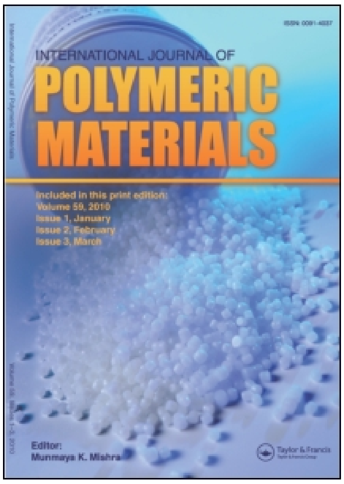

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Acrylonitrile butadiene styrene (ABS) was grafted using long chain molecules like oleic acid and dodecylamine. Grafting took place at the butadiene region of ABS. Grafted ABS (g-ABS) polymers were characterized using FTIR and blended with nylon-66 in various proportions. Physical, chemical, mechanical and thermal properties of the blends were analyzed. A physical blending technique was followed between nylon-66 and ABS and all properties were compared with the modified blends. SEM reveals that miscibility characteristics were found to be enhanced, as the modification of ABS makes it more compatible with nylon-66.

Keywords ABS, blending, engineering polymers, grafting, nylon-66

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INTRODUCTION

The ABS terpolymer is a good example of the combination of the rigidity of plastics and the elasticity of rubber. It is widely used nowadays in mobile industry and consumer products. Several reports have recently appeared on the subject of grafting of vinyl monomers onto ABS with various methods [1,2]. Nylons are attractive for this application because they have reactive functionality through amine and carboxyl end groups capable of reacting to form graft moieties [3–11]. Polyamides (nylon) are important engineering thermoplastics due to their excellent strength and stiffness, low friction and chemical resistance. However, polyamides are highly notch-sensitive. They are often ductile in the un-notched state, but fail in a brittle manner when notched [12]. Blending of immiscible polymers offers attractive opportunities for developing new material with a useful combination of properties [13]. However, simple blends often have poor mechanical properties and unstable morphologies. Compatibilization of such blends is necessary. Performed graft or blocked copolymers have traditionally been added to act as compatibilizers. However, it is often difficult to produce suitable graft or block copolymers for important commercial applications. A proactive alternative is to generate these copolymers in situ during the blend preparation through polymer-polymer grafting reactions using functionalized polymers [14], otherwise, reactive polymer blend. Although the interface of the reactive polymer blend is bound by chemical bond, the strength of interface adhesion is determined not only by the amount of the graft or block copolymer formed in situ, but also by the micro morphology and chain feature of graft or block copolymer formed in situ in interface [15]. The optimum compatibility is obtained by suitable chemical bond formed in situ in interface of reactive polymer blends, and the compatibility decreases when too much chemical bond is formed in interface [16]. Therefore, studying the reactivity of functionalized polymer is important.

In this work, oleic acid and dodecylamine were grafted onto ABS using a benzophenone initiator in a UV reaction chamber. Those grafted ABS (g-ABS) were blended with N-66 in various proportions by melt blending in an extruder. Various properties were estimated for those blends and compared with the physical blends of N-66/ABS.

EXPERIMENTAL

Materials

Nylon-66(N-66) – Dupont, Grade – Zytel – EPL-02–2E-30, ABS – Bayer ABS Ltd., Grade – Absolac −300, oleic acid, dodecylamine, xylene, methanol, and benzophenone are of laboratory grade.

Process

A UV reactor of a square-shaped closed metallic chamber with a glass container of 20-liter capacity surrounded by reflectors fitted with a stirring rod connected to a speed-controlled stirring motor was used. Four UV radiation-emitting tubes of 290–360 nm range are fitted symmetrically around the glass vessel. The reflectors are for increasing the efficiency of the lamp and 100% utilization of UV radiation. The glass vessel is covered by a glass lid to avoid the evaporation of solvents. There are no heating elements provided as reactions are done totally by the radiation effect. The g-ABS systems are synthesized in the laboratory by chemical process. Two different g-ABS were synthesized in which the functionalized compounds were grafted onto the main chain of ABS to study the improvement in interphase and the miscibility of the two polymers. The two g-ABS are: (1) ABS-g-oleic acid and (2) ABS-g-dodecylamine. The reactions were carried out in a UV reactor by solution technique. The 15% polymer solution was made in xylene. The amount of UV initiator was optimized by trial and error methods. 5% benzophenone (UV initiator) dissolved in xylene was added to the polymer solution under constant stirring for 15–30 mins. The polymeric solutions were exposed to the UV lights and constant stirring with 10% modifying chemicals (10% dissolved in suitable solvent) at room temperature. The reaction was carried under constant stirring for 7 d. The grafted polymer solution was precipitated in methanol and washed to remove the unreacted compounds. The characterizations of the g-ABS were done using the FTIR technique. The confirmation of the reaction taking place was done by studying the bands obtained in the FTIR spectra. Nylon-66 and ABS are hydrophilic materials that tend to absorb humidity present in the atmosphere. Thus to remove the humidity both the polymers were preheated up to 90°C for 6 h. g-ABS synthesized in the laboratory was added to N-66 in various proportions from 10 to 50 parts. The blending was done using the pelletizer at processing temperature. The blends are then used to prepare test specimens of tensile, flexural and impact properties in the injection molding machine.

Reactions

Figure 1(a) and (b) shows the possible reactions of ABS with oleic acid and dodecylamine, respectively.

The blends were tested for mechanical properties such as tensile strength [ASTM D 638], % elongation [ASTM D 638], tensile modulus, flexural strength [ASTM D 790], flexural modulus, Izod impact strength [ASTM D 265], Rockwell hardness [ASTM D 758], water absorption [ASTM D 570] and flame resistance [ASTM D 635] [17–19]. From all of the above properties for each blend, the optimized blend ratio was obtained and their thermal properties

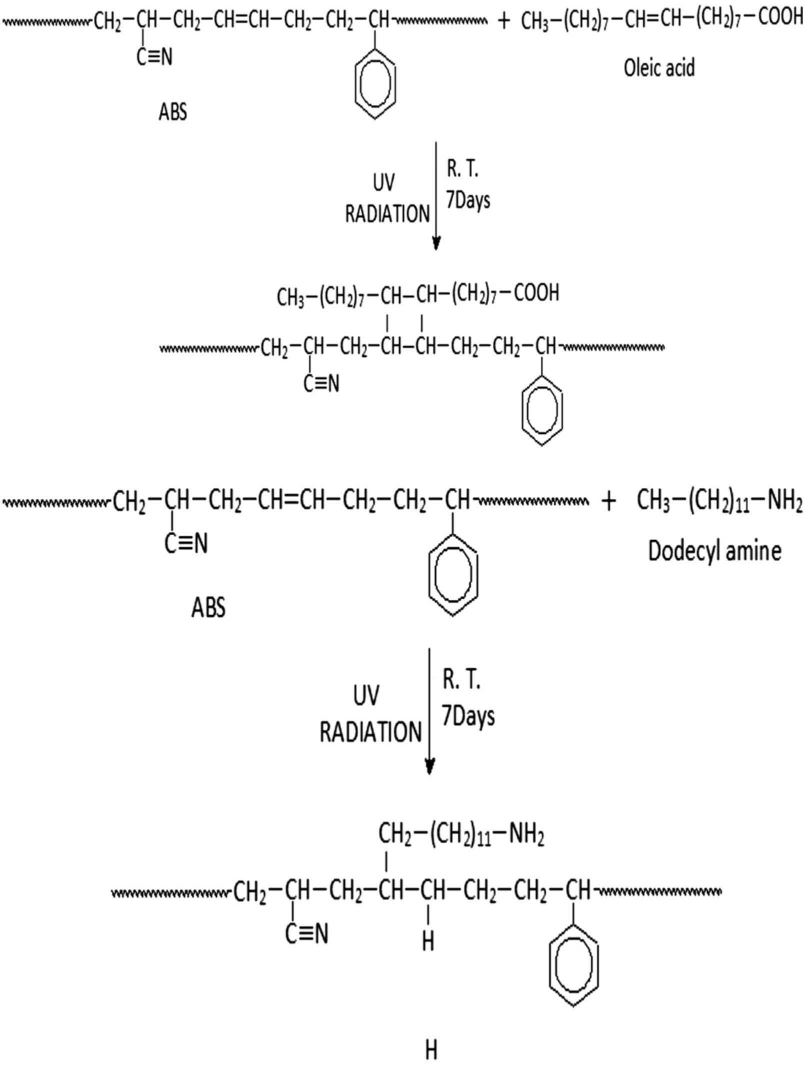


Figure 1: (a) ABS-g-oliec acid, and (b) ABS-g-dodecylamine.

were studied using DSC and TGA. The phase morphology for each optimized blend ratio was studied using SEM.

Compatibilizers were synthesized in the laboratory and characterized using FTIR.

1. VS−10 : ABS-g-oleic acid
2. VS−13 : ABS-g-dodecylamine

N-66/ABS blends

1. A : N-66/ABS conventional blend (without any grafting)
2. C(p) : N-66/ABS-g-oleic acid
3. C(q) : N-66/ABS-g-dodecylamine

RESULTS AND DISCUSSION

The g-ABS synthesized in the laboratory are confirmed for grafting using FTIR and results confirm the grafting of molecules to the respective main chains (Figures 2 and 3).

Figure 2 shows the following peaks: broad peak at 3425 for O-H stretching and 1721 and 1636 (due to hydrogen bonding) for C=O stretching of carboxylic acid, thus confirming the grafting of ABS with oleic acid. 3061 and 3027 for C-H stretching of aromatic ring; 2921 and 2850 for alkyl C-H stretching; 2237 for C≡N stretching of free nitrile group; 1637 and 1602 may be attributed to C=C stretching.

Figure 3 shows the following peaks: broad peak at 3434 for N-H stretching, thus confirming the grafting of ABS with dodecylamine. 3061 and 3027 for C-H stretching of aromatic ring; 2921 and 2850 for alkyl C-H stretching; 2237 for C≡N stretching of free nitrile group; 1637 and 1602 may be attributed to C=C stretching.

Figure 4 shows tensile strength of N-66/g-ABS blends with varying amount of g-ABS. As the g-ABS increases, the tensile strength increase

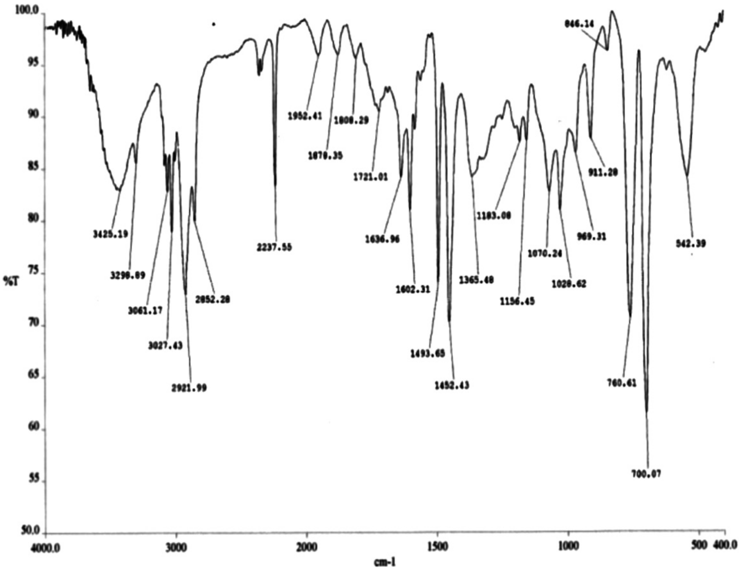


Figure 2: VS-10 shows FTIR of ABS-g-oleic acid.

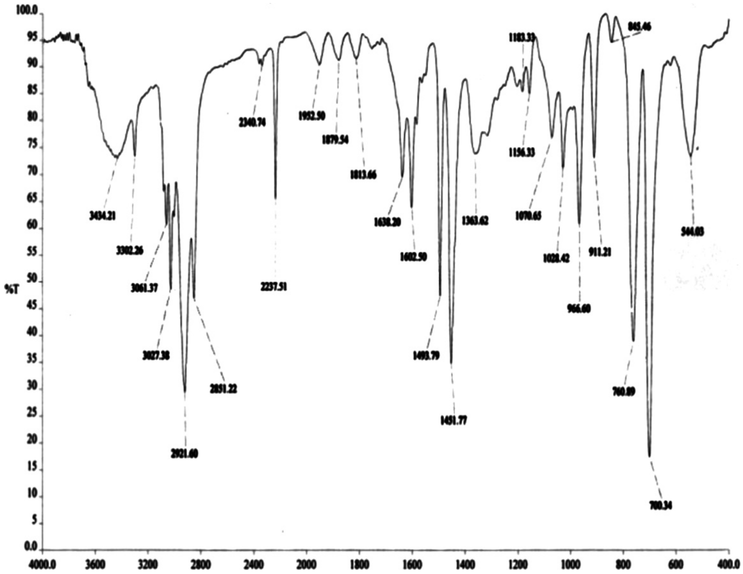


Figure 3: VS-13 shows FTIR of ABS-g-dodecylamine.

reaches a maximum at 30 parts and gradually decreases afterwards. Identical behavior was obtained in both types of grafting. The graph reveals that grafting of long chain compounds on ABS does not have a significant effect on the tensile properties of N-66/g-ABS blends, in comparison with physical blends.

Figure 5 shows % elongation at break of N-66/g-ABS blends with varying amount of g-ABS. % Elongation of the blends are found to be marginally decreasing in all grafted as well as in ungrafted blends. It is due to the change in crystalline behavior of N-66 by the addition of ABS. ABS impart into the

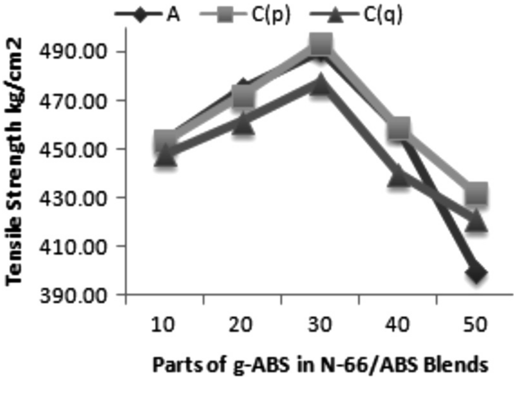


Figure 4: Shows tensile strength of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

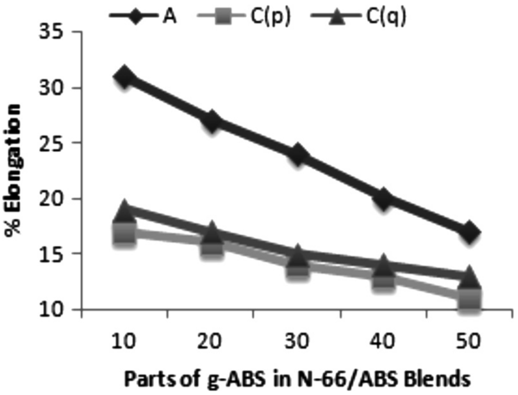


Figure 5: Shows % elongation of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

structure of N-66 and create amorphous regions into the N-66 matrix. The decrease in % elongation is found to be maximum in the case of grafted blends compared to ungrafted blends. Both the long chains show similar trends in the blends.

Figure 6 shows the tensile modulus of N-66/g-ABS blends with a varying amount of g-ABS. Tensile modulus is found to be increasing as an amount of g-ABS in the blends. All the grafted blends give higher properties compared to ungrafted physical blends. Amongst both g-ABS, oleic acid grafted ABS shows higher properties.

Figure 7 shows the flexural strength of N-66/g-ABS blends with varying amount of g-ABS. As the g-ABS increases, flexural strength increases, reaching a maximum at 30 parts and gradually decreasing afterwards. Identical

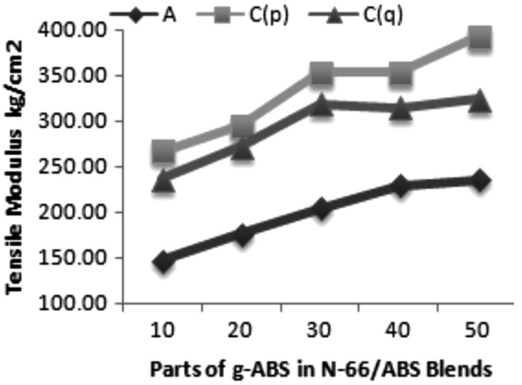


Figure 6: Shows tensile modulus of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

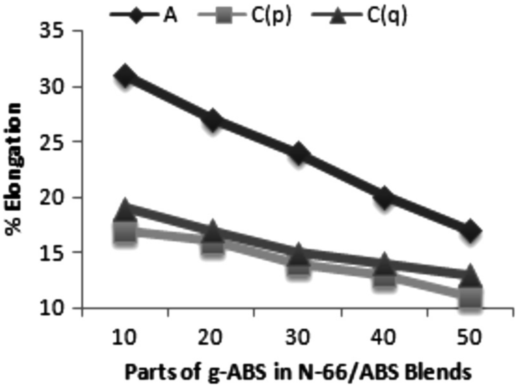


Figure 7: Shows flexural strength of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

behavior was obtained in all types of grafted blends. Among all blends ungrafted shows higher flexural strength.

Figure 8 shows the flexural modulus of N-66/g-ABS blends with varying amount of g-ABS blends. In all blends it is found that flexural modulus increases as the parts of g-ABS increases in the N-66/ABS blends. The flexural modulus is maximum for oleic acid grafted ABS.

Figure 9 shows the Izod impact strength of blends of N-66/g-ABS in various proportions. Izod impact strength increases as the amount of ABS increases in N-66, reaches the maximum, and slowly decreases after 30 parts of ABS in blend. The same trend is observed in all types of blend compositions. Dodecylamine grafted ABS gives the maximum properties compared to ungrafted and oleic acid grafted ABS.

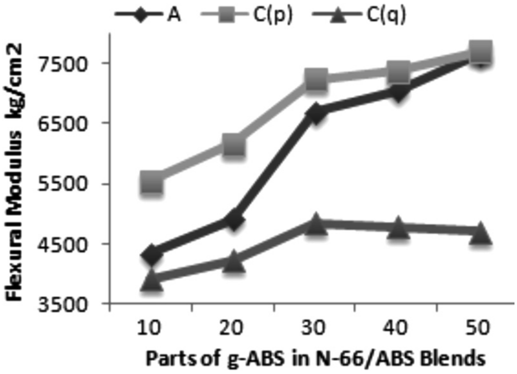


Figure 8: Shows flexural modulus of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

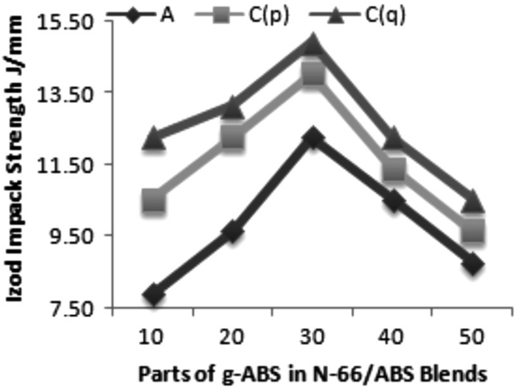


Figure 9: Shows izod impact strength of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

Figure 10 shows the Rockwell hardness of N-66/g-ABS blends with a varying amount of g-ABS. Addition of ABS gives a dilution effect on the N-66 rigidity after 30 parts. The decrease in the properties after 30 parts of ABS in the N-66/ABS blend is due to the increasing disturbance in the matrix of N-66. The highest hardness is observed in dodecylamine grafted ABS of all the grafted blends and physical blend of N-66/ABS as earlier.

Figure 11(a-c) shows the water resistance of N-66/g-ABS blends with a varying amount of g-ABS. By adding ABS, water absorption characteristics of N-66 are grafted drastically. It is found that water absorption decreases as the amount of ABS increases, which is similar in all types of grafted blends. The resistance is maximum in cold water in comparison with hot water. On functionalizing ABS with polar functionality, the hydrophilic nature of g-ABS increases. Due to this water absorption of the compound in hot water

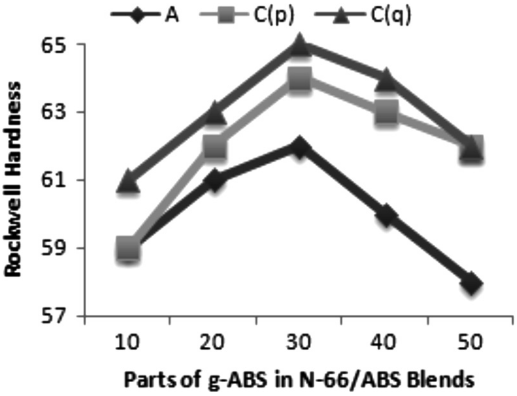
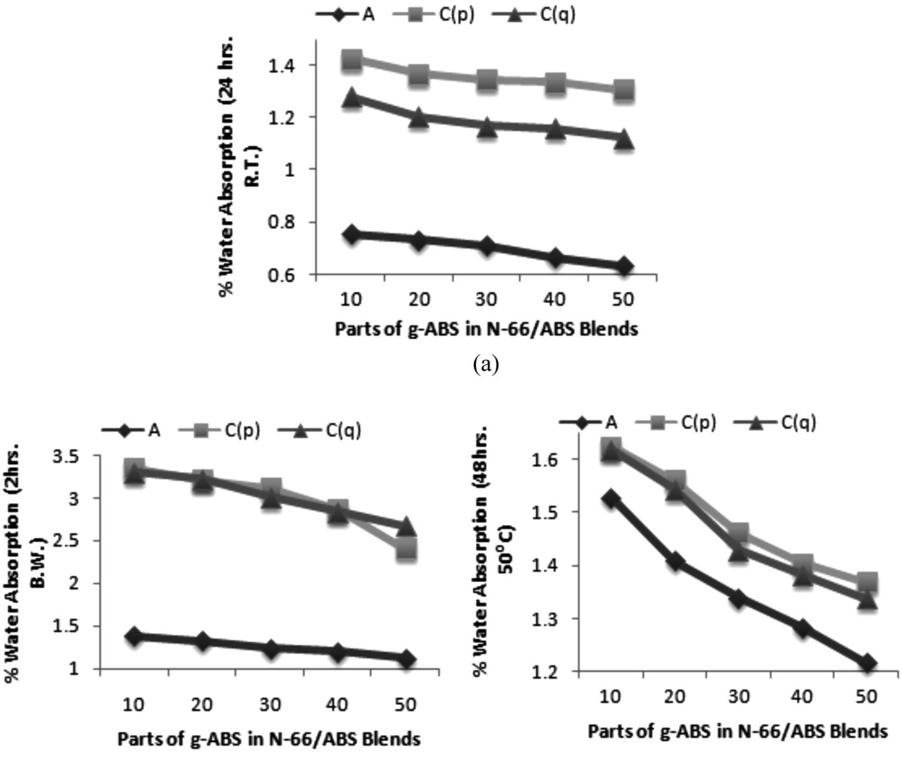


Figure 10: Shows Rockwell hardness of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.



(a)

(b) (c)

Figure 11: (a) Shows % water absorption for 24 h at room temperature of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine. (b) Shows % water absorption for 2 h in boiling water of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine. (c) Shows % water absorption for 48 h at 50°C of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.

is lower than ungrafted blends. An intermediate behavior is observed in water at 50°C.

Figure 12 shows the flame resistance of N-66/g-ABS blends with varying amount of g-ABS. Figure 12 shows the burning rate of specimens with respect to the amount of grafted ABS. It is found that as the amount of ABS increases, the burning rate increases. Nylons have superior flame resistance as compared to ABS, due to this the addition of ABS decreases the flame resistance of pure N-66.

Figure 13(a-c) shows DSC thermograms of blends of N-66/g-ABS blends with 30 parts of g-ABS. Figure 13a is for ungrafted N-66/ABS blend; 13b is for oleic acid grafted ABS and 13c is for dodecylamine grafted ABS. The graph reveals that on grafted ABS there is little difference in melting characteristics of the blends. All the blends show a melting point at 261°C with identical peak

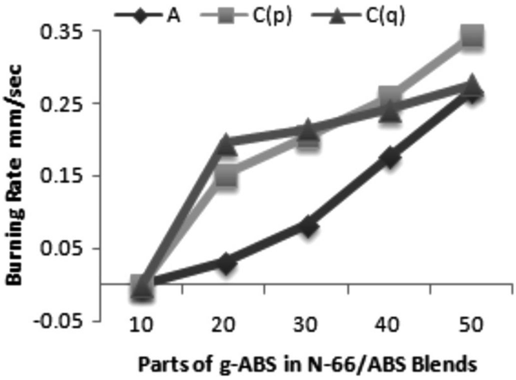
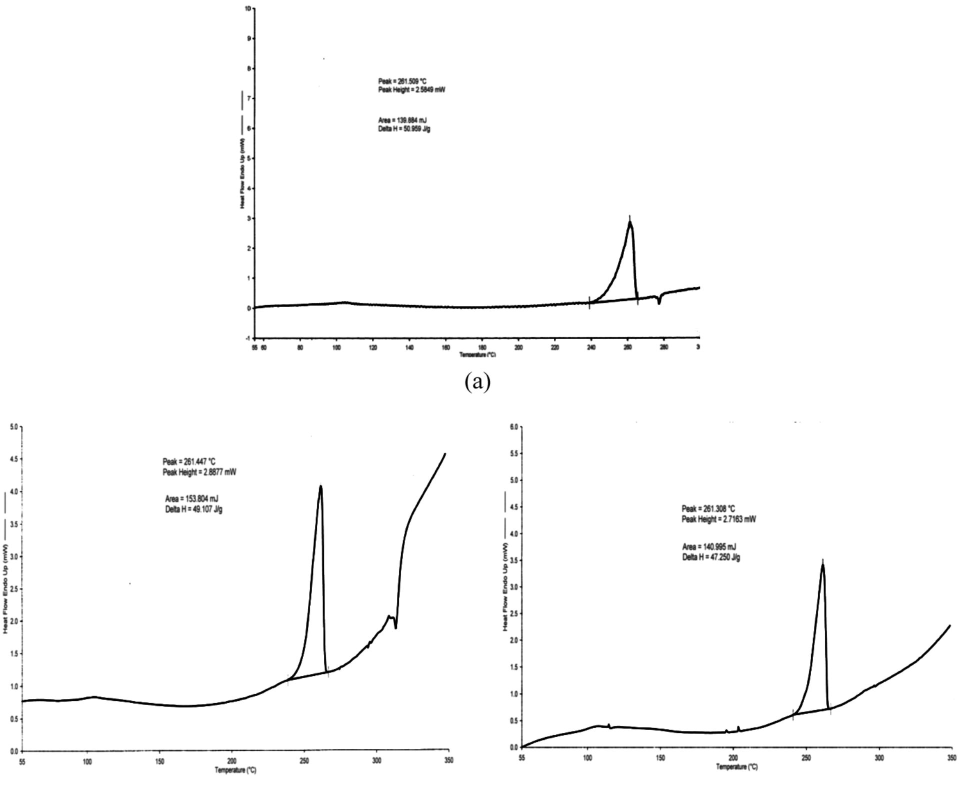


Figure 12: Shows burning rate of N-66/ABS blends. A is N-66/ABS conventional blend (without any grafting); C(p) is ABS-g-oleic acid; C(q) is ABS-g-dodecylamine.



(a)

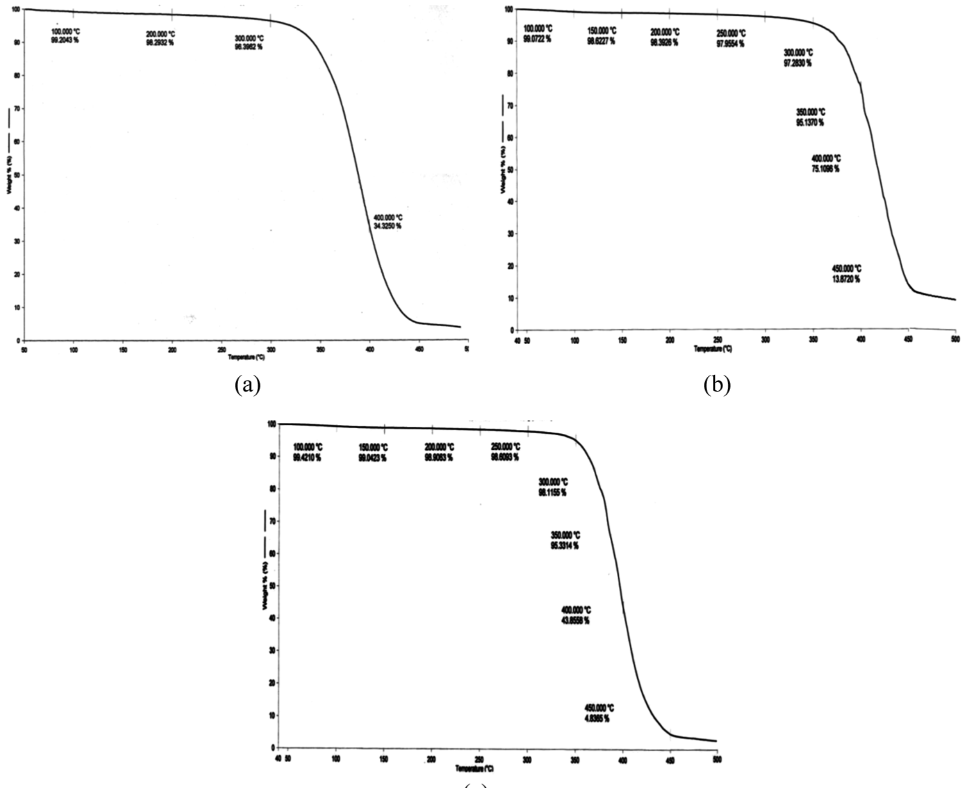
(b) (c)

Figure 13: (a) Shows DSC of 30 parts of ungrafted ABS in N-66/ABS blend. (b) Shows DSC of 30 parts of ABS-g-oleic acid in N-66/ABS blend. (c) Shows DSC of 30 parts of ABS-g-dodecylamine in N-66/ABS blend.

height. The graph 13b and 13c shows that after melting there is an endothermic stretch for the lines which reveals that the functional groups of N-66 and g-ABS are involved in chemical reactions, which is more significant in the case of oleic acid compared to dodecylamine.

Figure 14(a-c) shows TGA blends of N-66/g-ABS blends with 30 parts of g-ABS. Figure 14a is for ungrafted N-66/ABS blend; 14b is for oleic acid grafted ABS and 14c is for dodecylamine grafted ABS. It is evident from the s graphs that in the case of oleic acid, lower weight loss is observed as compared to dodecylamine, which is near about 3.5 times less at 450°C. Ungrafted blends give the least amount of material remaining compared to g-ABS blends. Thus, it is showing improvement in the thermal properties of the grafted blends compared to the ungrafted blends.

Figure 15(a-c) shows SEM blends of N-66/g-ABS blends with 30 parts of g-ABS. Figure 15a is for ungrafted N-66/ABS blend; 15b is for oleic acid grafted ABS and 15c is for dodecylamine grafted ABS. In case of N-66/ABS

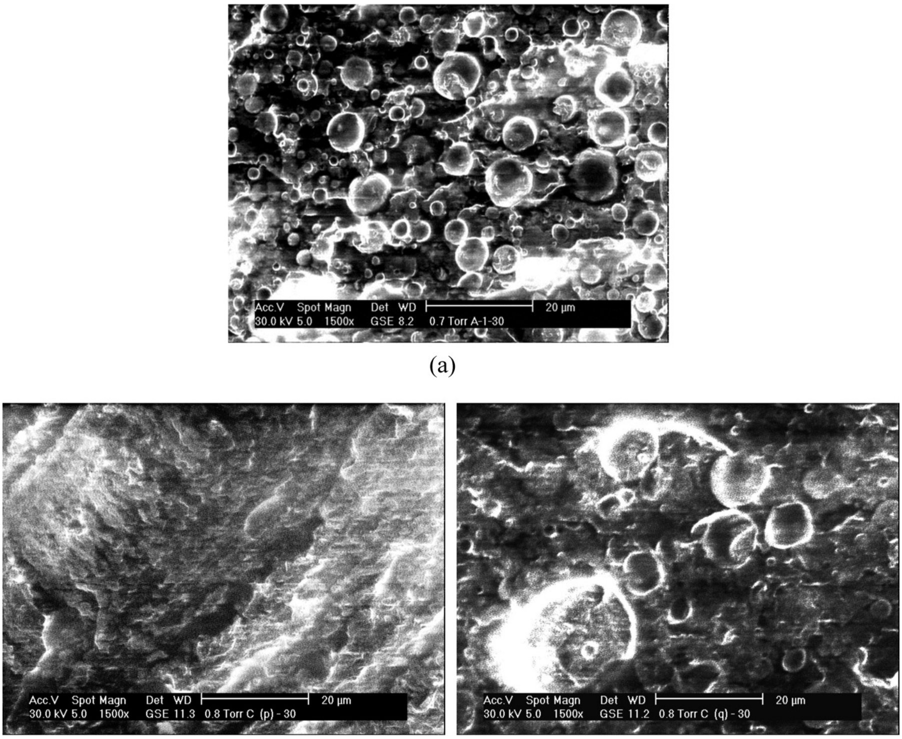


(a)

(b)

(c)

Figure 14: (a) Shows TGA of 30 parts of ungrafted ABS in N-66/ABS blend. (b) Shows TGA of 30 parts of ABS-g-oleic acid in N-66/ABS blend. (c) Shows DSC of 30 parts of ABS-g-dodecylamine in N-66/ABS blend.



(a)

(b) (c)

Figure 15: (a) 30 parts of ungrafted ABS in N-66/ABS blend. (b) 30 parts of ABS-g-oleic acid in N-66/ABS blend. (c) 30 parts of ABS-g-dodecylamine in N-66/ABS blend.

blends with 30 parts of ABS, N-66 acts as a continuous phase and ABS exists as bulky circular particles [20]. This indicates that blends are totally immiscible. Blending of completely immiscible polymers exhibits two or more isolated domains in the matrix [21] as shown in Figure 15a. In Figure 15b it is very clear that the circular particles disappear and a uniform phase appears, whereas in 15c a mixed image is seen which is intermediate of 15a and 15b comprising continuous phase and a few circular spheres in the matrix. This shows that oleic acid based grafting gives a more miscible phase compared to dodecylamine.

CONCLUSION

The graft copolymerization of oleic acid and dodecylamine onto acrylonitrile butadiene styrene (ABS) was initiated by benzophenone in xylene solvent at room temperature in a UV reaction chamber that utilized UV radiations. The double bond in the butadiene region of ABS absorbs the UV radiation to form free-radical active sites for the reaction. The copolymers were characterized by using FTIR and results confirm that oleic acid and dodecylamine long chains were successfully grafted on to an ABS backbone at the butadiene region. The long chain grafted ABS (g-ABS) was blended with N-66 in an extruder in various proportions. Mechanical properties, water absorption property, flame resistance and electrical properties were analyzed for both grafted and ungrafted blends of N-66/ABS. Both oleic acid and dodecylamine grafted-based blends showed similarities in properties. Thermal analyses like DSC and TGA and SEM were conducted. A comparative study was conducted between the grafted ABS (g-ABS) and ungrafted blends of N-66/ABS.

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