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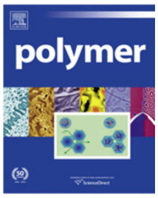

Polymer Communication

Nanodispersions of carbon nanofiber for polyurethane foaming

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ABSTRACT

Nanodispersions of polyurethane components with a three dimensional gelled network of filler is formed by the addition of a very small quantity of vapor grown carbon nanofiber (CNF). Reactive foaming of these nanodispersions produced polyurethane foams with superior properties. The kinetic profiles of polymerization and foaming reactions are not affected by the addition of filler. The cellular structure of nanocomposite foam becomes more uniform. Thermal conductivity and fire retarding tendency of the nanocomposite foams are superior at a very low loading of filler (1% by weight in components which corresponds to <0.5% by weight in foam). The filler did not open cells or induce structural defects.

1. Introduction

Rigid polyurethane foams find numerous applications as thermal insulation and construction materials [1]. Polyurethane foam formation consists of reactions of hydroxyl rich compounds with isocyanates, with simultaneous foaming. Generally, polyhydroxyl functional polyol are reacted with polyisocyanate compounds. In order to improve the properties of cured foam, several researchers have attempted the dispersion of nano scaled fillers such as silica nano particles and various clays to polyurethane components [2–7]. The dispersed nano-fillers failed to make a cross-linked network in any of the polyurethane components [7,8]. As a result, notable enhancements in properties of cured foam were not achieved, even at high filler loading [5–7]. Moreover, many of the nano-fillers acted detrimental to foaming process, making foams with inferior thermal and mechanical properties [5,6]. Vapor grown carbon nanofiber was shown to induce smaller cell size by inducing heterogeneous bubble nucleation in polystyrene thermoplastic foams [9,10]. This increased the cell uniformity and resulted in a higher cell density. In a recent report, by dispersing CNF in isocyanate component, Saha et al. found that the heat distortion temperature of polyurethane increased by 18 °C by the addition of 1% CNF [11]. They also found a moderate 57% increase in tensile strength. An increase in thermal insulation properties of rigid polyurethane foam would help in reducing the energy required to condition a building or device. Improved fire resistance could lead to the reduction or elimination of currently used halogenated flame retardants, which are being evaluated for a likely phase-out [12].

In this letter, we report the formation of a highly cross-linked network of CNF in both the polyurethane components. The foaming of the dispersion of CNF is carried out to estimate kinetic profiles during foaming and the post-foaming properties like morphology, thermal conductivity, fire properties, compressive modulus and closed cell content.

2. Experimental

2.1. Materials

Table 1 lists the formulation used in this study. Jeffol® SD361, polyol from Huntsman is a polyether polyol with a functionality of 4.2 and molecular weight of approximately 800. Polycat® 5 and Polycat® 8 are catalysts, both from Air products, are pentamethyldiethylenetriamine and dimethylcyclohexylamine respectively. Rubinate® M, isocyanate from Huntsman is polymethylenepolyphenyl polyisocyanate (MDI) with a functionality of 2.7 and molecular weight of approximately 365. Vapor grown carbon nanofiber with an average diameter of 70–100 nm and length of 50–100 μm (Pyrograf® PR-24-PS) was supplied by Applied Science Inc.

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Table 1
Formulation of polyol blend.

Component	Ratio (pbw)
Jeffol® SD361 Polyol	100
Polycat® 8 Catalyst	2.7
Polycat® 5 Catalyst	0.3
Tegostab® 8404 Silicone surfactant	2.0
Cyclopentane	9.0
Water	2.3

2.2. Dispersion, blending and in situ polymerization

The nanofiber was dried in a vacuum oven at about 70 °C for 48 h before dispersion. Calculated quantity of the filler was added to polyol and isocyanate separately, and stirred for about 45 min, in a closed container with moderate speed at a temperature of about 65 °C. This blend was sonicated in an ultrasonicator (L&R Company, NJ) for about 5 h. These blends were allowed to cool for 24 h, before conducting tests and making foams. For making polyurethane foams; catalysts, surfactant and blowing agents etc. were added to polyol/polyol – CNF blend and stirred at a speed of 2500 rpm for 15 s. After that, calculated quantity of MDI/MDI-CNF blend was added and stirred at 2500 rpm for 8 s. The isocyanate index used was 110. The reacting mixture was immediately poured into a paper lined rectangular wooden mold of size 32 × 32 × 7 cm^3 and the mould was quickly closed. The foam was de-molded after 1 h or more.

2.3. Characterizations

Rheological investigations on dispersions were carried out by a Rheometer (AR- G2, TA Instruments) with a parallel plate assembly. The kinetic profile of polymerization and foaming is estimated by making free rise foams (cup foams) and measuring the time of gelation and end of rise of the foam bun, the method for which is described elsewhere [6]. The cell morphology of foams was monitored by scanning electron microscopy (JEOL 6500). The cell window area was measured by using an image processing software (ImageJ). About 50 closed cells per sample were analyzed. The cell density N_f is calculated using a method described elsewhere [9]. The thermal conductivity of foams was measured by a thermal conductivity analyzer (Fox 150, Laser-Comp) following ASTM C518. The mean value of k for three foam samples is taken. The closed cell content was estimated by a pycnometer (AccuPyc 1330) as per ASTM D6226. The compressive modulus was measured in three perpendicular directions as per ASTM D 1621 (MTS UTM 1123) and the geometric mean of the three values was taken. The normalized compressive modulus was estimated at a density of 35 Kg/m^3. The fire properties were estimated by Butler chimney test (ASTM D3014). This test is used to compare relative time of burning and loss of mass of rigid thermoset cellular plastics. An increase in weight retention and/or a decrease in time to extinguish indicate an improvement in the fire characteristics.

3. Results and discussions

3.1. Rheology of nanodispersions

Fig. 1 shows the steady shear rheology of blends of CNF with polyol and isocyanate. While both polyol and isocyanate are Newtonian in behavior, the blends show significant shear thinning. It is seen from Fig. 1(a) that the increase in viscosity for 3% CNF in both the components is higher by approximately an order of magnitude and as a result, these dispersions could not be processed in to foam, by hand mixing. A Reaction Injection Molding Machine (RIM) must be used to handle such high viscosities. Fig. 2 shows the linear viscoelastic behavior of dispersions. For 1% CNF in components, although the dispersions show significant shear thinning as indicated by steady shear experiments, the storage modulus is shown to be a function of frequency indicating poor yield strength. In the case of 3% CNF in components, the storage modulus becomes independent of frequency, indicating the existence of a highly cross-linked, gelled 3D network [13,14]. Thus a loading as low as 3% CNF (~ 1.3% in foam) surpasses the percolation threshold for CNF in polyurethane components, to make a gelled 3D network.

3.2. Kinetic profile of foaming and polymerization

The gel and rise times of pure and nanocomposite foams are shown in Table 2. It is clearly seen that there is no significant change in kinetic profile of both polymerization and foaming reactions with CNF. This is due to the fact that there are no reactive functional groups in CNF which can couple with the functional groups of polyurethane components (hydroxyl or isocyanate) or that of chemical blowing agent (water). In the case of nano clays, the surface groups on clay are shown to alter the kinetic profile significantly by reacting with either –NCO groups of isocyanate or by binding to the chemical blowing agent (water) [4,6]. Thus, foaming with CNF does not require the alteration of the catalyst/blowing agent concentration in polyol blend to sustain the balance between blowing and gelling reaction.

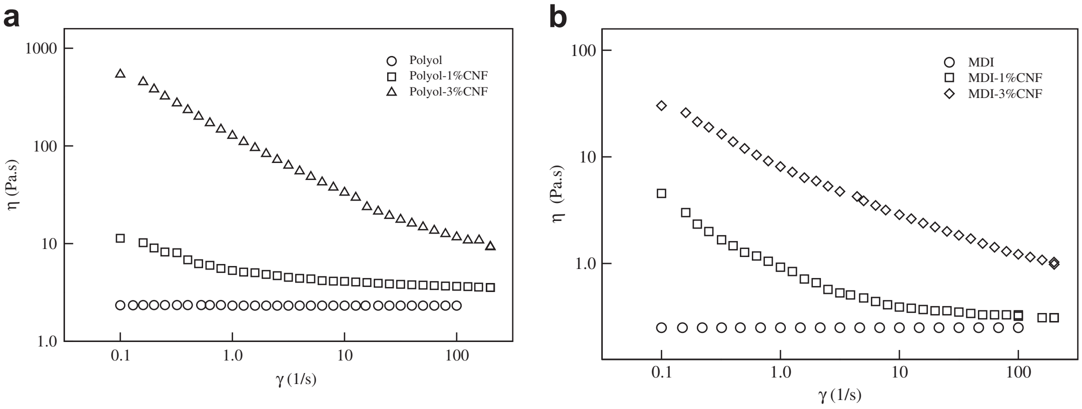

Fig. 1. Steady shear viscosities of CNF blends with (a) Polyol; (b) Isocyanate.

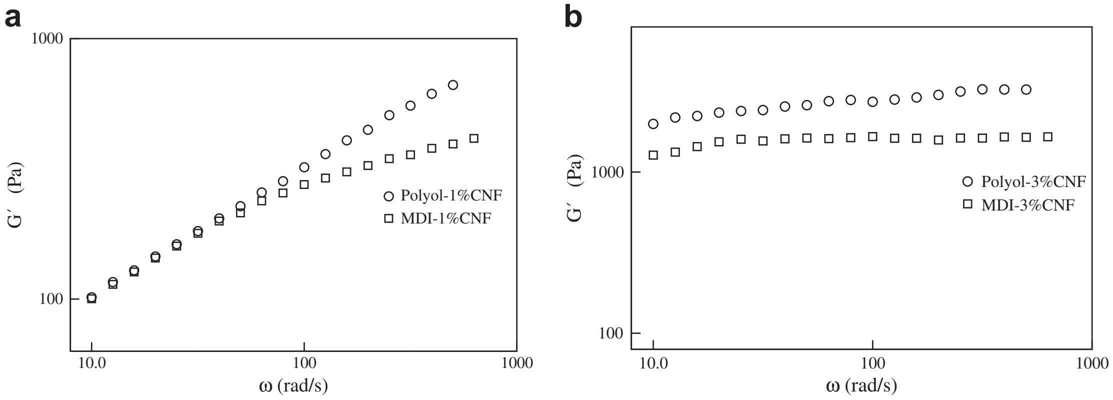

Fig. 2. Linear viscoelastic properties of CNF – component blends (a) 1% CNF in components (b) 3% CNF in components.

3.3. Cell morphology and closed cell content of cured foam

The scanning electron micrographs in Fig. 3 show the cell morphology of neat and CNF based foams. The cell size shows slight reduction by the addition of CNF. The corresponding cell densities are shown in Table 3. The potential nucleant density of filler during heterogeneous bubble nucleation can be calculated by the following equation [15].

$$PND = \frac{w}{\rho_P}\frac{\rho_{\text{composite}}}{V_P} \tag{1}$$

where *PND* denotes potential nucleant density, *w* the weight fraction of the particle in the composite, ρ_P is the density of the particle, $\rho_{\text{composite}}$ is the density of the polymer blend and V_P is the volume of individual particle. According to above equation, the potential nucleant density for 1% CNF in polyol (~ 0.42% in foam) is $1.17 \times 10^{12}/\text{cm}^3$. The observed cell density is $1.21 \times 10^4/\text{cm}^3$. In the case of polystyrene foams, the potential nucleant density and the observed cell density for 1% of CNF were $1.41 \times 10^{12}/\text{cm}^3$ and $2.78 \times 10^{10}/\text{cm}^3$, respectively [9]. This means that the nucleating efficiency of CNF in reactive foaming of PU is significantly inferior to that of non-reactive thermoplastic foaming. Fig. 3 (e) & (f) shows the high magnification SEM micrographs of neat and nanocomposite foams. It is clear from Fig. 3(f) that the nanofibers are located on the cell windows of the foam.

The closed cell content of both neat and nanocomposite foams is essentially the same (Table 3). This indicates that CNF did not induce cell opening and hence did not cause the loss of blowing agent. This is due to the fact that CNF particles are not antifoaming in nature, so that they do not induce film drainage and rupture. Particles which are phobic to polyurethane liquid matrix will have de-wetting effect on cell window lamellae and thus accelerates capillary drainage from the film resulting in coalescence and rupture [16]. It has been shown that montmorillonite based nano clays, owing to their antifoaming property, induced powerful cell opening in polyurethane foams, effectively increasing the *k*-value and decreasing the thermal insulating efficiency of the foam [6].

Table 2
Kinetic profile of foaming.

CNF (%wt)	Gel time ±2 (s)	Rise time ±3 (s)
0	49	70
1% (Polyol)	47	71
1% (MDI)	46	68

3.4. Thermal conductivity, compressive modulus and fire resistance

The thermal conductivity values shown in Table 3 fall in the range of *k*-values for commercial foams (0.01–0.02 W/mK). It is inferred that the thermal conductivity is reduced by 5.4% with the addition of 1% CNF in MDI (~0.5% in foam), effectively increasing the thermal insulating capacity of foam. This is much higher than the reported 2.8% reduction in *k*-value by the addition of up to 10% of organically modified montmorillonite [3]. The reduction in *k*-value may be due to the combined effect of nucleation and reduction in radiative heat transfer by CNF. In a foam, the thermal conductivity comprises of contributions from various mechanisms of heat transfer such as conduction, convection and radiation. In rigid polyurethane foam system, the contribution of convective heat transfer of blowing gas is shown to be insignificant [17,18]. The effective thermal conductivity in a gas-solid two phase foam system k_e (W/mK) could be represented as;

$$k_e = k_s + k_g + \frac{16\sigma T^3}{3\varepsilon} \tag{2}$$

where, k_s (W/mK) is the thermal conductivity of the solid, k_g is the vapor phase thermal conductivity of gas phase, σ is the Stephan–Boltzmann's constant, *T*, the temperature (K), ε (m^{-1}) is the extinction coefficient. The third term of above equation denotes the radiative contribution to thermal conductivity (k_r). The rate of radiative heat transfer contributes to about 25% of the total rate of heat transfer in the foam [19]. Carbonaceous materials such as carbon black have been shown to decrease the radiative heat transfer in PU foams by increasing the opacity to infrared radiation of the cell windows and struts and therefore decreasing the passage of infrared radiation through the foam [20].

From Table 3, it is seen that the normalized (for density) compressive modulus of the nanocomposite foams increases. Saha et al. also reported similar trend [11]. Regarding fire resistance of the foam, it is noted that the weight retention after the removal of the flame increases by 13% by the addition of 1% CNF in MDI (corresponding to 0.42% in foam) showing an enhanced fire resistance of the nanocomposite foam.

4. Conclusions

Nanodispersions of carbon nanofiber in polyurethane components have been prepared. Rheological estimations show that a filler loading as low as 3% in components is sufficient for making a highly cross-linked network. Reactive foaming of these nanodispersions was carried out to make polyurethane nanocomposite

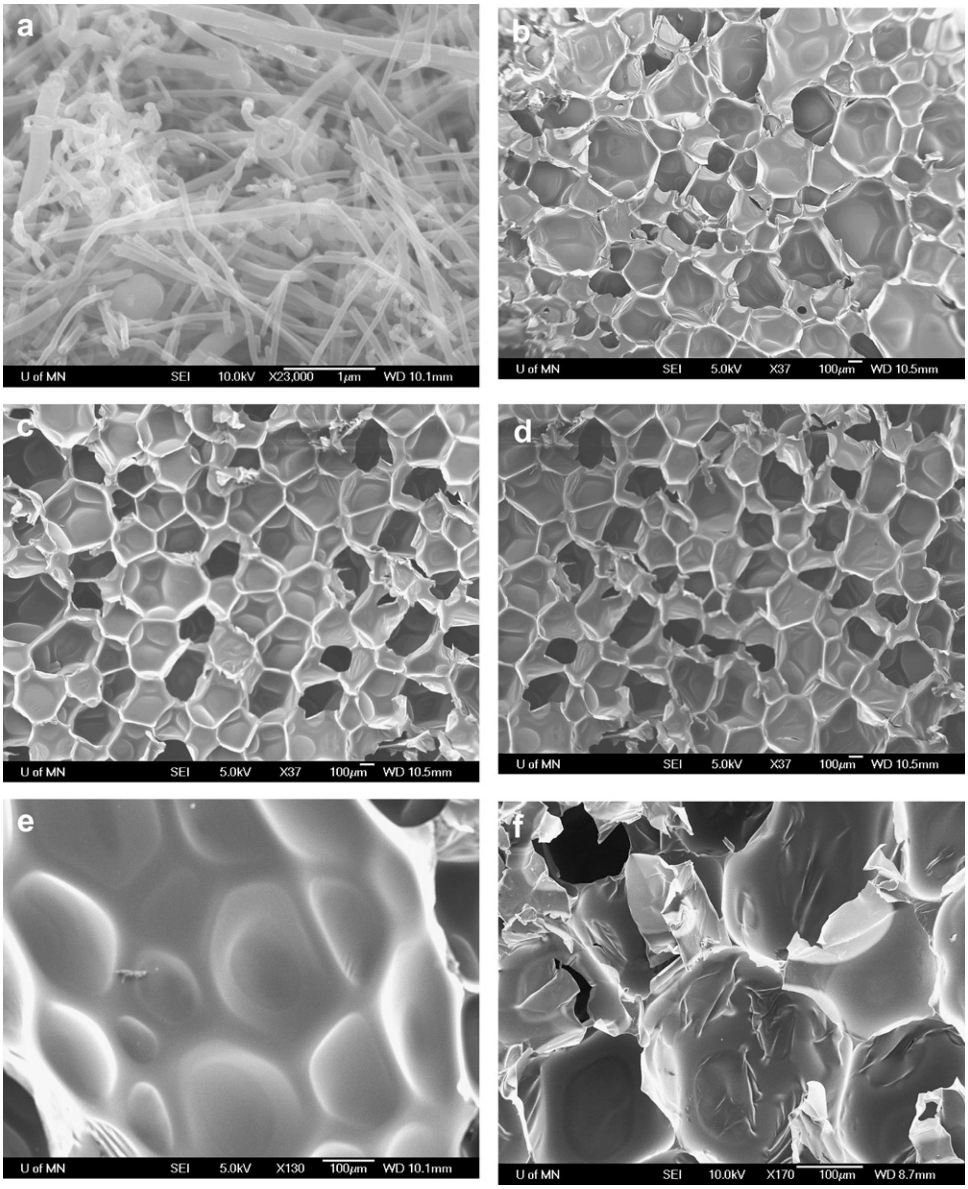

Fig. 3. SEM images of (a) CNF (b) Neat PU foam (c) PU foam from 1% CNF in polyol (d) PU foam from 1% CNF in MDI (e) high magnification image of neat PU foam (f) high magnification image of foam from 1% CNF in MDI showing the distribution of CNF on cell windows.

foams. Addition of CNF does not require a change in polyol formulation as the kinetic reaction profiles are unchanged. The nanofiber induced moderate heterogeneous bubble nucleation and the cell size became more uniform The thermal conductivity, compressive modulus and fire resistance of nanocomposite foams are better at a very low loading (<0.5% by weight of filler in foam). CNF did not induce structural defects in foam.

Table 3
Properties of conventional and nanocomposite foams.

Sample	Cell number density (#/cm^3)	Open cell content±2 (%)	k±0.0001 (W/mK)	Weight Retention±0.2 (%)	Normalized compressive modulus±0.3 (MPa)
Conventional	1.97×10^4	87	0.0162	19.8	31.2
1%CNF-Polyol	1.21×10^4	86	0.0157	20.5	35.3
1% CNF-MDI	1.01×10^4	86	0.0156	21.9	36.2

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