# Bifunctional monomers in photoinduced vinyl grafting on cotton cellulose: use of divinyl benzene in grafting of styrene

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*(Received 31 January 1991; revised 3 October 1991; accepted 30 October 1991)*

The effect of a bifunctional monomer, divinyl benzene (DVB) on the graft copolymerization of styrene onto cotton cellulose was studied using uranyl nitrate (UN) and benzoin ethyl ether (BEE) as photoinitiators. UN gave higher graft add-on as compared to BEE. Incorporation of DVB in the grafting bath containing styrene led to a great enhancement of graft add-on which was higher than that obtained by using cotton preswollen with sodium hydroxide as substrate. With increase in the graft add-on, the moisture regain and tenacity decreased, whereas thermal stability of cotton improved.

**(Keywords: cotton cellulose; styrene; graft copolymerization; divinyl benzene; uranyl nitrate; benzoin ethyl ether; moisture regain; tenacity; thermal stability)**

## INTRODUCTION

The photoinitiated grafting of vinyl monomers onto natural and synthetic polymers has been extensively studied. The chemical modification of cotton by graft copolymerization reaction causes a significant change in its physical and mechanical properties. Since u.v. radiation is not quite energetic enough to dissociate any but the weakest bond in the polymer backbone, the photoinitiators are required to increase the free radical formation on the backbone during graft copolymerization reactions. Various photoinitiators such as dyes[1], metal ions[2] and hydrogen peroxide[3] have been used for u.v. radiation-induced grafting of cotton; however, benzoin ethers are most widely used[4].

The graft copolymerization of styrene onto cotton has been studied using different inorganic photoinitiators such as uranyl nitrate and ceric ammonium nitrate[5–7]. The effect of solvent on grafting of styrene onto cotton has been studied[8–10] and methanol was found to give maximum graft yield. Very little work seems to have been reported on the effect of addition of a bifunctional monomer during grafting of cotton with vinyl monomers. Dorwianyn and Garnett[11] have reported that the grafting of styrene onto cellulose in the presence of divinyl benzene results in a synergistic effect on the graft yield. A similar observation was made by Garnett and co-workers[12,13].

This paper presents results on the effect of adding a bifunctional monomer, divinyl benzene, during grafting of styrene onto unswollen and sodium hydroxide-swollen cotton cellulose. The photoinitiators used were uranyl nitrate and benzoin ethyl ether, both of which give free radicals[12,14–19]. The changes in the properties of grafted substrates, such as moisture regain, tenacity and thermal behaviour, have also been investigated.

## EXPERIMENTAL

### Materials

*Substrates.* The cellulose sample used was scoured and bleached 30-count cotton yarn. The swollen samples of cotton were prepared by using 24% (w/w) sodium hydroxide at 20°C for 1 h, followed by thorough washing with water and then drying in air at room temperature.

*Chemicals.* Styrene (supplied by LOBA Chemie Indoaustranal Co.) and divinyl benzene (DVB, supplied by Ion Exchange (India) Ltd) were vacuum distilled to eliminate inhibitors. Uranyl nitrate (UN) and benzoin ethyl ether (BEE) were used as the photoinitiators. Methanol, benzene and sodium hydroxide of chemically pure grade were used.

### Methods

*Graft copolymerization.* The cotton samples to be grafted were weighed to 1 g and immersed in 100 ml methanol bath containing different concentrations of styrene and a photoinitiator in 250 ml quartz flasks. A Phillips HPW 125 W mercury lamp was used as a source of u.v. radiation. The temperature was varied in the range 30–60°C and controlled using a glycerine bath. The quartz flasks were irradiated for different time intervals varying from 1 to 6 h in an enclosed wooden chamber containing a u.v. lamp. After completion of the reaction, the grafted samples were removed, washed with methanol, Soxhlet-extracted with benzene for at least 72 h and then air-dried as per the method suggested by Garnett[20,21] and co-workers. Thus, the parameters of grafting, namely initiator and monomer concentrations, time and temperature of reaction were optimized. The

0032-3861/92/173729-05

bifunctional monomer, DVB, was added in the required amount to the grafting bath after addition of methanol and styrene under optimized conditions. A similar procedure was followed for sodium hydroxide-swollen samples.

The graft add-on of the samples was determined gravimetrically using the relation:

$$\text{Graft add-on } (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where $W_1$ = weight of the original sample and $W_2$ = weight of the grafted sample.

*Moisture regain.* The moisture regain of the control and grafted cotton samples was determined by the oven-drying method[22].

*Tenacity.* Samples of 1 cm length of the control and grafted cotton were tested for tenacity on an Instron tensile tester which recorded load–elongation curves with a chart speed of 50 mm $\text{min}^{-1}$. The full scale of the recorder was adjusted for a load corresponding to 500 g. The tenacity was measured in terms of breaking load.

*Thermal analysis of grafted cotton.* Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) were carried out using a Stanton Redcroft Thermal Analyser STA 780. The cotton sample was cut to lengths of approximately 1–2 mm and 20 ± 5 mg was taken for each analysis. The analysis was carried out from room temperature (30°C) to 500°C at a heating rate of 10°C $\text{min}^{-1}$ and with a chart speed of 200 mm $\text{h}^{-1}$.

## RESULTS AND DISCUSSION

The parameters of graft copolymerization of styrene onto cotton cellulose, namely concentrations of the photoinitiators and styrene as well as the time and temperature of reaction, were optimized to obtain maximum graft add-on.

### *Optimization of parameters of styrene grafting*

The effect of concentration of both photoinitiators was initially studied by varying it between 0.1 and 0.4% (w/v) at 50°C for 3 h, keeping the styrene concentration at 20% (w/v) in the methanol bath. The reaction time was then varied between 1 and 6 h with these optimized concentrations of the photoinitiators at 50°C and 20% (w/v) styrene. The reaction time of 4 h gave maximum graft add-on. With these optimized conditions of time and photoinitiator concentrations, a temperature of 50°C gave maximum graft add-on. Finally, when the styrene concentration was varied from 5 to 40% (w/v), it was found that the graft add-on increased gradually up to 30% (w/v) followed by a decrease with further increase in the styrene concentration. The decrease in the level of grafting at higher monomer concentrations may have been due to the decrease in the amount of methanol in the grafting bath which must be present in sufficient quantity to permit efficient swelling of fibre and also to allow grafting reaction to take place. Thus, it was not possible to increase the monomer concentration indiscriminately to obtain higher amounts of graft in the u.v. radiation-induced graft copolymerization reaction. The optimum conditions of styrene grafting and the graft add-on values obtained under these conditions are given in *Table 1*. It is evident that UN is a slightly better photoinitiator than BEE under optimized conditions.

**Table 1** Optimum conditions for grafting of styrene onto cotton

| Grafting parameter | Photoinitiator UN | Photoinitiator BEE |
|---|---|---|
| Initiator concentration (%, w/v) | 0.20 | 0.30 |
| Time (h) | 4 | 4 |
| Temperature (°C) | 50 | 50 |
| Monomer concentration (%, w/v) | 30 | 30 |
| Maximum graft add-on (%) | 19.12 | 18.00 |

The homolytic cleavage of BEE photoinitiator is likely to form loose polystyrene chains, whereas the simultaneous hydrogen abstraction from the trunk polymer, namely cellulose, initiates the grafting reaction. Grafting of polystyrene chains is thus retarded due to simultaneous homopolymer formation. This is confirmed since the values of graft yield increased only up to a certain concentration of monomer in the bath beyond which, although the graft add-on increased slightly, the graft yield decreased, mainly due to the predominance of homopolymer formation over graft copolymerization. In the present work, maximum graft yield of 0.613% was observed at 15% (w/v) styrene concentration.

### *Effect of bifunctional monomer*

Since the graft add-on values obtained were not very high, even at the higher concentrations of styrene, it was decided to study the effect of addition of DVB to the grafting bath containing 30% (w/v) styrene at 50°C for 4 h in the presence of 0.30% (w/v) BEE. Use of the bifunctional monomer DVB in the styrene grafting bath has been shown[11–13] to enhance the graft level.

The graft copolymerization of DVB alone onto cotton cellulose using 0.30% BEE for 4 h at 50°C was not found to take place up to a DVB concentration of 2% (w/v). However, using a higher concentration of 8% (w/v) DVB and Soxhlet extracting the grafted cotton with benzene for 72 h, a graft add-on value of 3% was obtained.

In the present work, the DVB concentration in the styrene grafting bath was increased up to 2% (w/v) (*Figure 1*). The graft add-on value was found to increase with increase in the DVB concentration only up to 0.20% (w/v), beyond which it decreased drastically, reaching a value of 23.26% at 1.0% and 20.96% at 2.0% (w/v) DVB, almost equivalent to the value obtained in the absence of DVB in the styrene grafting bath. This was attributed to the fact that when the concentration of DVB in the styrene bath is very low, it does not form graft chains onto the cellulose backbone and only the styrene chains are grafted. This very small amount of DVB can only form crosslinks between polystyrene chains which are already grafted onto cotton or which are present in the loose homopolymer form in the bath. At higher concentrations, it is likely that the DVB predominantly forms the homopolymer. Another possibility is that the branching of growing styrene graft chains takes place when one end of the DVB molecule is bonded to the growing chain and the other end is saturated and free to initiate a new chain growth via scavenging reactions. The new branched polystyrene chain may eventually terminate by reacting with a neighbouring polystyrene

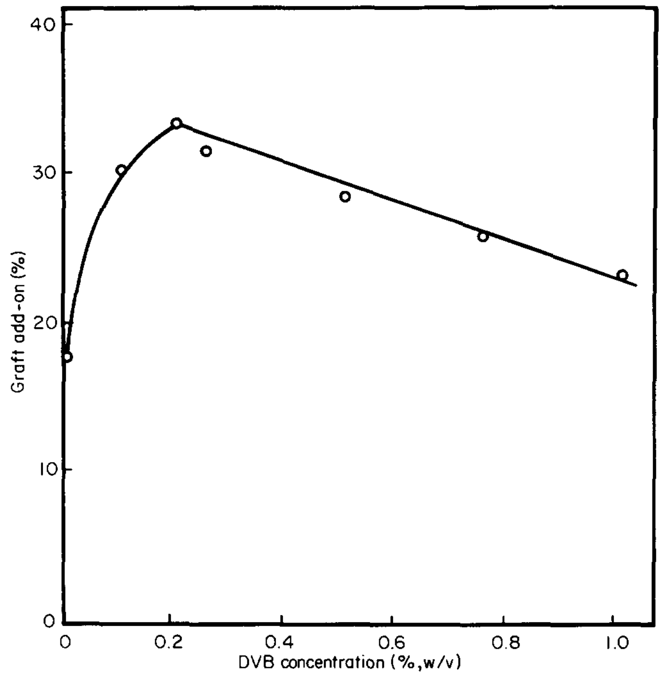

**Figure 1** Graph of DVB concentration *versus* graft add-on value (BEE photoinitiator at 30% (w/v) styrene concentration)

chain or crosslinking with an immobilized DVB radical.

At the very low concentration of DVB used (0.20% (w/v) in the grafting bath containing 30% (w/v) styrene), the amount of crosslinks formed is extremely small and hence there was no difficulty in extracting the homopolymer of styrene, DVB, as well as the slightly crosslinked product of loose polystyrene chains from the substrate by the specified method[11]. To confirm this, copolymerization of 30% (w/v) styrene and 0.20% (w/v) DVB under the conditions used for grafting was carried out and the product was found to dissolve in benzene over a period of time (12 h) which is considerably less than that used for extracting the grafted samples.

*Figure 2* shows the effect on graft add-on value of changing the styrene concentration at 0.20% (w/v) DVB. The graft add-on increased with the increase in the styrene concentration from 5 to 30% (w/v) and then decreased slightly. However, the graft add-on value at each styrene concentration was significantly higher in the presence of DVB than that observed in the absence of DVB.

The i.r. spectra of styrene-grafted cotton samples in the absence and presence of DVB in the grafting bath, shown in *Figure 3*, indicate the appearance of a peak at 1620 $cm^{-1}$ due to the introduction of aromatic C–C stretch in the fibre structure. This was also observed by Guthrie and Haq[23]. As both styrene and DVB have the same functional groups, the i.r. spectra of the two do not exhibit any difference, although the levels of graft add-on vary considerably.

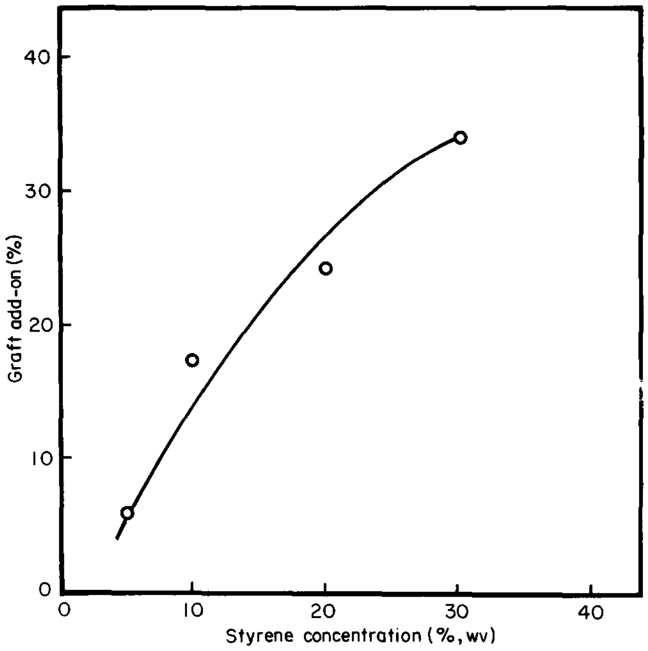

**Figure 2** Graph of styrene concentration *versus* graft add-on (BEE photoinitiator at 0.20% (w/v) DVB concentration)

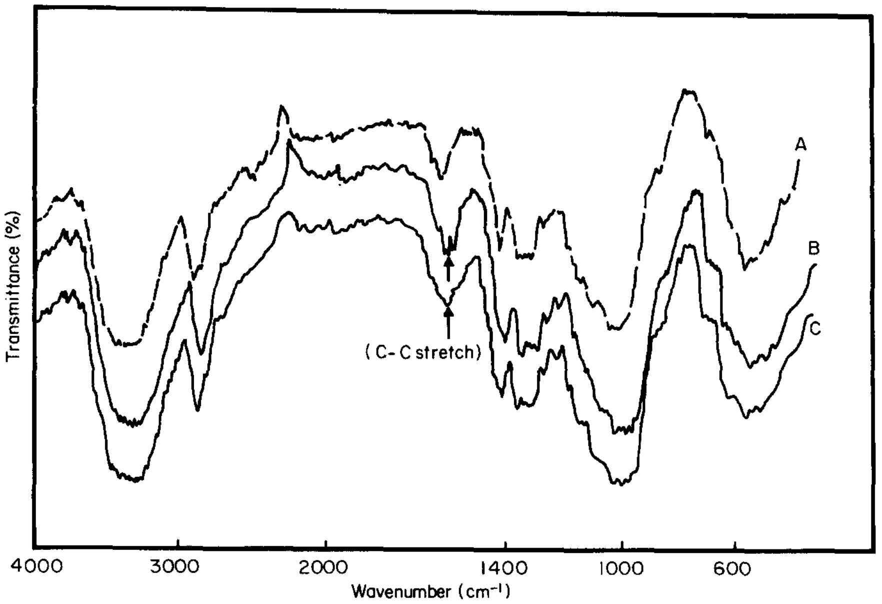

**Figure 3** I.r. spectra of samples: A, control cotton; B, styrene-grafted cotton; C, styrene-DVB grafted cotton

### *Effect of preswelling*

*Figure 4* shows the graft add-on onto unswollen and swollen cotton with variation in concentration of styrene in the grafting bath, with and without addition of 0.20% (w/v) DVB. It may be observed that the swollen cotton shows a higher level of grafting than the unswollen cotton at each concentration of styrene used, which has been attributed to the higher accessibility and greater reactivity of the swollen cotton than of the unswollen cotton. Similarly, swollen cotton samples grafted with styrene in the presence of DVB showed further enhancement in graft add-on. It is thus clear that although preswelling of the substrate improves the graft add-on to a certain extent, addition of a bifunctional monomer to the grafting bath is a more efficient and simpler technique.

### *Moisture regain and tenacity*

The moisture regain values for the control cotton and for the sodium hydroxide-swollen cotton samples were found to be 6.13% and 9.18%, respectively. On grafting with styrene, it was observed that the moisture regain decreased gradually with increase in the graft add-on. These results are given in *Table 2*. The decrease in moisture regain was attributed to the introduction of hydrophobic groups in the fibre structure.

The breaking load of the grafted fibre was also found to decrease (*Figure 5*). As the graft add-on increases, the extent of crosslinking in the fibre substrate increases, which makes the fibre brittle and rigid, thus decreasing its breaking load.

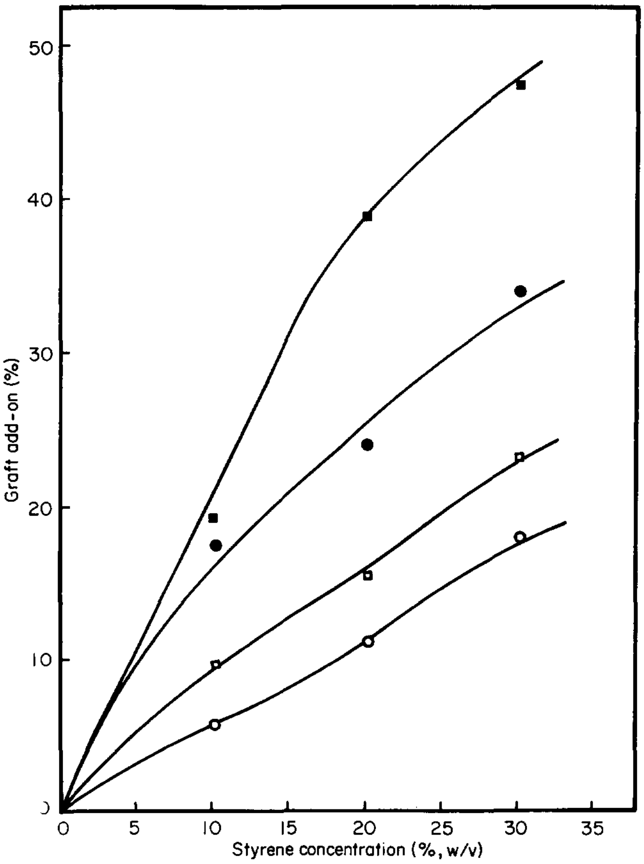

**Figure 4** Graph of styrene concentration *versus* graft add-on (BEE photoinitiator): ○, unswollen without DVB; ●, unswollen with DVB; □, swollen without DVB; ■, swollen with DVB

**Table 2** Effect of styrene on moisture regain (m.r.) of cotton cellulose (BEE photoinitiator)

| | | | Sample grafted in presence of DVB | |
|---|---|---|---|---|
| Styrene concentration (%, w/v) | Cotton sample | M.r. of untreated sample | Graft add-on (%) | M.r. (%) |
| 10 | Unswollen | 6.13 | 17.48 | 4.39 |
| | NaOH-swollen | 9.18 | 19.24 | 7.02 |
| 20 | Unswollen | 6.13 | 23.92 | 3.90 |
| | NaOH-swollen | 9.18 | 39.12 | 6.02 |
| 30 | Unswollen | 6.13 | 33.70 | 3.13 |
| | NaOH-swollen | 9.18 | 47.16 | 4.37 |

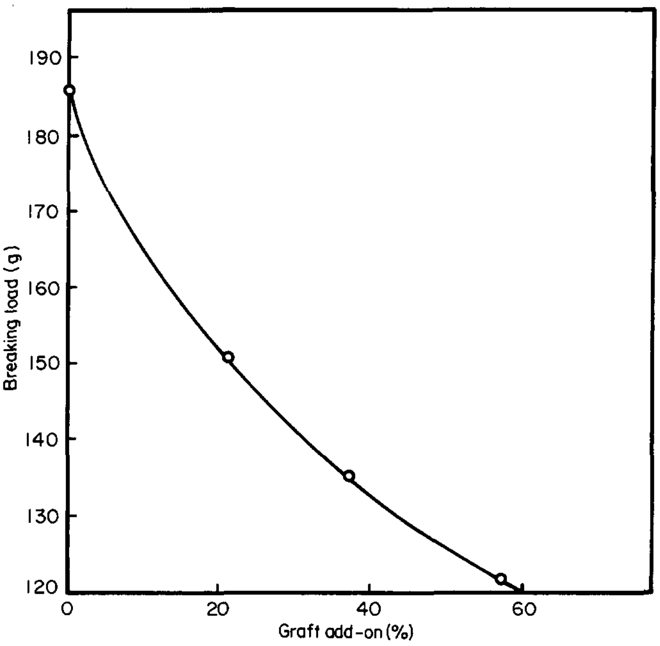

**Figure 5** Graph of graft add-on *versus* breaking load (preswollen fibre grafting using UN photoinitiator with DVB)

### *Thermal behaviour of grafted cotton*

The d.t.a. curves of control and grafted cotton samples are shown in *Figure 6*. In the d.t.a. curve of ungrafted cotton (curve A), an endotherm is observed at 100°C due to moisture desorption, followed by an exothermic process starting at about 260°C due to the oxidative attack at the carbonyl groups and C–H bonds of the substrate. The major endothermic reaction was observed to start at 305°C with a peak at 341°C reflecting the thermal depolymerization of cellulose. The d.t.a. curves of styrene-grafted cotton in the absence as well as in the presence of DVB (*Figure 6* curves B and C) show a new endothermic peak at around 410–425°C, representing the presence of polystyrene copolymer. This peak becomes larger with the increase in graft add-on with simultaneous decrease in the cellulose decomposition endothermic peak at 341°C. The endothermic peak around 100–110°C, corresponding to moisture desorption, seems to be disappearing with increasing styrene graft add-on due to the increased hydrophobicity of the grafted sample. A small endothermic peak at 75–80°C in the d.t.a. curves of samples containing higher styrene graft

**Table 3** Temperature of decomposition at different weight losses of swollen cotton grafted with styrene (UN photoinitiator)

| Cotton sample | Graft add-on (%) | Decomposition temperature (°C) at various weight loss values (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
| Control | 0.00 | 248 | 310 | 325 | 336 | 342 | 335 | 370 | 433 | 460 |
| Styrene-grafted | 23.14 | 296 | 326 | 341 | 346 | 355 | 366 | 385 | 429 | 484 |
| Styrene-grafted in presence of DVB | 56.80 | 310 | 325 | 346 | 350 | 370 | 375 | 394 | 440 | 490 |

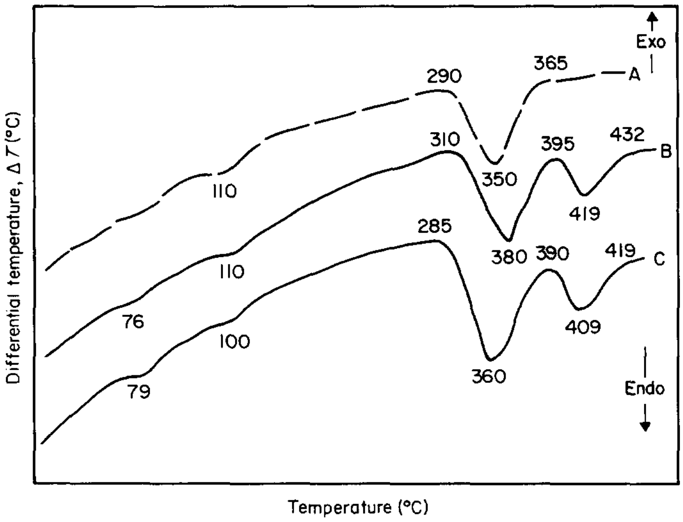

**Figure 6** Graph of temperature *versus* differential temperature: A, control cotton; B, styrene grafted cotton; C, styrene–DVB grafted cotton

may be due to the glass transition temperature of polystyrene.

The decomposition temperature of the grafted samples at different weight losses are given in *Table 3*. The data indicate that the thermal stability of the styrene-grafted cotton cellulose increases with the level of graft add-on. The results also indicate that the thermal decomposition of grafted cotton starts at correspondingly higher temperatures with increase in the graft level.

It may be concluded that the incorporation of DVB in the grafting bath containing styrene greatly enhances the graft add-on as compared to that obtained by preswelling of cotton cellulose. The moisture regain and tenacity decreased, whereas the thermal stability increased due to grafting, depending on the level of graft add-on.

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