Influence of Reaction Temperature on the Polymerization of GAP-E.

During the initial reaction, an excessive amount of MDI was added, and there was a large number of \(-\text{NCO}\) groups in the initial reaction system. Because the \(-\text{NCO}\) groups in MDI have a mutual induction effect and high reaction activity, the reaction temperature has a great influence on the reaction rate and reaction stability of the polymerization at the initial stage. In this study, the di-\(n\)-butylamine titration method was adopted to investigate the content of isocyanate groups at three prepolymerization temperatures of 60, 80, and 90 \(^\circ\text{C}\) to determine the reaction rate. The measured relationship between \(-\text{NCO}\) mole fraction and the reaction temperature/reaction time is shown in Figure 2.

It can be seen from Figure 2 that under the same reaction time, with the increase of the reaction temperature, the content of residual \(-\text{NCO}\) in the system decreases, indicating that heating up can accelerate the reaction speed. At 90 \(^\circ\text{C}\), the content of \(-\text{NCO}\) decreased rapidly to 2.8% (less than the theoretical value of 3.58%) with the reaction time. This is because at higher temperatures, excessive \(-\text{NCO}\) can react with \(-\text{H}\) in carbamate, \(-\text{COOH}\) in DMPA, and even itself. With the increase in time, the viscosity of the system increases rapidly and gelation occurs. At 60 \(^\circ\text{C}\), the residual \(-\text{NCO}\) is higher than the theoretical value of 3.58%, and prolonging the reaction time cannot make the \(-\text{NCO}\) and \(-\text{OH}\) completely react. The residual \(-\text{NCO}\) at 80 \(^\circ\text{C}\) is close to the theoretical value, which means there are few side reactions at 80 \(^\circ\text{C}\), and the reaction period is moderate. Therefore, the reaction temperature selected for this experiment is 80 \(^\circ\text{C}\).

2.1.3. Molecular Structure of the GAP-E Emulsion.

In this study, the molecular weight and its distribution of the GAP-E emulsion was measured by gel permeation chromatography.
(GPC), as shown in Figure 3. The number average molecular weight ($M_n$) of the GAP-E emulsion is measured to be 76,600. The ratio of the weight average molecular weight ($M_w$) and the polydispersity index ($M_w/M_n$) is calculated to be 1.6, which indicates that the molecular weight distribution is narrow and the molecular weight is relatively uniform.

Fourier transform infrared (FTIR) measurement of GAP-E films is shown in Figure 4. It can be observed that the $\text{−NCO}$ absorption peak at 2250 cm$^{-1}$ disappears, which indicates that the reaction of MDI has been completed. The $\text{−NH}$ stretching and bending vibration peaks can be observed at 3380 and 1600 cm$^{-1}$. Besides, the $\text{C=O}$ stretching vibration peaks in carbamate and the characteristic peak of $\text{−N=}$ can also be found at 1710 and 2100 cm$^{-1}$ respectively. All of these peaks show that the carbamate structure of the GAP-E was successfully synthesized.

2.2. Mechanical Properties of the GAP-E Films.

2.2.1. Influence of the R Value on the Mechanical Properties of the GAP-E Films. The GAP-E films with different $R$ values were cut into a dumbbell shape for mechanical property measurement. The obtained results are presented in Table 1. It can be seen that the tensile strength of the films increases, while the elongation at break decreases when the $R$ value of NCO/OH increases. This is mainly because the number of polar groups increases with the increase of the hard segment content, which results in the improvement of the molecular chain rigidity and the tensile strength. However, there is no obvious change on the tensile strength when the $R$ value is greater than 3.5. With further increase of $R$, the system undergoes microphase separation with the increase of the hard segment content. Because the tensile strength mainly depends on the soft phase area and the increase of $R$ value does not lead to a softer phase area, there will be no significant change in the tensile strength thereafter. Moreover, the content of rigid chain linkages such as the urethane bonds and urea bonds in the main chain increases with the increasing $R$ value, which enhances the rigidity of the molecular chain and weakens the deformation of the molecular chain. As a result, the elongation at break decreases with the increasing $R$ value.

In addition, the particle size of the emulsion gradually increases with the increasing $R$ value. It can be observed from Table 1 that the prepolymer molecular chains cannot be completely terminated by the $\text{−NCO}$ groups when the $R$ value is 2. The $\text{−OH}$ groups of the prepolymer molecules that are not terminated by $\text{−NCO}$ groups will have an addition condensation reaction with the terminal $\text{−NCO}$ groups of the prepolymer that have been terminated by $\text{−NCO}$ groups. It can increase the viscosity of the prepolymer and make it difficult to emulsify in water, leading to the formation of gel.

When the $R$ value is between 2.5 and 4.0, an ideal prepolymer that is terminated by $\text{−NCO}$ with uniform molecular weight can be obtained. In this $R$ range, the low viscosity makes the system easy to disperse, and the emulsion of milky white with blue light appearance can be obtained. When the $R$ value is greater than 4.0, a large number of residual $\text{−NCO}$ groups exist in the prepolymer, which can easily form urea bonds when they react with water during emulsification. The size of the obtained emulsion particles is increased due to the strong hydrophobicity of the urea bonds. It therefore causes poor storage stability,
were synthesized with di
the GAP-E Films. 

stability of the emulsion was greater than 6 months. 

3.0, and 3.5 showed no precipitation, indicating that the storage 
acceleration centrifugal test of the samples with 
weakens the dispersity, and makes it easy to gel. Moreover, the 
the appearance of the emulsion changes from white layered to 
interfacial compatibility between GAP-E and TEGN/NC. 

2.2.3. Influence of DMPA on the Mechanical Properties of 
the GAP-E Films. The fixed R value is 3.5, and GAP-E emulsions 
prepared emulsions were cast into films for the mechanical property 
Table 3. Mechanical properties of GAP-E films with different DMPA contents.

| DMPA content/% | tensile strength/MPa | elongation at break/% | stability of the emulsion |
|----------------|----------------------|-----------------------|---------------------------|
| 3              | 2.91                 | 610                   | white, stratiﬁcation, unstable |
| 4              | 12.8                 | 485                   | white emulsion, stable     |
| 5              | 13.3                 | 415                   | white emulsion with blue light, stable |
| 6              | 13.8                 | 398                   | white emulsion with blue light, stable |
| 7              | 13.9                 | 310                   | white emulsion, viscous, stable |

As presented in Table 2, with the content of DMPA increases, 
the appearance of the emulsion changes from white layered to 
white with blue light emulsion, and ﬁnally to white viscous 
emulsion, indicating that the average particle size of the 
emulsion decreases with the increase of hydrophilic groups. In 
addition, the tensile strength of the GAP-E ﬁlms gradually 
increases, while the elongation at break gradually decreases with 
the increasing DMPA content. This is because the content of the 
hard segment increases with the increasing hydrophilic group, 
which results in the enhancement of the hydrogen bonds and the 
intra-molecular Coulomb force. As a result, both the crystallinity 
of the hard segment and the degree of microphase separation 
between the soft and hard segments were increased, resulting in 
the improved tensile strength of the ﬁlms.

2.2.3. Influence of the Chain Extender on the Mechanical Properties of GAP-E Films. With a ﬁxed R value of 3.5 and a 
DMPA content of 6%, GAP-E ﬁlms with different chain extender ratios were prepared for the mechanical property measurement, 
as shown in Table 3.

In Figure 6, the thermal decomposition of GAP-E emulsion consists of three stages. The ﬁrst stage represents the decomposition of azide groups, which have a mass loss of about 25%. The second stage is the decomposition of the hard segment carbamate groups, with a mass loss of about 30%. The third stage shows the decomposition of long chain polymers in the soft segment, with a mass loss of about 16%. In 
Figure 6, it can also be seen that the initial decomposition temperature (242 °C) of GAP-E emulsion is slightly lower than 
that of GAP prepolymers (247 °C). In the second and third 
stages of decomposition, the decomposition rate of GAP-E is 
lower than that of the GAP prepolymer. The improved thermal 
Stability of GAP-E emulsion is mainly attributed to the cross-linking 
enhancement with the addition of a cross-link agent into the system.

2.5. Properties of GAP-E/TEGN/NC Blends. 2.5.1. Molecular Structure of GAP-E/TEGN/NC Blends. 
FTIR spectra of GAP/TEGN/NC blends are presented in Figure 7. Because the 
peaks of C=O and −O−NO2 are close, it presents one peak on 
the spectra, which can be seen clearly after peak division by 
Gaussian ﬁtting. There are characteristic peaks of −O−NO2 at 
1627 and 1276 cm−1, 833 cm−1 is −O−NO2 bending vibration, 1067 cm−1 is the stretching vibration of C−O, the characteristic 
peak of −N3 is at 2100 cm−1. The carbonyl region of GAP-E is 
1710 cm−1, while the C=O of GAP-E/TEGN/NC blends move to 1657 cm−1. It can be seen that the carbonyl region of 
GAP-E/TEGN/NC blends moves to a low wave number. This is 
because in addition to the hydrogen bond between −NH and 
C=O, the hydrogen bond between −OH and C=O in NC is 
also formed, which enhances the hydrogen bond and leads to the 
movement of the hydrogen bond carbonyl toward a low wave 
number. 

2.5.2. Morphology of GAP-E/TEGN/NC Blends. The properties 
of polymer blends are closely related to their morphological 
structure, and the investigation of the properties of the blends is 
 inseparable from the study of their morphological structure. The 
scanning electron microscopy (SEM) image of the GAP-E/ 
TEGN/NC blends is shown in Figure 8a–c. 

Because GAP-E is a ﬂexible material with microphase 
separation of soft and hard segments, it presents a ﬂexible 
microstructure, as observed from the smooth fracture surface in 
Figure 8a. Compared with GAP-E, TEGN/NC is a rigid material 
with a rough fracture surface, as shown in Figure 8b. With 
the addition of GAP-E (5%), the morphology of blends has obvious 
changes, with a rougher fracture surface when compared with 
pure GAP-E, as shown in Figure 8b. It can also be seen from 
Figure 8c that there is no phase separation between GAP-E and 
TEGN/NC, indicating that the blends are well mixed with good 
interfacial compatibility between GAP-E and TEGN/NC.
2.5.3. Mechanical Properties of GAP-E/TEGN/NC Blends.

The GAP-E/TEGN/NC film was prepared as presented in Experimental Section for the mechanical property measurement. The results of the films with different component ratios are shown in Table 4. As the content of GAP-E emulsion increases, both the tensile strength and elongation at break of the samples increase first and then decrease. When the content of GAP-E is 5%, both the tensile strength and elongation at break of the blends have been greatly enhanced. The tensile strength has been increased from initial 24.7−32.1 MPa at 5% loading, and the elongation at break has been increased from 37.0 to 54.4%. After adding GAP-E, the hydrogen bonds between GAP-E and NC are enhanced, which results in the improvement of interfacial compatibility and the tensile strength. Besides, the GAP molecules serve as soft segments in the blends, which can improve the flexibility and reduce the rigidity of the blends. Therefore, the elongation at break at 5% GAP loading can be improved. However, further loading of GAP will bring about inhomogeneous blending of the composite system, which leads to reduced mechanical properties of the blends.

2.5.4. Thermal Stability of the GAP-E/TEGN/NC Blends.

GTN-5 is selected for thermal stability test, and the results are shown in Figure 9. It can be seen from Figure 9 that the initial mass loss in the thermal decomposition process of TEGN/NC was attributed to the volatilization and thermal decomposition of TEGN, and the maximum decomposition peak comes from the thermal decomposition of NC at 201 °C.17 The initial decomposition temperature of TEGN/NC is 127 °C; after adding GAP-E, the thermal decomposition temperature was advanced to about 110 °C. Meanwhile the maximum temperature of the thermal weight loss peak advanced from 201 to 193 °C. It shows that GAP-E could accelerate the thermal decomposition process of TEGN/NC and reduced the thermal decomposition temperature.

2.5.5. Dynamic Mechanical Properties of GAP-E/TEGN/NC Blends.

Dynamic mechanical properties of GAP-E/TEGN/NC blends were tested at 1 Hz, as presented in Figure 10 and Table 5. There are two characteristic peaks observed in the high and low temperature zones, respectively. The low temperature one ($T_{g1}$) and the high temperature one ($T_{g2}$) result from the molecular chain motion of GAP-E and NC,18 respectively. With the increasing mass fraction of GAP-E, $T_{g1}$ increases slightly, while $T_{g2}$ decreases obviously. It is probable that the glass transition temperature decreases due to the increase of flexible...
segments. Besides, the glass transition temperature difference ($\Delta T_g$) of the two phases in GAP-E/TEGN/NC decreases from the original 121.4−97.6 °C with the increasing content of GAP-E. If the polymer system is partially mixed, $T_g$ of the different components will be close to each other due to the mutual diffusion of the components. The better the blending, the closer the two peaks of $T_g$. Therefore, the results show that GAP-E has good compatibility with TEGN/NC and exhibits good plasticizing capability for the blends.

3. CONCLUSIONS

In summary, a novel energetic aqueous GAP-E emulsion was developed by an anionic self-emulsion polymerization method with a number average molecular weight of 76,600 and polydispersity index of 1.6. Among the influences of the $R$ value, DMPA content, and cross-link agent TMP, the amount of TMP plays a key role in the tensile strength. When $m$(BDO)/$m$(TMP) equals to 1:3, the tensile strength and the elongation at break of the film reached up to 17.8 MPa and 415%, respectively, while the glass transition temperature slightly increased to −28.5 °C. The uniform GAP-E/TEGN/NC was successfully fabricated by blending the GAP-E emulsion and TEGN/NC homogeneously in the aqueous phase through the demulsification method. FIRT showed that there was a certain hydrogen bond interaction between GAP-E and TEGN/NC molecules, which was conducive to the improvement of the mechanical properties. The results of SEM indicated that GAP-E could obviously soften the rigid fiber structure of TEGN/GN, and the blends were well mixed with good interfacial compatibility between the GAP-E (5%) and TEGN/NC. When the content of GAP-E is 5%, the tensile strength of the sample reached up to 32.1 MPa, and the glass transition temperature still remained −21.6 °C. Our study provided a green and safe strategy for preparing the GAP/NC blends under the aqueous phase with enhanced mechanical properties and thus will help develop the azide polymer systems through a green way in the future.

4. EXPERIMENTAL SECTION

4.1. Materials. The GAP prepolymer was provided by Liming Chemical Research and Design Institute Co., Ltd (Luoyang, China), with the hydroxyl value is 53.24 mgKOH/g and the molecular weight is 2000. 4,4′-Diphenylmethane diisocyanate (MDI, AR) was purchased from Aladdin Industrial.
Corporation. 1,4-Butanediol (BDO, AR), dimethylolpropionic acid (DMPA, AR), trimethylolpropane (TMP, AR), triethylamine (AR), and acetone (AR) were purchased by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Aluminum potassium sulfate dodecahydrate (Alum, AR) was purchased from Xilong Chemical Co., Ltd. NC (nitrogen content, 12.0%) and nitrotriethylene glycol (TEGN) were purchased from Luzhou North Chemical Industries Co., Ltd (Luzhou, China), and the mass ratio of TEGN/NC blends used in this paper was 68/32.

4.1.1. Synthesis of GAP-E Emulsion. According to Figure 11, the reaction for preparing GAP-E emulsion was carried out by a two-step method. First, the GAP prepolymer was reacted with excess MDI to form a prepolymer with hydroxyl-terminated −NCO. Then, the DMPA and chain extender were added to introduce hydrophilic groups on the GAP macromolecular chain; meanwhile, the prepolymer had a certain molecular weight. Finally, triethylamine was added to the prepolymer and neutralized with −COOH to form ammonium salt, which was then dispersed in deionized water to form the GAP-E emulsion.

The preparation process of synthesizing GAP-E emulsion is shown in Figure 12. Before the formal experiment, the GAP prepolymer was vacuum-degassed at 90 °C for 2 h and then filled with N₂ for protection. After that, a predetermined amount of preheated MDI was added and reacted with the GAP prepolymer at 80 °C for 2 h. Then, the desirable amount of DMPA, BDO, and TMP as well as a small amount of acetone were added to continue the reaction for 3 h. Subsequently, the reaction temperature was cooled down to 40 °C. Afterward, a predetermined amount of triethylamine and deionized water were added to form a prepolymer with hydroxyl-terminated −NCO. Then, the DMPA and chain extender were added to the prepolymer, and the reaction was continued for 3 h. Finally, the reaction mixture was cooled down to 40 °C and filtered.

Figure 11. Two-step synthetic illustration of GAP-E emulsion.

Figure 12. Preparation process of GAP-E emulsion.

Figure 13. Synthesis process of GAP-E/TEGN/NC blend.

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was added and reacted under strong stirring for 30 min. Finally, acetone was removed by vacuum distillation to obtain the GAP-E emulsion with milky white and blue light appearance, with a solid content of 35% and a pH value of 7.0.

4.1.2. Preparation of GAP-E/TEGN/NC Blend. By adopting the absorption process, the GAP-E emulsion and TEGN/NC (TEGN/NC = 68:32) were blended, demulsified, and adsorbed in water, which reduced the use of solvents and provided a safe and environmentally friendly preparation process. The specific steps are presented in Figure 13.

First, a stoichiometric amount of TEGN/NC and GAP-E emulsion was added to the flask with the deionized water ($m_{H_2O}/m_{TEGN/NC} = 10:1$) and stirred at 40 °C until it was dispersed into the homogeneous suspension. Then, an appropriate amount of alum with a concentration of 10% was added for demulsification. Stirring was continued for 30 min, and when the milky white liquid became clear, the demulsification was completed. After that, the blend was obtained by suction filtration and washing for three times and drying at 50 °C.

4.1.3. Preparation of GAP-E Films and GAP-E/TEGN/NC Films. In order to facilitate the subsequent tests, the samples needed to be prepared into the films.

4.1.3.1. GAP-E Films. The emulsion was poured into the polytetrafluoroethylene mould, dried at room temperature for 12 h, and then dried at 80 °C for 48 h for performance testing. GAP-E film is presented in Figure 14.

4.1.3.2. GAP-E/TEGN/NC Films. The GAP-E/TEGN/NC blend was prepared into a 15 wt % acetone solution. Then, the solution was placed still until the bubbles were eliminated completely. Finally, it was poured into the polytetrafluoroethylene mould, and the GAP-E/TEGN/NC films were obtained after drying at 50 °C until constant weight. The thickness of the films is about 3 mm.

4.2. Characterization. The stability of GAP-E emulsion was tested by simulating the storage stability of the emulsion using centrifugal acceleration. The samples were placed in the centrifugal machine at 3000 rpm for 15 min. The storage stability can last for 6 months when there is no precipitation; otherwise, the storage stability is poor.

The relative molecular weight and its distribution of GAP-E emulsion were tested by GPC (Wyatt Technology Co.) through using tetrahydrofuran as the solvent.

FTIR measurement was carried out under diffuse reflection mode (27 Tensor, Bruker Spectroscopy, Germany) with resolution of 4 cm⁻¹ and scan frequency of 20 times. In the GAP-E/TEGN/NC blend samples, GAP-E:TEGN/NC = 1:1.

The mechanical performance was measured according to GB/T528-1998. Typically, to obtain the tensile strength and elongation at break, the samples were cut into dumbbell shape according to ASTM 1708-95 standard and tested by a precision universal material testing machine (INSTRON-3367, American Instron) under the temperature of 20 ± 2 °C and tensile rate of 100 mm/min. The mechanical property of each sample was calculated by the average value of every three samples.

The thermogravimetric analysis (TGA/SDTA85/e Instrument) was carried out by weighing the 0.8 ± 0.01 mg sample under the argon atmosphere with a flow rate of 30 mL/min, heating rate of 10 °C/min, and temperature range from 50 to 600 °C.

Dynamic thermomechanical performances of the film, such as the loss modulus, storage modulus, and loss tangent (tan δ), were measured according to dynamic mechanical analyzer (DMA) Q800 V7.0 Build 113, with the temperature range from −75 to −150 °C, the frequency of 1 Hz, the amplitude of 5 μm, and the heating rate of 2 °C/min.

Thermogravimetric analysis of the sample was carried out by a TGA/SDTA85/e TGA instrument with the sample mass of 0.8 ± 0.01 mg, the test atmosphere of argon, the argon flow rate of 30 mL/min, the heating rate of 20 °C/min, and the temperature ranged from 50 to 600 °C.

The particle size and zeta potential were measured by the laser particle analyzer (Zetasizer Nano SZ, Malvern, UK). The sample was diluted by 1:1000 to obtain a blue transparent emulsion and measured at 25 °C. Each sample was measured for three times, and the results were obtained by calculating the average value of each sample.

SEM (JSM-6380LV, JEOL) was used to observe the morphology of the films. The samples were vacuum-dried and then fractured in liquid nitrogen to expose the cross section for scanning.

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Notes
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