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Gels from acrylic acid and hydroxypropyl cellulose via free radical polymerization

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Abstract: A hydrogel from acrylic acid and hydroxypropyl cellulose was made. The percentages of raw materials and crosslinkers were varied and its swelling behavior was evaluated. Some of the gels obtained absorbed more than 300% wt. The gels with higher swelling percentages were characterized by means of IR spectroscopy, differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), and scanning electron microscopy (SEM). The FTIR showed the presence of the main reactants in the gel, while the DSC showed a phase separation in the gel. This gel is partly biodegradable because of the content of hydroxypropyl cellulose and has the viscoelastic properties of poly(acrylic acid).

Introduction

Gels are materials that absorb and desorb solvents; they swell in the process, normally conserving their shape. Nowadays, they have many practical uses, from diapers to sensors; however, many of them are made from synthetic materials, and therefore, they contribute to environmental pollution. One way to make them partially biodegradable is to use natural materials; this objective can be accomplished by making a gel that combines a synthetic material with a natural one. Acrylic acid (AA) is a synthetic material derived from oil cracking. Poly(acrylic acid) (PAA) is widely used in pharmaceutics as a gel for drug delivery; it is also used with polyacrylamide for tumour treatment [1]. Hydroxypropyl cellulose (HPC) is a material derived from cellulose [2]; it is a polysaccharide and can be degraded via microbiological activity to produce glucose [3]. HPC can form many mesophases according to the solvent and its concentration in it, with the cholesteric phase presenting birefringent properties [4, 5]. The HPC, as many polysaccharides, tends to form nanomaterials [3]. It is also a material approved by the U. S. Food and Drug Administration for use in medicines and food [6]. The cellulose derivatives are used to dissimulate the bad taste of medical drugs [1]. These properties make HPC an interesting material to work with. HPC presents a lower critical solution temperature (LCST) of 45 °C in water [5], this is the cloud point, which varies according to the pH of the surrounding media. The HPC phase transition may be caused by the delicate hydrophilic-hydrophobic balance of the HPC itself, which has a large bipolar moment. When the temperature is increased, the bipolar moment is reduced, and the HPC phase transition occurs [7]. HPC has been used as a raw material for artificial muscles; high concentrations have the biggest moduli but less elasticity, and thus, are easier to break [8]. Lu *et al.*

[7] studied the phase transition behaviour of HPC under interpolymer complexation with PAA, creating several mixtures of HPC and PAA, starting with the polymer, and not the monomer, of PAA. It was found that with pure HPC, nanospheres are formed at 41 °C, and microspheres at room temperature. They also found that the interpolymer complex is formed due to hydrogen bondings.

In this work, a gel from poly(acrylic acid) and HPC was synthesized starting from acrylic acid with the goal of combining the mechanical properties of the first, and the biodegradability of the second. A catalyst and crosslinkers were used, the content of raw materials and crosslinkers was varied, and the effect of that variation on the swelling of the resulting PAA/HPC gels was studied. A biodegradable gel with good absorbtion properties for pharmaceutical and agricultural use is desired.

Results and Discussion

The gels produced clear coloured films, going from slightly yellow to slightly blue, depending on the concentration of monomers. PAA gives a yellowish colour and HPC gives a bluish one. Divinyl sulfone (DVS) was used as a crosslinker for HPC [7, 8, 11]. Initially, the experiment used glutaraldehide [12] as a crosslinker, however it was changed to DVS because many gels dissolved in water, thus yielding a poor degree of crosslinking and low percentages of absorbed water. The swelling behaviour of all the gels was evaluated. Table 1 shows the swelling values for gels with the highest percentages of water absorption.

Tab. 1. Swelling percentages for gels PAA/HPC.

Name of the Sample	%wt AA	% wt HPC	Crosslinker		Swelling at 24 hr (%wt)
			%wt MBAm	% wt DVS	
B111	90	10	0.1	1.8	200%
B131	90	10	0.05	1.8	328%
B113	90	10	0.1	0.9	240%
C111	70	30	0.1	1.8	120%
D211	50	50	0.1	1.8	340%
E212	30	70	0.1	3.6	190%
F112	10	90	0.1	3.6	190 %
F113	10	90	0.1	0.9	322%
F121	10	90	0.2	1.8	212%
G102	0	100	0	3.6	280%
G103	0	100	0	0.9	265%

It can be observed that the highest swelling values were obtained for the samples containing high percentages of HPC, followed by the samples with a lesser content of crosslinkers. This led to less stiffness in the gels and to bigger pores in the network [10]. This fact can be proven with a comparison between B111 and B131, both with the same quantity of PAA and HPC: the latter had less crosslinker and yielded a much bigger swelling percentage. The sample with the highest swelling percentage was D211, which had a concentration of PAA/HPC 50/50 with 0.1% of MBAm and 1.8% of DVS, and a swelling percentage of 340%. This is because the crosslinker percentages were not too high and the network was stabilized with the stiffness of the PAA/MBAm chains and the water absorbing HPC/DVS chains. These results are compared with many samples that are not listed in this article because their swelling percentage was lower; the crosslinker percentages used for D211 were at the medium level of the three possible. As D211 was the most absorbent gel, the results of this paper will be focused on that sample.

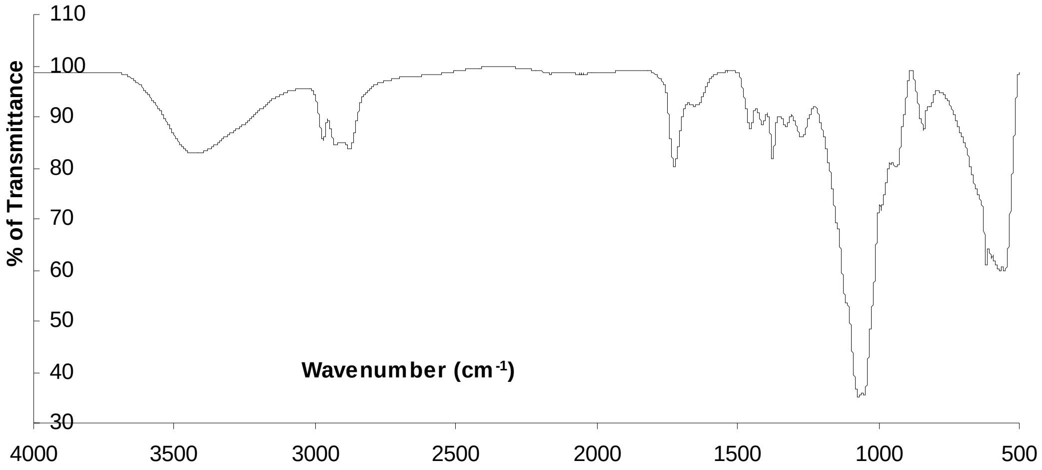

Fig. 1. IR spectrum of sample D211.

Figure 1 shows the IR spectrum of sample D211. The characteristic bands of the main functional groups of both raw materials are presented.

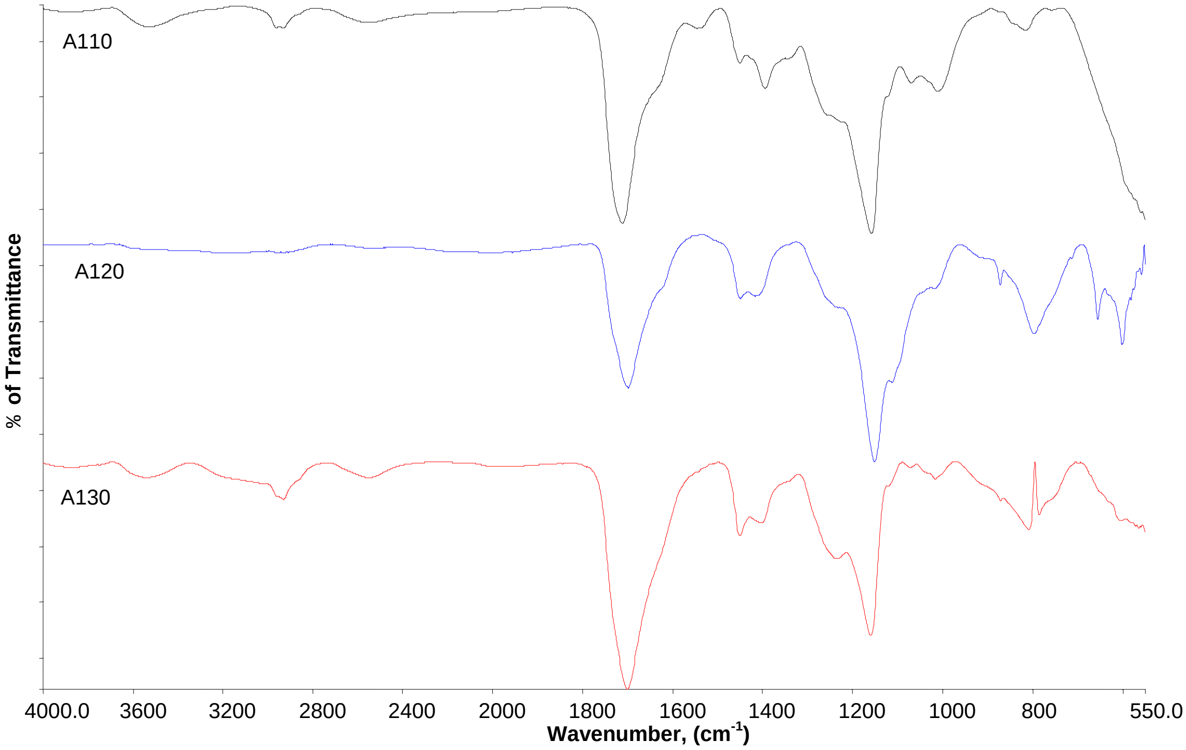

Fig. 2. IR spectra of PAA samples, A110 (100% PAA with 0.1% of MBAm), A120 (100% PAA with 0.2% of MBAm), and A130 (100% PAA with 0.05% of MBAm).

At 3600 cm^{-1} there is a peak attributed to stretching the OH bond of the HPC and PAA. At 2870 – 2970 cm^{-1} there is a peak corresponding to the stretching of the CH_2 and CH_3 groups of HPC. At 1710 cm^{-1} a peak appears that is attributed to the stretching of the C = O bond of the PAA. At 1100 cm^{-1} there is a peak corresponding to the C – O – C cm^{-1} of the HPC, as well as those bonds formed during crosslinking. This is a signal of the presence of the main reactives in the gel.

IR analysis was also conducted on pure PAA samples with variations in the amount of MBAm. In Figure 2, the IR spectra of A110 (100% PAA with 0.1% of MBAm), A120 (100% PAA with 0.2% of MBAm), and A130 (100% PAA with 0.05% of MBAm) are presented. These analyses showed that C=C groups of MBAm reacted with the OH of the PAA because the band at 3300 cm^{-1} almost disappeared while increasing the percentage of MBAm, and the band at 1000 cm^{-1} had a strong increase with the same pattern of MBAm content. This is an indication that the hydroxyl of the PAA reacts with the C=C of the MBAm in an anti-Markovnikov way, and ether is formed. This gives an idea of how the PAA/MBAm network is formed. The proposed reaction is shown in Figure 3, the HPC/DVS network is formed by an additional reaction between the OH of the HPC and the C=C of the DVS [11]. Here, one reaction of PAA/MBAm, and another of HPC/DVS, is thought to occur based on literature and on their affinities, and based on the fact that each crosslinker mentioned is specific to the proposed reactant. However, side reactions of PAA/DVS and HPC/MBAm may occur.

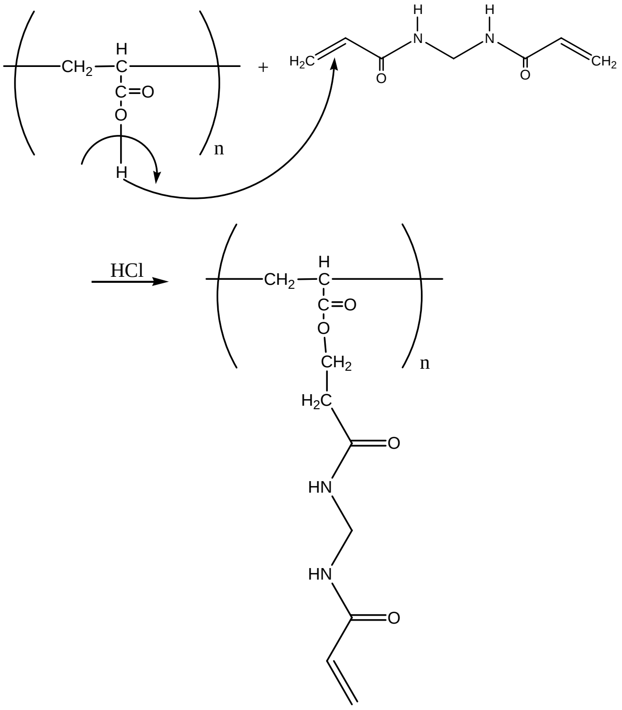

Fig. 3. Crosslinking of the PAA and the MBAm.

The DSC showed the presence of two glass transition temperatures (T_g) in the gels. This suggests that there is a phase separation in the said gels. The tendency of the DSC is that the greater the crosslinker is, the higher the T_g. Figure 4 shows the DSC thermogram for sample D211. There are two T_g's: one at 41 °C that is attributed to HPC, and another one at 70 °C; this is in the range of the T_g pertaining to the PAA, which is easily notable, while the step of T_g pertaining to the HPC is small and difficult to see. This is because cellulose ethers usually show a glass transition temperature of low intensity, and the associated change in heat capacity is too small to be detected using conventional DSC [13].

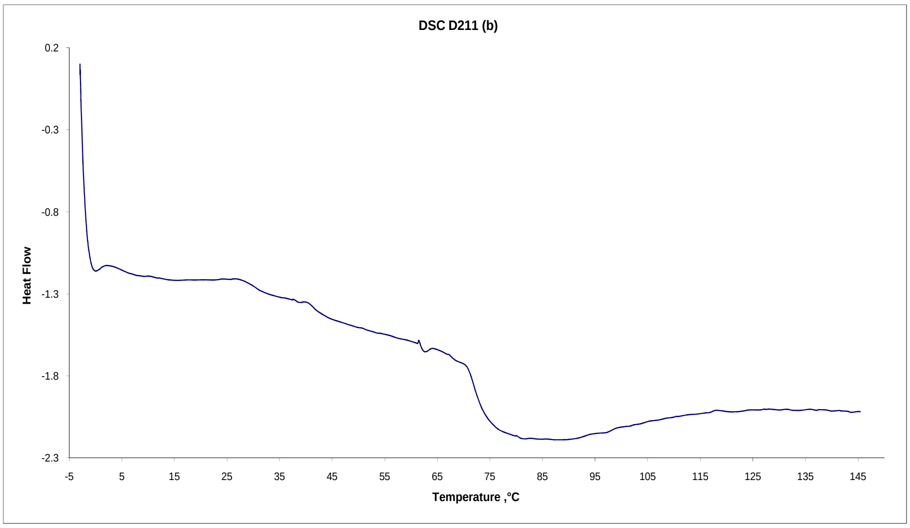

Fig. 4. DSC thermogram of sample D211, second scanning.

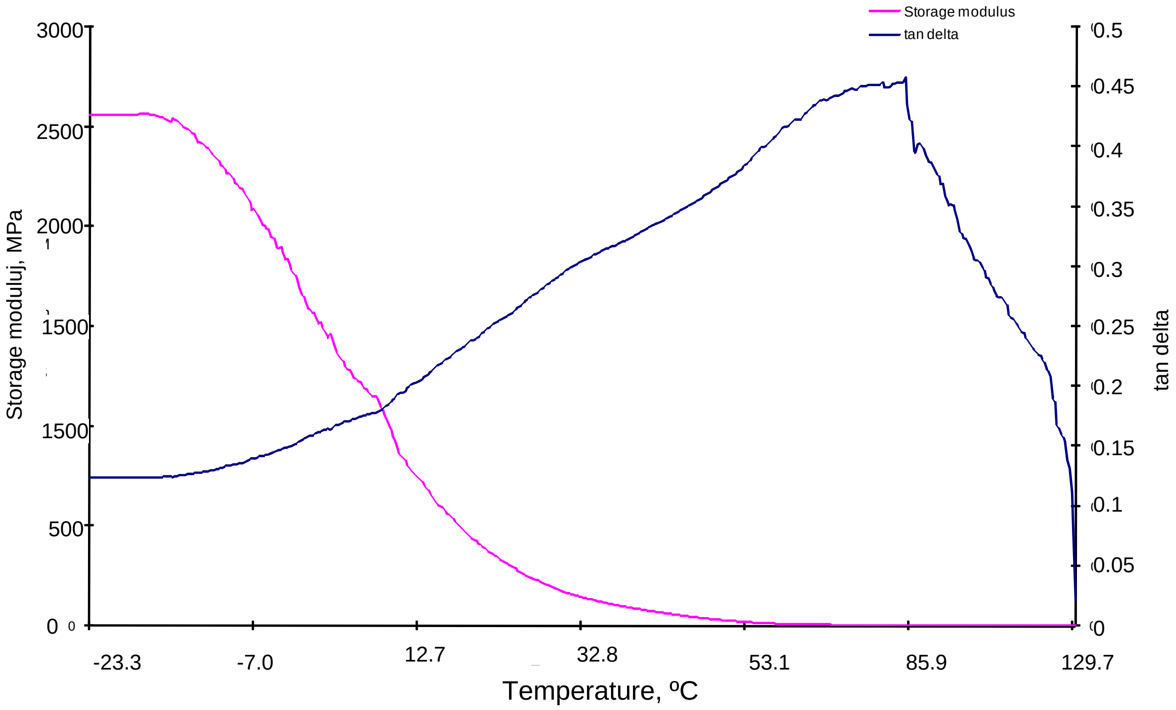

Fig. 5. DMA thermogram, curves temperature vs. tan delta and temperature vs. storage modulus of D211.

In Figure 5, the DMA thermogram of sample D211 is shown. DMA was performed on the xerogel and not on the hydogel, because the hydrogel will not bear the analysis without quickly breaking. In Table 2, the T_g's values and the storage modulus of some samples are presented. The highest storage modulus is for sample C111 (4616 MPa), said sample being PAA/HPC 70/30 with 0.1% of MBAm and 1.8% of DVS. The PAA network in this gel gives high viscoelastic properties. On the other hand, as can be seen in Table 1, sample C111 has a low swelling percentage (120%). F112 and F113 are gels made up of PAA/HPC 10/90 with 0.1% of MBAm; the former has 3.6% of DVS, and the latter, 0.9%. Sample F112 has a higher modulus than F113, due to the fact that the first gel has 400% more crosslinker than the second sample, and thus a stiffer chain is obtained. Here, only one T_g is given, but the peaks are wide so it is possible that the T_g's are very close and there is more than one glass transition temperature, as suggested by DSC. The width of the peaks also indicates that the gels are soft, which is corroborated with the storage modulus values. The change in the transitions is a clear indication of the changes in the viscoelastic properties of the gels. The discrepancies in T_g between DSC and DMA are related to the different physical parameters measured with each procedure [15], as some authors suggest that DMA is more precise than DSC [16]. Since HPC can form liquid crystal phases and present a complex substitution pattern, it is not clear if the endothermic transition is due to a glass transition, the melting of the crystalline phase, or a liquid crystal isotropic transition.

Tab. 2. Values of T_g and storage modulus of some samples.

Gel	T_g (Tan delta), °C	Storage Modulus, MPa (at -30°C)
C111	55	4616
D211	76	2568 (at -20°C)
D121	38	2122
F121	65	2800
F112	102	3340
F113	78	1002
G103	--	3134 (at -20 °C)

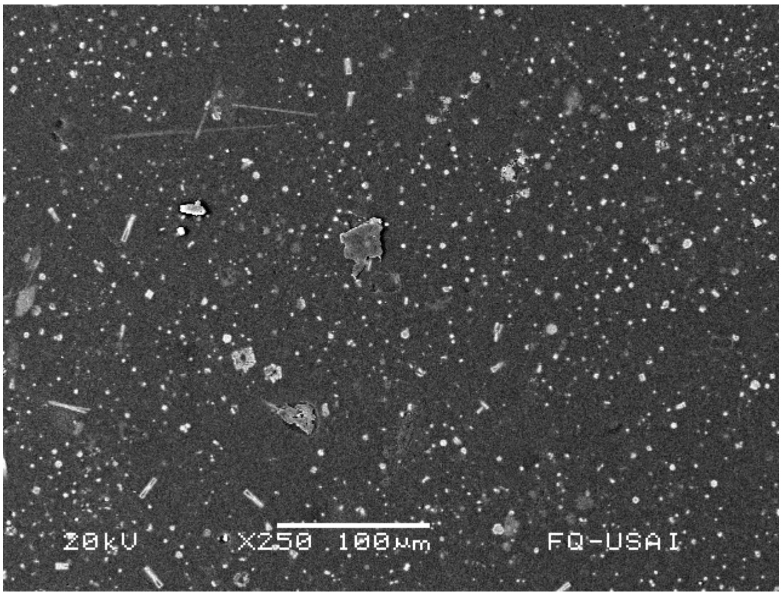

Fig. 6. SEM micrograph of the D211 gel.

The SEM micrograph of the D211 gel is shown in Figure 6. There are no pores on the surface of the gel which may catch and absorb the solvent; the swelling is then explained as taking place when the solvent is caught between the gel's networks. The gel is of a smooth texture attributable to the PAA chain with hexagonal particles dispersed throughout the gel; these particles are attributed to the presence of the HPC. These globules are similar to the fingerprint pattern observed by Bhadani in solutions of benzoic acid ether of HPC-acetone liquid crystal [17]. At a higher density of aggregation of such granules, they may coalesce to appear as a coating. With this, the conclusion is that two phases occur in the gel with HPC particles dispersed by the PAA. The globules also resemble the particles observed by Changez [18] in a PAA gel charged with gentamicin sulphate, but here they are made of HPC and not of gentamicin sulphate.

Conclusions

The characterization shows that there was a phase separation in the gels with a network of PAA/MBAm and HPC/DVS, with both chains being joined by hydrogen bonding. This conclusion is based on the two T_g's observed in DSC and the wide peaks in DMA, and also on the SEM micrographs where some particles, possibly of HPC, can be seen scattered on the surface; the broad tan delta peaks from the DMA suggest the presence of two very close T_g's merged into one. The best results of swelling behavior were for a sample of PAA/HPC 50/50, this was because the DVS chain was fixed by the PAA chain, and because the best crosslinker for the HPC in this system was DVS, not glutaraldehide, as was described in the swelling behavior section. The higher quantities of crosslinker, 0.2% of MBAm and 3.6% of DVS, led to smaller percentages of swelling, but to higher storage moduli. The gels with a higher concentration of PAA had better viscoelastic properties because of the rigidity of the PAA/MBAm chain. Homogeneous gels were produced, and they should be biodegradable because they had a cellulose derivative as one of the raw materials.

Experimental Part

In a glass reactor, under a nitrogen atmosphere, 30 g of solution were prepared, in which 10%wt of the solution corresponded to the main reactants. HPC (Aldrich) with M_w = 10,000 and MS = 3.6 was dissolved in 27 g of methanol (Fermont, 99.9%) until a homogeneous solution was achieved. Then, acrylic acid (Aldrich, 99%) was added and the mixture was stirred for one hour at 50 °C. Afterward, the initiator, 1% wt of potassium persulfate (Productos Químicos de Monterrey, 99%), methylenebisacrylamide (MBAm, Aldrich, 99%), and divinyl sulfone (Aldrich, 97%), which acted as crosslinkers, were added. Next, 1%wt of hydrochloric acid (Productos Químicos de Monterrey, assay of 37.2%) was injected, and the mixture reacted for 3 hours at 60 °C under constant stirring. After the reaction, the mixture was poured into a silicone dish and dried for seven days at 50 °C. Once dried, it was washed with distilled water and dried again [9]; this washing was done in order to remove the non-reacted monomer. The percentages of acrylic acid, HPC, methylenebisacrylamide, and divinyl sulfone were varied to study their effect on swelling, as the variations in raw materials and crosslinker will affect the structure of the network and the pore size. The swelling behaviour of the resulting gels was evaluated via the gravimetric method with the addition of distilled water at room temperature. The swelling percentage of the gels was calculated with Equation 1 [10]:

$$S = \frac{W_S - W_D}{W_D} \times 100 \qquad (1)$$

where S is the swelling percentage, W_S is the weight of the swollen sample, and W_D is the weight of the dry sample.

A Perkin Elmer spectrophotometer model Spectrum One was used for FTIR; a TA Instruments model 2010 was used for the DSC characterization in the range from 0 to 150 °C, scanned twice using the latter for analysis. The ramps used were 10 °C/min and 5 °C/min. The DMA was carried out by a TA Instruments (model 2980) in the multifrequency mode with 1Hz frequency, 5 °C/min ramp, and a film tension clamp. JEOL JSM5900 equipment was used for SEM characterization.

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