

PP 용융혼합에 의한 폐폴리우레탄 재활용에서 상용화제의 효과

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Effect of Compatibilizers in recycling of waste PU by PP melt blending

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INTRODUCTION

Polyurethanes (PU) have been used in industrial and commercial applications in the past few decades as a dependable workhorse and as a result increasing amount of it are ended as scraps after end use after their lifetime. Although, PU can be tailor made from thermoplastics to elastomers, thermosets are the main contenders in mass usage-particularly in the form of rigid polyurethane foams. The recycling of these thermoset materials suffers certain limitations, for example in the remolding process, due to a crosslinked structure as against their thermoplastic counterpart. The usual way of recycling this kind of products is by mechanical recycling, thermo-chemical recycling or entirely chemical recycling [1,2], depending on the viability of the process or the cost/benefit involved. In recent times, the blending of post consumer waste polymers has become a promising approach to the ecological and economical exploitation of waste plastics. Crosslinked thermoset wastes like waste ground rubber tire (GRT) powder has been successfully blended with numerous thermoplastics [3] to get technologically high strength materials for making products for engineering and commercial applications. Taking this into consideration, we have investigated the mechanical behavior of melt blends of waste PU with impact grade Polypropylene (PP). Since, this blend has been well known to be immiscible, we were interested in increasing the miscibility by using a series of maleic anhydride based compatibilizers (COM) like EPDM-g-MA, PP-g-Ma and SEBS-g-MA. Reactive compatibilization *ie* generating graft or block copymers *in situ* during the process of melt blending was used to produce the best blend compatibilization [4].

EXPERIMENTAL

Materials

Waste PUR powder procured from cryogenic grinding of industrial waste with average particle size of 10-30 μm and isotactic PP (1088, Korea petrochemical, Korea) was the main raw materials. Maleic anhydride-grafted polypropylene (RE 340B, SK Corporation, Korea) and maleic anhydride-grafted EPDM (RE 340B, SK Corporation, Korea) was purchased locally. The triblock copolymers, SEBS (Kraton G1652)and SEBS-g-MA (Kraton FG1901X) were supplied by Shell Chemical Co. Ltd., USA. Blending of various percentage of different compatibilizers/PP/PU was done in a Brabender Plasticorder PLE-330 at 190°C and 60 rpm screw speed for 10 minutes and sheeted in a two-roll mill. With the addition of compatibilizers, the PP weight fraction was reduced accordingly to maintain the weight fraction of PU.

Testing

Tensile properties were determined in a UTM (LLOYD INSTRUMENTS, LR10K, UK) as per ASTM D638 at a crosshead speed of 50 mm/min. The phase morphology of the blends was studied by a scanning electron microscopy (FE-SEM, model Philips XL 30S, Netherland). Perkin-Elmer 2000 spectrophotometer was used in the attenuated total reflectance mode (FTIR-ATR). Thermogravimetric analysis (TGA) was carried out in a DuPont TA2100 thermo gravimetric analyzer in the temperature range of 50-700°C at a heating rate of 20°C/min. Contact Angle Analyzer (Phoenix 300, Surface Electro Optics Co. Ltd., Korea) was used for measuring Polar and dispersive surface free energy but only the contact angle was reported here. Owens-Wendt Geometric Mean Method [5] was used taking water and diiodomethane as the solvents.

RESULTS AND DISCUSSIONS

Mechanical Properties

The PP reference compound had a Tensile strength (TS) of 25 MPa but a very poor elongation at break (%EB) of only 38%. So, with increase in the waste PU content both properties decrease drastically as shown in Fig.1. With the addition of only 5% compatibilizer in PP/PU/COM ratio 75/20/5 we observed a decrease in TS in the order PP-g-MA > SEBS-g-MA > EPDM-g-MA > SEBS with the SEBS based blend having a tremendous decrease as shown in Fig.2. With further increase in the compatibilizer keeping the PU constant at 20% and only changing the PP accordingly, the decrease in TS has the same trend although for PP-g-MA it is only marginal decrease. On the contrary in the %EB front for the same 5 % addition, % EB increases in the order PP-g-MA < SEBS-g-MA < EPDM-g-MA < SEBS as shown in Fig.3 with the SEBS based blend having the maximum value of 50%. With increase in the compatibilizer, the increase in %EB is only marginal except for SEBS which is increasing very drastically reaching as high as 200% for 20% addition and to some extent in SEBS-g-MA at higher concentrations. In spite of the brittle behavior observed in PP, the compatibilized blends shows some ductility at their higher concentration. Although, waste PU was known to induce brittle characteristics, SEBS was found to be the most effective while EPDM-g-MA the least in modifying it. There is only a marginal change in the impact properties with both the type and content of compatibilizers although 5% SEBS-g-MA is found to be better impact resistant of all as shown in Fig.2.

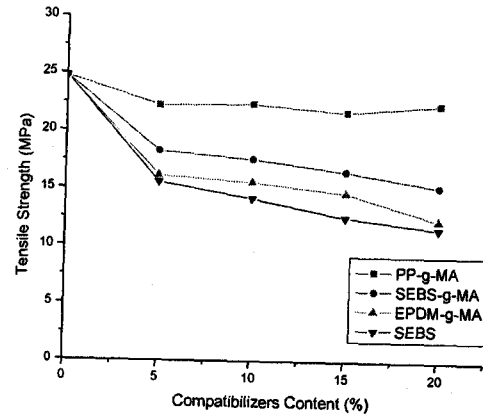
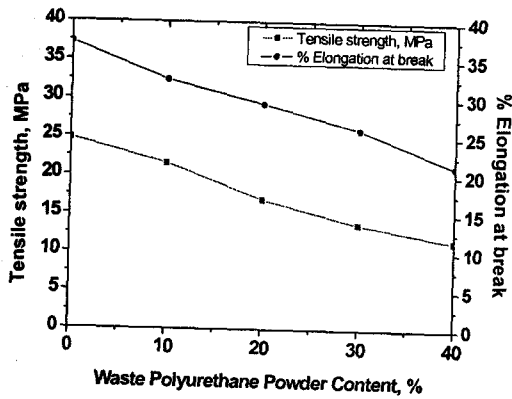


Fig:1 Effect of PU on Mechanical properties Fig:2 Effect of compatibilizers on TS

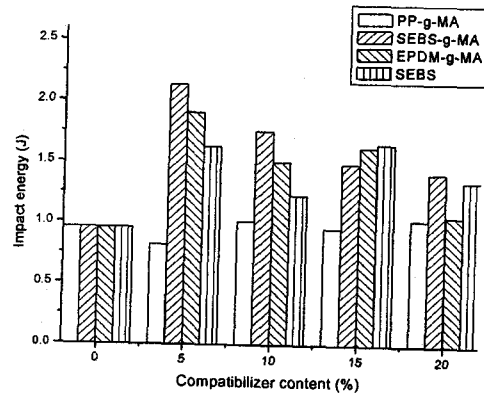
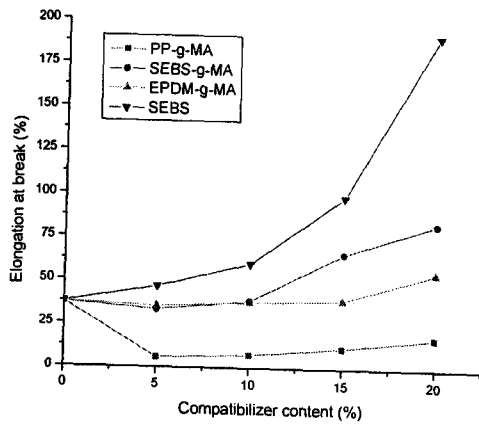


Fig:3 Effect of compatibilizers on %EB Fig:4 Effect of compatibilizers on Impact energy

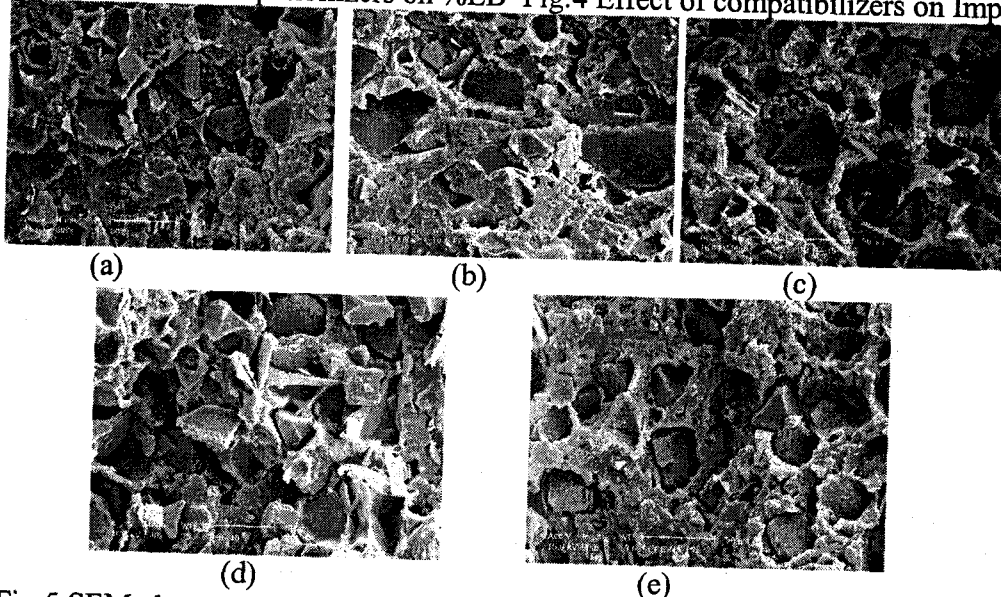


Fig:5 SEM photos 500X of (a) PP/PU and with 15% (b) PP-g-MA (c) EPDM-g-MA (d) SEBS-g-MA (e) SEBS

Morphology of the blends reveals interesting results as seen in Fig.5. With PP-g-MA addition, the formation of interfacial copolymer due to the reaction of the carbonyl group of MA with amino groups of PU is expected and hence domain size remains unchanged. But, in the case of the other two MA based compatibilizers we can see clearly the PU particles separate out from the matrix thereby confirming the poor adhesion as observed earlier by the weak mechanical properties. It is very distinct in the case of EPDM-g-MA which has the weakest TS and %EB while the highest %EB by SEBS can be explained by the good miscibility as clearly seen in SEM. Waste PU powder has a characteristic absorbance at 1728 cm^{-1} corresponding to the ester carbonyl group. But, the PP/PU/MA blends exhibit one more evident peak at 1760 cm^{-1} due to the formation of imide group. This absorption band is attributed to the carbonyl vibration of imide group which is due to the reaction between the amino group in PU and the carbonyl group of maleic anhydride of compatibilizers. Vermeesch et al. [6] has shown that imide group absorbances at 1799 cm^{-1} , 1726 cm^{-1} and 1710 cm^{-1} are due to in-phase, free and hydrogen bonded out-of-phase carbonyl vibrations. Phan et al. [7] assigned 1703 and 1774 cm^{-1} to correspond to the imide structure, thereby indicating the copolymer formation.

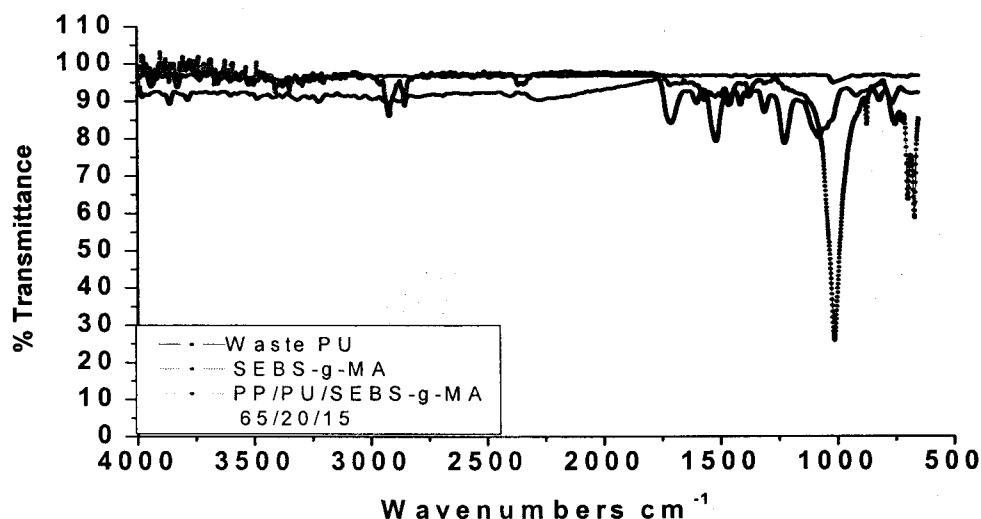


Fig: 6 Representative FT-IR spectrum of the PP/PU/SEBS-g-MA blend

Contact angle [8] is widely used to characterize the surface properties of solid polymers. It can also be seen that the contact angle decreases with increasing the waste PU content (Fig.7) as well as the degree of compatibilization (Fig.8). The decrease in the contact angle is attributed to the increase of the polarity of the graft copolymer formation. This is also confirmed by the TGA thermograms (Fig.9). Interestingly, we can see that the decomposition temperature of the compatibilized blends are shifted to higher temperatures from both the base PP and also PP/PU 80/20 blend. As expected, this is not very effective in the case of EPDM-g-MA while it is very good in PP-g-MA based blends by the shift in the temperature to higher degree. All SEBS based blends gave a slightly lesser decomposition temperature than the PP-g-MA based blends thereby confirming the order of efficiency.

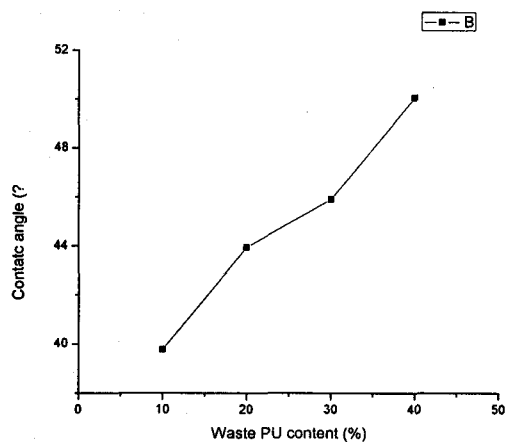


Fig:7 Effect of waste PU on contact angle

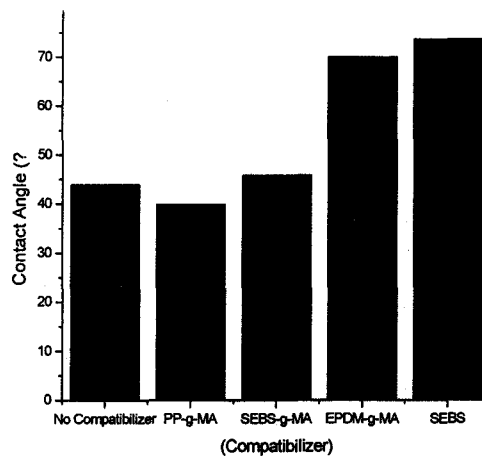


Fig:8 Effect of compatibilizers on contact angle

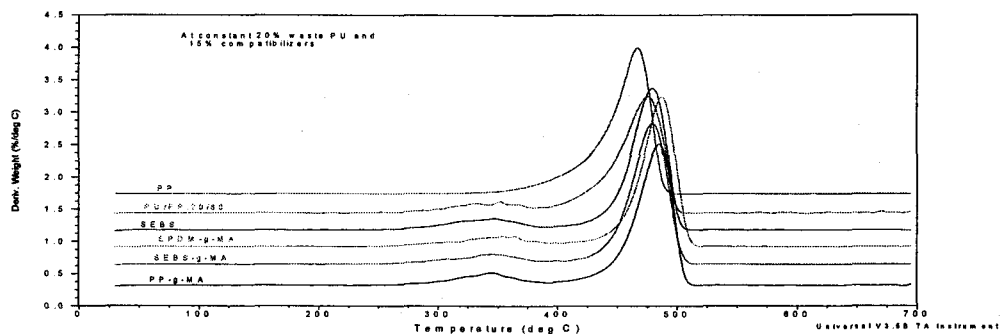


Fig:9 TGA thermograms of the base and compatibilized polymers

CONCLUSIONS

(1) Waste PU can be recycled by melt blending with PP and compatibilizers like PP-g-MA, SEBS-g-M, EPDM-g-MA and SEBS. (2) The Tensile strength decreases in the order PP-g-MA > SEBS-g-MA > EPDM-g-MA > SEBS and also with increase in their % individually while %EB increases MA < SEBS-g-MA < EPDM-g-MA < SEBS confirmed by morphology. There was marginal increase in impact properties (3) FTIR and Contact angle studies indicates copolymer formation using PP-g-MA.

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