Mechanical properties of diacetylene functionalized polyamides

H. W. Beckham and M. F. Rubner†
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
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An aliphatic diacetylene functionalized polyamide has been synthesized and successfully processed into high quality fibres and films for mechanical property measurements. The reactive diacetylene functional groups positioned in the backbone of this polymer remained dormant during a wide variety of processing schemes but were activated in a controlled manner by exposure to fixed dosages of high energy electrons. Solid state ^{13}C nuclear magnetic resonance revealed that exposure to high energy electrons crosslinks the polymer via the formation of conjugated polydiacetylene chains. In general, crosslinking via the formation of polydiacetylene chains was found to increase the ultimate tensile strength and modulus of the material and reduce its critical failure strain. For specific fibres, the tensile strength of the material was doubled, its modulus increased by 50%, and the failure strain only reduced to 30% thereby maintaining a high degree of toughness in this system even after an 80 Mrad dose of electrons.

(Keywords: polyamide; diacetylene; tensile properties; functionalized; crosslinking)

INTRODUCTION

Over 20 years ago, Wegner described the synthesis of linear polyesters and polyurethanes containing diacetylene groups in their repeat units and confirmed that these polymers undergo the same type of solid state topochemical reaction observed in diacetylene monomers[1]. Since that time, a number of different diacetylene-containing host polymers have been synthesized and characterized[2–5]. The presence of crosslinkable diacetylene groups in the backbone structure of a host polymer provides a unique opportunity to systematically adjust the optical and mechanical properties of these materials in the solid state. Compared to existing crosslinking schemes for polymeric materials, the diacetylene functionality provides many attractive advantages. For example, the diacetylene group can be readily incorporated into a wide variety of host polymers, remains dormant during processing, and can be activated either thermally or via radiation to form conjugated polymeric crosslinks without the creation of volatile byproducts. In addition, since the reaction proceeds as a diffusionless topochemical process, the molecular organization of the host polymer is not disrupted during crosslinking. This latter characteristic is especially important for highly aligned polymer fibres in which destruction of a highly ordered morphology may be deleterious to the ultimate mechanical properties of the material.

Recently, our work on diacetylene containing segmented polyurethanes has shown that diacetylene functionalization of a host polymer can be used to significantly improve the mechanical performance of a polymer[6]. For these systems, it was found that the ultimate tensile strength in some cases could be more than doubled by simply controlling the level of radiation-induced diacetylene crosslinking taking place after processing. In general, the ultimate tensile strength of these materials was found to initially increase, reach a maximum, and finally decrease as the level of diacetylene crosslinking increased. Significant increases in the moduli of some of these new materials were also realized by diacetylene crosslinking. Most recently, studies were conducted to monitor the orientation of the polydiacetylene conjugated crosslinks during tensile elongation via the use of visible dichroism techniques. These studies have provided new insights into the deformation mechanisms active in segmented polyurethanes[7]. These results coupled with the development of additional novel optical properties, such as thermochromism and mechanochromism[7], prompted the extension of this technique to other host systems. In particular, the investigation of a variety of fibre-forming host polymers based on polyamides is currently underway.

The synthesis and optical properties of the diacetylene-containing polyamides have been previously reported[8]. Polyamides were chosen as the host polymer because they represent a class of semicrystalline, fibre-forming polymers that may be prepared with either flexible or rigid polymer backbones. It was important to be able to spin fibres from the new diacetylene-functionalized materials as a fibre possessing an intrinsic mechanism for systematic controlled crosslinking is expected to exhibit highly interesting properties as well as enormous technological potential. For example, a well oriented fibre in which the polymer chains are highly aligned along the fibre direction would give crosslinks in the transverse direction to the fibre axis upon irradiation. Thus, with this system, it is possible to examine in a controlled manner the influence of interchain strength on the traditionally poor compressive behaviour of rigid rod polymer fibres. As a first step to such materials, we report

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† To whom correspondence should be addressed

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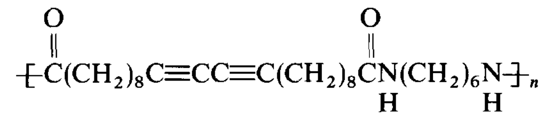
the processing of aliphatic functionalized polyamides into both fibres and films and the study of their mechanical properties as a function of systematically increasing the degree of diacetylene cross-polymerization.

EXPERIMENTAL

The diacetylene functionalized polyamide discussed in this paper, PADA 6,22:



$$\left[\overset{O}{\overset{\|}{C}}(CH_2)_8C\equiv CC\equiv C(CH_2)_8\overset{O}{\overset{\|}{C}}\underset{H}{N}(CH_2)_6\underset{H}{N}\right]_n$$

was prepared from 10,12-docosadiyn-1,22-dioyl chloride and 1,6-hexanediamine by using an adaptation of the previously reported interfacial polymerization procedure[8]. Specifically, an equimolar mixture of the monomers was reacted in the presence of NaOH (2 × molar excess based on the monomers) and sodium dodecyl sulphate (1% based on the volume of aqueous phase) in a high speed blender. The diamine, base, and surface active agent were first dissolved in ultrapure water to give the aqueous solution. The diacid chloride, used immediately following its synthesis from the corresponding diacid and thionyl chloride, was dissolved in dry chloroform and charged to the blender before the aqueous solution was added in one quick motion. Blending commenced immediately and was continued at high speed for 5 min. The resulting suspension was broken up by pouring the contents of the blender into a large volume of methanol. The precipitated white polymer was collected by filtration and subsequently washed thoroughly with water, methanol, and acetone to remove byproducts, impurities, and the surface active agent (SDS). Typically, starting monomer quantities were controlled to generate 5 g batches of white, fluffy PADA 6,22 after drying at room temperature under high vacuum.

Inherent viscosities (η_{inh}) were determined for 5 g l^{-1} *m*-cresol solutions at 30°C for all batches of polymer produced. For the work reported here, PADA 6,22 was consistently prepared having inherent viscosities of about 1.0 dl g^{-1}. It is worth noting that polymers of higher molecular weights, as evidenced by η_{inh} values of 1.4 and higher, were also prepared. The fibres and films processed from these polymers did not exhibit any significant differences in mechanical behaviour when compared to their lower molecular weight counterparts. This is important in that materials processed from different batches of polymers may be comparatively evaluated without concern for attributing property variations to differences in molecular weight, at least as long as a minimum molecular weight is obtained.

The details of the solid state ^{13}C nuclear magnetic resonance (n.m.r.) spectroscopy were reported previously[8]. For the spectra displayed here, a cross-polarization pulse sequence was employed with a contact time of 1 ms, a 5 μs 90° proton pulse, and a 3 s recycle delay.

The polymer was processed into fibres and films for mechanical property assessment. Films were produced by both compression moulding and solvent casting techniques. The compression-moulded films were prepared with a table-top hydraulic press in which the blocks were heated to 170°C (the processing window for this material lies between its melting point of 160°C and its diacetylene polymerization initiation temperature of about 240°C). Because of the possibility of thermally activating the diacetylene polymerization, the polymer was placed between the blocks only long enough for melting to occur, pressed for 30–60 s at 55 MPa and then taken out of the press while the flat plates cooled slowly to ambient temperature. The cast films were prepared by static evaporation of hexafluoroisopropanol from solutions containing 3 wt% polymer under a carefully controlled nitrogen stream. The solutions were filtered into casting dishes through a fine stainless steel mesh screen to remove any large impurities and insolubles. Nylon 6,12 (Aldrich Chemical) was processed into films in a similar manner in order to assess the influence of high energy electrons on the mechanical properties of a non-functionalized aliphatic polyamide.

The polymers synthesized were spun into fibres at the DuPont experimental station. This was highly successful as evidenced by the variety of morphologically diverse samples of PADA 6,22 that could be produced by varying the processing conditions. During the process optimization period, fibres were produced by both wet and dry spinning techniques. By adjusting or introducing such processing parameters as drawing, air-gap height (between spinneret and coagulating bath), and constitution of coagulant, fibres were collected with a wide range of properties. Only data from a few of these samples are presented to illustrate the changes in mechanical properties caused by cross-polymerization of the diacetylene groups. Details concerning the processing of this material into fibres will be published shortly.

Fibres and films were crosslinked in air by exposure to controlled dosages of electrons generated by a Van de Graaff accelerator operated at 2.6 MeV. Dosages ranging from 1–80 Mrad were administered. Precautions were taken in order to minimize sample heating during radiation exposure.

Tensile properties were measured with an Instron model 1122 at an initial gauge length of 2.54 cm and a strain rate of 0.04 min^{-1} for both the fibres and films. All samples were tested at 25°C whereas the relative humidity varied slightly during tensile testing but was always near 45%. All fibres of a particular type were tested under identical conditions so that trends in the mechanical properties could be attributed directly to diacetylene cross-polymerization instead of variations in relative humidity. Although the fibres appear to be quite sensitive to variations in relative humidity, the films were found to be essentially insensitive to moisture effects.

RESULTS AND DISCUSSION

In order to confirm that the crosslinks created during exposure to high energy electrons are due to the production of polydiacetylene (PDA) chains via polymerization of the diacetylene units, an analysis of the polymer by solid state ^{13}C n.m.r. was conducted prior to mechanical property evaluation. Due to the topochemical nature of the solid state diacetylene polymerization, specific packing requirements must be met for high reactivity to be realized. In semicrystalline diacetylene functionalized polymers, highly ordered arrays suitable for diacetylene polymerization are most likely to be found in the crystalline regions of the host polymer. Our expectation was therefore that the formation of PDA chains would be essentially restricted to the crystalline or paracrystalline regions within the polymer. A schematic representation showing the polymerization of diacetylene groups in an ordered array of PADA 6,22 chain segments is shown in *Figure 1*.

Figure 2 shows the n.m.r. spectrum of a sample of as-prepared powder of PADA 6,22 and the spectrum of the same material after an 80 Mrad dose of high energy electrons. The 85–135 ppm regions of these spectra are shown in expanded form to show the evolution of the peaks associated with the PDA chains. Comprehensive peak assignments are given elsewhere[8] and are based on previous reports in the literature[9–11]. The peak appearing in both spectra at 100 ppm is simply a spinning side band of the carbonyl carbon resonance (173 ppm). This was confirmed by varying the sample spinning speed which altered both the chemical shift and intensity of this peak. Other spinning side bands at 151 and 139 ppm can also be seen in these spectra and are due to the resonances of the unreacted diacetylene carbons (77 and 65 ppm).

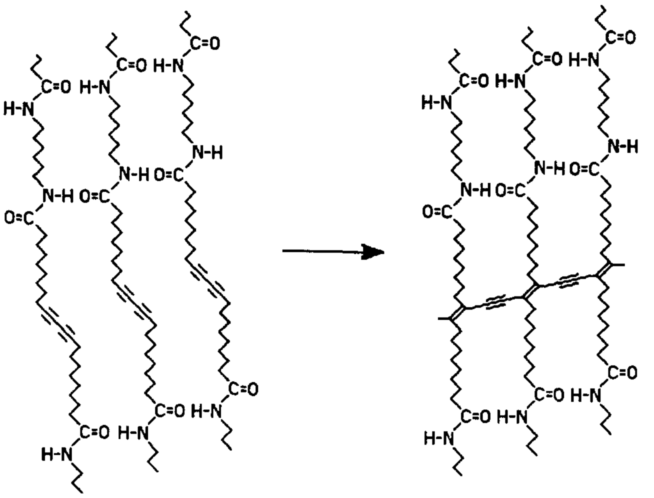


Figure 1 Schematic representation of diacetylene cross-polymerization within an ordered array of PADA 6,22 repeat units

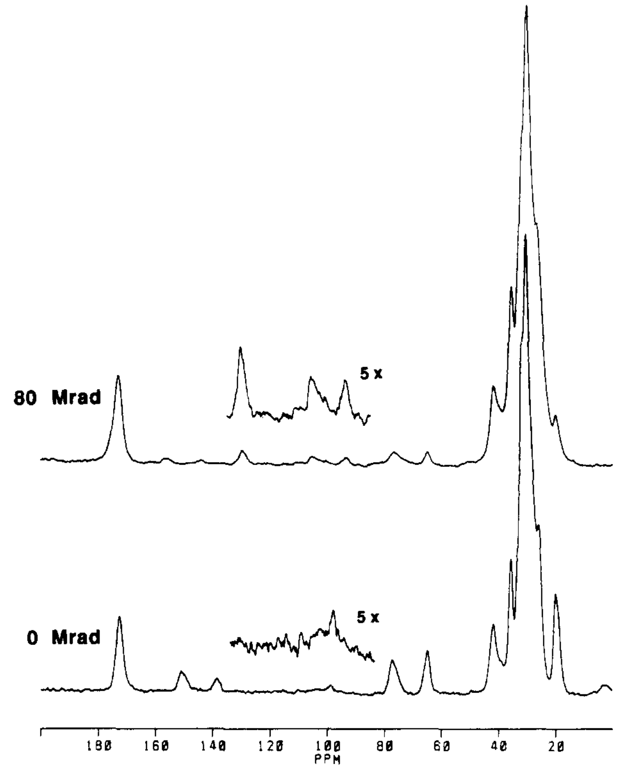


Figure 2 Solid state ^{13}C n.m.r. spectra of PADA 6,22 before and after exposure to electron beam radiation

The resonance that appears at 130 ppm in the spectrum of the irradiated material is due to the vinylic carbons (–C=) of the newly created PDA backbones, and the peak around 106 ppm can be attributed to the acetylenic PDA carbons (–C≡). This latter resonance is broadened due to the strong chemical shift dependence of this particular carbon on conjugation length as reported by other researchers[11,12]. The planarity of the PDA backbone, and hence its effective conjugation length, is strongly influenced by the conformational states of its pendant side chains. In this particular polyamide diacetylene, the side chains are attached to the PDA backbone via a sequence of eight methylene units which can adopt a wide range of stable conformations (depending on local chain environment) thereby distorting the planarity of the backbone to varying degrees and broadening the –C≡ chemical shift. In any event, the development of these peaks in the irradiated material and the decrease in intensity of the diacetylene peaks (77 and 65 ppm) clearly show that conjugated PDA chains are formed during crosslinking.

The details of the ^{13}C n.m.r. studies will be presented in a future publication. The spectra are displayed here only to provide evidence that the diacetylene groups residing in linear polyamide chains crystallize in a manner favourable for the 1,4 solid state addition polymerization to occur. In fact, the degree of conversion of the diacetylene groups to PDA chains has been estimated by solid state ^{13}C n.m.r.[8]. For a 60 Mrad dose of electrons, the percentage of diacetylenes polymerized to PDA chains in an as-prepared sample has been estimated to be about 60%. Furthermore, recent findings have demonstrated that reducing the crystallinity of the polymer also reduces the extent of diacetylene conversion for a given radiation dosage. Since the percentage conversion is strongly linked to the morphology of a sample, direct extensions of conversion/dosage data to fibres and films should be taken only as convenient references. Nevertheless, we have found that the degree of conversion in these materials can be quite high. This is important as it provides a wide range over which to vary the degree of crosslinking, and therefore systematically adjust the mechanical properties.

In order to examine the influence of diacetylene polymerization on the mechanical properties of the polyamide host polymer, samples were evaluated as both films and fibres. By examining the polymer in these various forms, it was also possible to evaluate how different processing methods and conditions influenced diacetylene reactivity and mechanical performance.

Figure 3 shows the stress–strain curves of a solvent-cast film of PADA 6,22 after exposure to radiation dosages of 0, 1, 5, 10, 20, 30 and 60 Mrad. As can be seen, the modulus and ultimate tensile strength (UTS) of the film increase with increasing level of diacetylene polymerization whereas the ultimate strain to failure decreases during this process. This trend was observed in most of the samples evaluated. In this case, the modulus of the film is more than doubled by a 60 Mrad dose while the UTS is increased by more than 50%. Thus, the introduction of PDA crosslinks does not render the

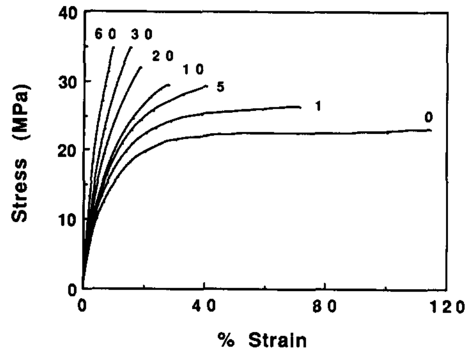


Figure 3 Stress–strain curves of PADA 6,22 solvent-cast film as a function of radiation dosage. Numbers indicate radiation dosage (in Mrad)

material overly brittle (it still exhibits a modest strain to failure), but instead produces a significantly stiffer and stronger material. In fact, even after a 60 Mrad dosage, the films are still quite flexible and can be reversibly bent without breakage. Similar property changes were observed for compression-moulded films (data not shown). It is important to note that the dose levels to which these polymers are being subjected are quite excessive for an aliphatic organic polymer.

To examine the effects of electron irradiation on non-functionalized aliphatic polyamides, the same analysis was performed on solvent-cast films of nylon 6,12. The films were tested in tension after high energy electron dosages of 0, 1, 5, 10, 20 and 42.5 Mrad. The results revealed a trend commonly observed for polymers exposed to high energy electrons. After 1 Mrad, the UTS of nylon 6,12 displayed an increase of 20%. However, at 5 Mrad, the UTS had already fallen to 80% of the strength of the non-irradiated polymer. At progressively higher dosages, the UTS continued to fall until at 42.5 Mrad the strength had been reduced to less than half the strength of the non-irradiated film. The failure strain was likewise reduced after a slight increase for the sample exposed to 1 Mrad.

The two possible physico-chemical consequences of exposing polymeric materials to high energy radiation in air are crosslinking and chain scission. The initial mechanical property enhancement observed in nylon 6,12 after a 1 Mrad exposure is most likely due to radiation-induced crosslinking. At higher doses however, the chain scission mechanism apparently begins to dominate and the mechanical properties become severely compromised. Other nylons as well as polyethylene have been shown to exhibit similar behaviour[13,14]. These findings rule out the possibility that the strength and modulus increases found for PADA 6,22 are due simply to random radiation-induced crosslinking and point instead to the controlled systematic crosslinking afforded by the incorporated diacetylene groups.

While the host polyamide chains present in the films of PADA 6,22 did not display any significant degree of preferred orientation, the chains present in fibres spun from this polymer exhibited varying degrees of orientation depending on the specific processing method and conditions. For example, wet spun fibres were tested both before and after drawing. Their mechanical properties and responses to radiation were markedly different as manifested in the tensile curves displayed in *Figures 4* and *5*. It is immediately apparent that processing history has a major influence on the mechanical properties of the fibre. As expected, the drawn fibre is much stronger due to the additional shear-induced alignment of the polymer chains that is introduced during the drawing step. The UTS of the non-irradiated drawn fibre reaches about 100 MPa, whereas the equivalent non-drawn fibre breaks at a stress of about 30 MPa. In addition, the UTS of the drawn fibre appears to be less sensitive to radiation exposure than that of the non-drawn material. In fact above 40 Mrad, diacetylene cross-polymerization does not provide additional strength improvements in the drawn fibre whereas the non-drawn fibre shows a strength enhancement even at larger dosages.

It is interesting to compare the relative percentage changes in UTS between the two fibres resulting from diacetylene polymerization. At 40 Mrad, for instance, the drawn fibre has registered its maximum increase in UTS of about 25% while the non-drawn fibre exhibits a 50% UTS improvement with this dosage. Visual observations of colour changes indicate that the drawn fibres are less cross-polymerized than the non-drawn fibres; although this observation has yet to be verified. If this relative increase difference is indeed due to variations in the extent of crosslinking, then it appears that the molecular organization of the non-drawn fibre is more favourably suited for diacetylene polymerization than that of the drawn fibre. To account for the lower reactivity of the drawn fibre, it is possible that the drawing process, although responsible for enhanced alignment of the host polymer chains, also mechanically disrupts the crystalline regions of the polymer thereby limiting the amount of

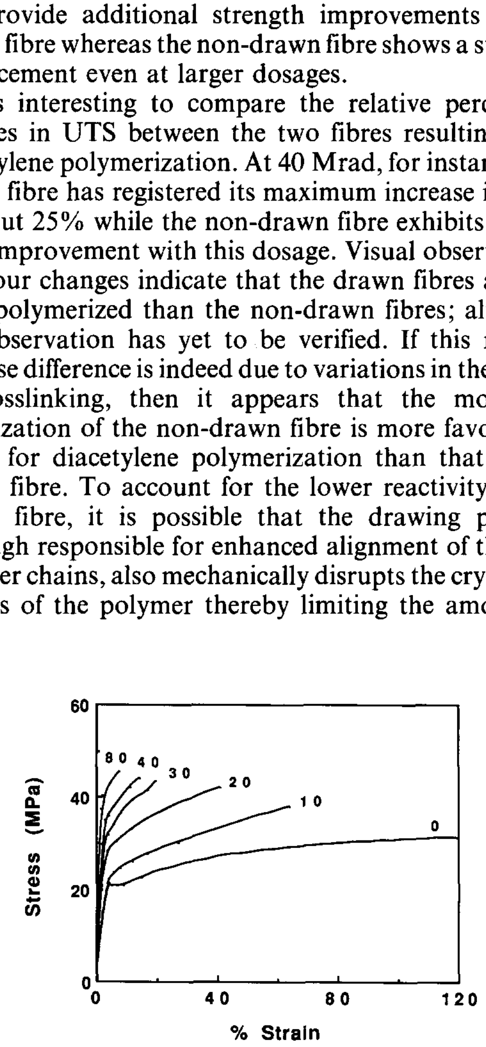


Figure 4 Stress–strain curves of PADA 6,22 wet spun fibre as a function of radiation dosage. Numbers indicate radiation dosage (in Mrad)

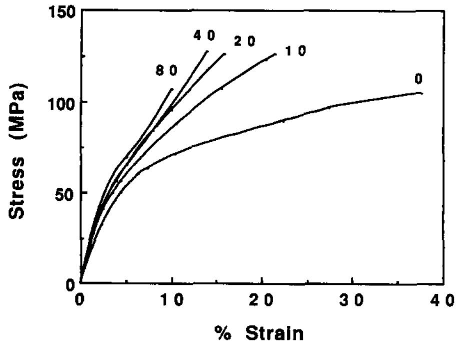


Figure 5 Stress–strain curves of PADA 6,22 drawn wet spun fibre as a function of radiation dosage. Numbers indicate radiation dosage (in Mrad)

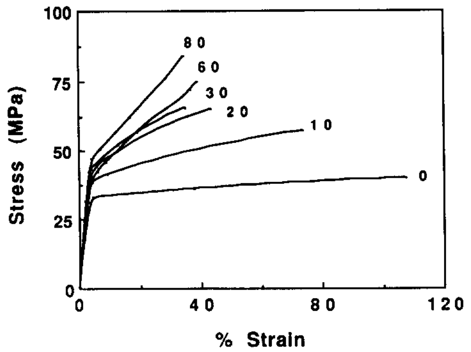


Figure 6 Stress–strain curves of PADA 6,22 air-gap wet spun fibre as a function of radiation dosage. Numbers indicate radiation dosage (in Mrad)

diacetylene polymerization that is possible. Alternatively, these differences may simply reflect different strengthening mechanisms operating within the fibres due to the differences in chain organization (the number of chain-folded crystallites *versus* the number of more extended chains) developed during processing. Diacetylene polymerization in a fibre already strengthened by a high degree of chain alignment may not influence the mechanical properties as much as in a less aligned fibre comprised of crystallites linked together with amorphous tie molecules. X-ray studies are now underway to answer these pertinent questions.

One of the more striking features of these data is the retention of some degree of strain ability even after high radiation dosages. This is especially evident in *Figure 6* which shows the mechanical data of a fibre processed with a variation that introduces an air gap between the spinneret and coagulating bath. This particular fibre exhibits tensile properties intermediate to the previously shown drawn and non-drawn wet spun varieties. Besides an UTS enhancement of over 100%, the interesting point to note is the greater than 30% strain level to which this fibre still reaches even after an 80 Mrad dosage of high energy electrons. Thus, the fibre has been strengthened without significantly compromising its toughness.

These data raise a number of important points. Since the fibres still retain a relatively high strain ability, a fair volume of the fibre must remain uncrosslinked even after an 80 Mrad dosage. This might be expected considering the nature of the crosslinking reaction. As indicated earlier, diacetylene cross-polymerization is mostly restricted to the ordered regions of the polymer. Thus, if the bulk of the crosslinking occurs in the crystallites of this semicrystalline polymer, then the data suggest that improvements in the rigidity and cohesion of the crystallites can effectively increase tensile strengths. Studies of the mechanisms of deformation active in these materials and their dependence on morphology and molecular organization are currently in progress.

CONCLUSIONS

Incorporation of diacetylene functionalities into the backbone of linear polymers is emerging as a very attractive and flexible method for post-synthesis post-processing modification of material properties. Linear polyamides have been shown to be highly suitable host materials for this purpose. The diacetylene-containing polyamides were successfully processed into films by high temperature compression moulding and solvent casting techniques. Fibres were also successfully spun from these materials by a variety of adaptations on wet and dry spinning techniques. Thus, the processability of the functionalized polymer was not compromised by the presence of reactive groups in the backbone.

The processed materials were irradiated with controlled dosages of electrons to promote systematic enhancements in tensile strengths and moduli. For the best fibre, the mechanical property gains were achieved without significant losses of toughness for dosages up to 80 Mrad. In general, the polymers were able to withstand radiation dosages that would severely reduce the mechanical response of many non-functionalized aliphatic polymeric materials.

The promise of novel diacetylene-containing polymers is extremely broad. The crosslinking method is novel because the controlled manner of introduction allows the specific tailoring of polymer mechanical and material properties. Besides the mechanical properties described, marked improvements are also realized in solvent resistance, radiation resistance, and temperature utility range. Also, the potential use of these materials for investigating deformation mechanisms of semicrystalline polymers was demonstrated.

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